

**HEAVY-METAL GEOACCUMULATION ASSESSMENT
OF THE EGOR LOCAL GOVERNMENT AREA
LITHOLOGY, BENIN CITY, SOUTHERN NIGERIA.**

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FACULTY OF LIFE SCIENCES
UNIVERSITY OF BENIN, BENIN CITY.**

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**A PROJECT WORK SUBMITTED TO THE
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AWARD OF BACHELOR OF SCIENCE DEGREE (B.Sc.)
IN SCIENCE LABORATORY TECHNOLOGY.**

MAY 2024.

CERTIFICATION

This is to certify that this project work was carried out by Victor CHIBUNNA with matriculation number, LSC1807185 of the Department of Science Laboratory Technology, Faculty of Life Sciences, University of Benin, Benin City.



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DEDICATION

I dedicate this work to God Almighty, my lovely parents and to those committed in understanding the intricate dynamics of heavy metal geoaccumulation.

ACKNOWLEDGEMENT

First and foremost, I offer my unreserved gratitude to the Almighty for granting me the strength, guidance, and perseverance throughout this academic endeavour.

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ABSTRACT

This study was carried out to determine the toxicity level of heavy metals at Egor Local Government Area of Edo State (Uwelu Mechanic/Spare-parts Market) in Benin-City, by evaluating the soil pollution accumulation and distribution resulting from the activities of automobile spare parts market and workshops in the study area. Nine (9) sample points including control were profiled at 0-5 cm, 5-10 cm, 10-15cm and 15-30cm. The control site which was east of the study area was situated about 1km away, and instruments used for sample collection are hand auger, Global Positioning System (GPS), ruler, sample bags, marker, and masking tapes. Laboratory analysis carried out revealed the physicochemical properties and heavy metals presence. Statistical analyses employed to investigate the heavy metal concentration, accumulation and distribution in the soil samples were performed using Pearson Correlation analysis and ANOVA analysis. Thereafter, Contamination factor, Geoaccumulation Index and Pollution Load Index. At profile depth 0-5 cm and 15-30 cm, there is no significant difference with control values. At profile depth 5-10 cm and 10-15 cm, there was significant difference between control and Chromium, Vanadium, Lead, Cadmium, Zinc and Electrical Conductivity. There was positive strong correlation between all the heavy metals except Nickel and Chromium which showed only significant correlation. Cadmium, Vanadium, Lead, Zinc and Chromium showed Contamination Factor value greater than 1.5 in all the profile samples which translates to Contamination from anthropogenic sources. Cadmium and Lead recorded high geo-accumulation index values which implies moderate to heavy contamination. Pollution Load Index of the profiles revealed that the sub soil at 10-15 cm and 15-30 cm where the most contaminated with the highest PLI values. In conclusion, the soil within the study area is heavily polluted with heavy metals due to the spilling of spent oil and dumping of scrap metals.

CHAPTER ONE

1.0

INTRODUCTION

1.1 GENERAL INTRODUCTION

Environmental pollution refers to the negative changes that occur in our surroundings due to various factors such as waste generated by human activities, alterations in radiation levels, the physical and chemical properties of substances, and the abundance of harmful organisms (Miller, 1988). Therefore, pollutants are substances that are present in the environment, at least partially as a result of human actions, and have harmful effects on the environment (Bayero, 2004). Land pollution specifically pertains to the terrestrial environment, which encompasses everything from the surface of vegetation to the uppermost layer of groundwater, which is the primary habitat for many living organisms on Earth. When it rains, non-biodegradable pollutants and waste materials are carried into the soil, groundwater, and nearby streams (Maduka, 2004).

The environment encompasses all living and non-living factors that influence the life of an organism, including both biotic (plants, animals, living or dead) and abiotic components such as land, water, and air (Bayero, 2004). Natural and artificial causes can bring about various changes in the environment. Key factors contributing to environmental issues include population growth, industrial development, urbanization, unsustainable resource utilization, and localized alterations (Botkin and Keller, 1997). Pollution, as defined by Maduka (2004), is the introduction of substances or energy into the environment by humans that have the potential to pose risks to human health, harm living resources and ecological systems, damage structures or amenities, or interfere with the legitimate uses of the environment.

According to USEPA (1993), common undesirable elements that contaminate the environment include natural organic compounds (e.g., phenols, formaldehyde), heavy

metals (e.g., lead, nickel, zinc, cadmium, copper, chromium), inorganic substances (e.g., ammonia, cyanides, fluorides, nitrites, sulphites), synthetic organic compounds (e.g., pesticides, herbicides, detergents), acidic and alkaline substances, and mineral oils.

fats and floatable substances and suspended solids, as well as nutrient substances like nitrogen, phosphorus, sulphates, and radioactive materials, are among the undesirable elements commonly found in environmental pollution. Nigeria, with a land area of approximately 950,000 km², is blessed with abundant resources. However, the nation is faced with severe environmental problems that manifest in various forms, posing significant challenges to soil sustainability. Pollution, erosion, loss of fertility, and rapid urbanization are major threats to soil resources in Nigeria (Bankole, 2005). Various types of waste, including plastics, discarded cans and cartons, tins, pails, motor and machine parts, dry cells, and paints, are dumped on the soil in dumpsites.

Furthermore, the increase in automobile repair and workshop activities in Nigeria, mainly due to the influx of used vehicles into the country in the late 1990s, has contributed significantly to soil contamination in most cities. Waste generated in automobile spare parts markets or workshops primarily comes from artisan activities. These activities involve the disposal of metal scraps, used batteries, packaging materials, spent lubricants, and worn-out parts containing contaminants such as heavy metals (Pam et al., 2013a; Pam et al., 2013b). Many of these petroleum products are organic chemicals that can be highly toxic and hazardous to soil organisms and humans. The use of automobiles has also resulted in soil contamination by trace elements and heavy metals, which have serious consequences for soil-dwelling organisms (Gupta and Gupta, 1998). According to Gupta and Gupta (1998), the toxicity and effects of heavy metals depend on an organism's position in the food chain, while in some cases, they are based on genetic abnormalities resulting from physiological impairments. Without proper management of these activities, if waste disposal and

automobile-related activities are not properly monitored and regulated, they can lead to increased levels of heavy metals and hydrocarbons in the environment. The contamination of soil by heavy metals is a significant concern due to their toxicity and the risks they pose to human life and the environment (Begum *et al.*, 2009). Heavy metals tend to have a long residence time in the soil, with estimates suggesting that metals like copper, nickel, lead, and zinc can persist for 1000-3000 years in certain temperature conditions (Bowen, 1977).

Soil pH plays a crucial role in nutrient solubility and the activity of microorganisms responsible for organic matter decomposition and chemical processes in the soil. Most garden plants thrive in a pH range of 6 to 7. Under acidic conditions, many heavy metals become more soluble in water and can leach through the soil, potentially reaching aquifers, surface streams, or lakes. Decreasing soil pH can also reduce the availability of nutrients like phosphorus due to reactions with aluminum and iron (Dirisu and Alao, 2010). Acidic soils generally have higher solubility and availability of minerals and nutrients compared to neutral or slightly alkaline soils. Phosphorus, for example, is most readily available in soils with a pH of 6.5. Incorrect or excessive use of certain fertilizers can contribute to soil acidification (Dirisu and Alao, 2010). Additionally, research by Martin (2010) showed that continuously and conventionally tilled plots tended to have the lowest soil pH.

Soil, unlike water and air, responds more slowly to external influences because it has the ability to bind substances into complex structures. Clay minerals and humic acids play a role in the binding of ions on the soil surface. Consequently, soil serves as a reservoir for both organic and inorganic substances, providing nutrients for plants and microorganisms (Bloemen *et al.*, 1995).

Based on these considerations, this study is undertaken to assess soil pollution resulting from the activities of mechanic workshops and spare parts markets in the Benin City metropolis.

1.2 STATEMENT OF PROBLEM

Benin City is located in the southern part of Nigeria with a growing population of about 1.5 million. Benin City is a hub for Tokunbo cars which has led to the people engaging in town services such as Tricycle, taxi and bus driving as their occupation and has led to the existence of many automobile mechanic shops and workshops as can be seen in Uwelu. Also, indiscriminate disposal of their spent oil subjects the soil of this environment to high risk of pollution with heavy metals and other harmful substances. Since heavy metals at elevated levels can be dangerous to lives and environment, there is need to check their concentration and mobility. The lack of strict application of environmental protection legislation and the need for better control of the pollution situation and absence of basic data about heavy metal pollution from automobile shops and mechanic workshops in this vicinity is the background for the present work.

1.3 AIM AND OBJECTIVES

The aim of this study is to examine the impact of mechanic workshops on soil within the study area.

The objectives are as follows

- ❖ To determine the extent soil around the automobile shops and workshops are contaminated or polluted
- ❖ To determine the profile of leachate towards groundwater systems
- ❖ To determine the Contamination Factor of soil from the study area
- ❖ To determine the Pollution Load Index and Geo accumulation Index of soil from the study area

- ❖ To determine the relationship between the heavy metal concentration in the study area

1.4 ACCESSIBILITY

The area of study is thickly populated with automobile shops and workshops and very assessable. Some of the roads leading to this area include Uwelu Road, Power Line Road, Edobor Street, etc. The terrain is flat and the streets in the vicinity around are well connected.

1.5 HYDROGEOLOGY

The man made drainages in the study area carries storm water from the study area to a nearby moat which is channeled to the Ikpoba river.

1.6 CLIMATE

The study area has a tropical climate. Average annual temperature is 26.1oC while 2025mm of precipitation falls annually. There are mainly two seasons, the wet and dry. The wet seasons starts in April and ends in October while the dry season starts in November and ends in March. The wet season is usually characterized by heavy rainfall and in some recent years there have be 5 – 8 days of nonstop rainfall. The dry seasons is characterized by intermittent Harmattan periods due to climate change. Change over periods of the dry and wet seasons are characterized by heavy winds and thunder storms due to the mixing of the North-East and South West trade winds.

1.7 LOCATION OF THE STUDY AREA

The study area is located in Uwelu, Egor Local Government Area of Benin city. It is about 2.2km from Wasota Junction along the Benin Shagamu Express Way and lies on N6° 24' 57'' & E5° 54' 33'' and N6° 26' 45'' & E5° 45' 49.5'' (Figure 1.1).

1.8 SIGNIFICANCE OF THE STUDY

It is crucial to prioritize environmental preservation and recognize the adverse impacts of heightened industrialization, agricultural practices, and pollution processes. It is essential to minimize these influences as swiftly as possible. The importance of this research lies in assessing the extent of toxic heavy metal contamination in the soil of the study area and finding solutions to eliminate or prevent further accumulation of these contaminants in the environment.

1.9 SCOPE OF WORK

This includes desk or reconnaissance study, sample collection, digestion of samples, laboratory analysis, statistical analysis, presentation of results and discussion, summary, conclusion and recommendation.

CHAPTER TWO

2.0 LITERATURE REVIEW AND GEOLOGY OF THE STUDY AREA

2.1 LITERATURE REVIEW

Oguntimehin and Ipinmoroti (2008) conducted a study on heavy metals in automobile workshops in Akure, Nigeria. They found high concentrations of iron and zinc in all samples, while some samples showed elevated levels of barium, copper, lead, chromium, nickel, and cobalt. Cadmium was not detected in any of the collected samples. The severity of heavy metal pollution followed the order of Ijapo, Ilesha garage, Ondo Road, Oyemekun, and Oke-ijebu.

Nwachukwu *et al.* (2010, 2011, 2017) and Udebuani *et al.* (2011) reported significant soil degradation in the Nekede mechanic village due to excessive heavy metal pollution. This degradation was attributed to poor management of automobile waste.

Pam *et al.* (2013) conducted studies in Gboko and Makurdi and found that mechanic workshop clusters in these areas were contaminated with heavy metals such as lead, copper, zinc, manganese, nickel, and cadmium. The contamination levels were significant and indicated a considerable degree of pollution. The researchers concluded that auto mechanic workshops have a negative impact on the surrounding environment and called for stricter regulations on their location within cities and proper disposal of waste from these clusters.

Ogunmodede *et al.* (2015) observed high concentrations of chromium, cadmium, lead, nickel, zinc, manganese, iron, and copper in soil located in dumpsites within Ado-Ekiti. They suggested that the heavy metal pollution originated mainly from the dumping of industrial waste or uncontrolled release of effluents into the ground, which could eventually contaminate water bodies and streams in the study area. The study emphasized the urgent need for control measures to address the severe heavy metal pollution in the area and its impact on the soils urgent actions such as bioremediation and other remediation

technologies, including phyto-remediation involving the cultivation of specific plants, were recommended to minimize contamination rates and mitigate future pollution issues.

According to Nwachukwu *et al.* (2017) poor management of occupational waste, specifically used battery acid, was identified as the main cause of soil acidity within the Nekede mechanic village. The study recorded a pH in the range of 1.6 to 2.1, with a mean value of 1.8 for the potential acidity (Pi) and a pH in the range of 1.7 to 2.0, with the same mean value of 1.8 for the exchangeable acidity (pHeF). These findings suggested that in heavy metal-contaminated topsoil, the exchangeable acidity tends to be similar to the potential acidity.

In the soil area of the Agbabu bitumen deposit, Fagbote and Olanipekun (2010) found relatively low mean concentrations of cadmium (Cd) in the soil, which did not exceed the maximum allowable limits used in different countries. However, they recorded high concentrations of other heavy metals in the soil. The enrichment factor of heavy metals in the study area ranged from no enrichment to moderate enrichment.

Iwegwe *et al.* (2006) observed elevated levels of heavy metal concentrations in soil profiles of automobile mechanic waste dumps in Port Harcourt municipal, compared to background concentrations. The distribution pattern of heavy metals in the soil profiles followed the order of lead (Pb) > zinc (Zn) > copper (Cu) > cadmium (Cd) > nickel (Ni) > chromium (Cr). The researchers concluded that the mechanic waste dumps represented potential sources of heavy metal pollution to the environment and posed a serious threat to both surface and groundwater.

Adewoyin *et al.* (2013) conducted a study in the auto mechanic villages of Ibadan metropolis, assessing the physicochemical properties and heavy metal concentrations in both soil and groundwater. The results indicated a high degree of contamination and pollution. Various pollutants, including heavy metals, oil, and grease, were found to

accumulate in the soil, eventually seeping or percolating into the groundwater. This posed significant hazards to those consuming the water and also posed risks to the soil.

Amos-Tuatua *et al.* (2014) assessed lead, cadmium, chromium, and physicochemical properties of soils collected from an open dumpsite in Yenogoa, Nigeria. The study found that all soil samples had very high base saturation (>90%) and exchangeable calcium, magnesium, potassium, and sodium, surpassing critical levels set by FAO for agricultural soil. However, lead, chromium, and cadmium concentrations were below the maximum tolerable levels set by FAO and WHO for agricultural soils. The researchers concluded that the dumpsites, along with the control area characterized by adequate soil nutrients and low levels of heavy metals, could eventually be converted into agricultural farmland and did not require immediate remediation at the time of the study.

Akoto *et al.* (2008) investigated heavy metal pollution in soils around a railway servicing workshop in Kumasi, Ghana. The study found that the I-geo (geoaccumulation index) values of the metals in the studied soils indicated that cadmium and nickel concentrations could generally be considered as background levels, while zinc exhibited moderate pollution and lead and copper showed high to very high pollution levels. Anthropogenic sources were identified as contributors to the elevated concentrations of lead, copper, and zinc. Overall, the soils in the vicinity were described as moderately to very highly polluted, as all collected samples showed moderately high levels of contamination in at least one metal.

Deka and Sarma (2012) reported that increased concentrations of lead, manganese, and iron were associated with high levels of organic matter, pH, and conductivity in the soil. Heavy metal contamination in the soil was likely due to atmospheric deposition of contaminated dust and industrial discharge. The investigations revealed that all analyzed soil samples were contaminated with lead and manganese. The researchers concluded that based on their

study, the soil quality in the study area was found to be unsatisfactory, emphasizing the need for appropriate measures to improve soil health.

In their study on soils from auto-mechanic shops and refuse dumpsites in Makurdi, Nigeria, Luter *et al.* (2011) reported significant concentrations of cadmium, chromium, copper, lead, and nickel in these areas compared to control values, indicating clear pollution. The presence of heavy metals in the soil was suspected to be derived from the waste materials.

Pam *et al.* (2013a) conducted research on the impact of automobile mechanic sites on heavy metal contamination in soil, using the North Bank Mechanic village in Makurdi, Benue State as a case study. They found that lead, copper, zinc, manganese, nickel, and cadmium all recorded values above background levels and threshold limits established for soil in the collected samples. The distribution pattern of heavy metals in the soil followed the order of lead > manganese > zinc > copper > nickel > cadmium. The geoaccumulation index values indicated high pollution levels with lead and copper, moderate pollution with cadmium and manganese, while the soil remained unpolluted with zinc.

Akujieze and Irabor, 2014) assessed the extent of environmental degradation of soil and groundwater using the Benin West Moat-Ekenwan gully as a case study. Their findings revealed contamination of the soil with aluminum, cadmium, iron, lead, and total hydrocarbons (THC) at a statistically significant level ($p < 0.05$). The groundwater was also found to be polluted with presumptive coliform and heavy metals such as aluminum, cadmium, and lead at a high significant level ($p < 0.01$). The researchers concluded that the once protective moat has now become an area of potential phytotoxicity and overall environmental toxicity to humans, especially if chronic exposure continues due to ongoing waste disposal.

2.2 REGIONAL GEOLOGY

The study area is located within the Niger Delta region, which consists of three lithostratigraphic units: The Akata Formation, the Agbada Formation, and the Benin Formation, arranged in chronological order from oldest to youngest (Weber and Daukoru, 1975). These formations have ages ranging from the Paleocene period to the present (Weber, 1986). Similar stratigraphic units can be observed in southern Nigeria, as documented in Table 2.1 by (Short and Stauble 1967). The formations represent a clastic wedge that progressively coarsens upward, indicating deposition in marine, deltaic, and fluvial environments.

Table 2.1: Age of the formation ranges from Paleocene to Recent (Doust and Omatsola, 1989)

Subsurface			Surface Outcrops		
Youngest Known Age		Oldest Known Age	Youngest Known Age		Oldest Known Age
Recent	Benin Formation(Afam clay member)	Oligocene	Plio/Pleistocene	Benin Formation	
Recent	Agbada Formation	Eocene	Miocene Eocene	Ogwashi-Asaba Formation Akeki formation	Oligocene Eocene
Recent	Akata Formation	Eocene	Lower Eocene	Imo Shale Formation	Paleocene

2.2.1 THE AKATA FORMATION

The upper boundary of the Akata Formation is determined by the deepest occurrence of deltaic sandstone beds. In the central part of the clastic wedge, the Formation is estimated to have a thickness of approximately 21,000 feet. The lithologies within the Akata Formation consist of dark gray shales and silts, occasionally interbedded with sandstone layers that are

likely the result of turbidite flows. As one moves vertically, the Akata Formation transitions into the Agbada Formation, characterized by an increased presence of plant remains and micas (Doust and Omatsol, 1989).

2.2.2 THE AGBADA FORMATION

The Agbada Formation is widespread within the clastic wedge of the Niger Delta and reaches a maximum thickness of approximately 13,000 feet. In the southern region of Nigeria, specifically between Ogwashi and Asaba, it is referred to as the Ogwashi-Asaba Formation (Doust and Omatsola, 1989). The lithologies comprising the Agbada Formation consist of alternating layers of sand, silt, and shale, organized into successions ranging from tens to hundreds of feet in thickness. These successions demonstrate progressive upward changes in grain size and bed thickness. The strata are generally interpreted as having been deposited in fluvial-deltaic environments. The Agbada Formation spans in age from the Eocene epoch to the Pleistocene epoch.

2.2.3 THE BENIN FORMATION

The Benin Formation represents the uppermost portion of the Niger Delta clastic wedge, extending from the Benin-Onitsha area in the north to beyond the current coastline (Short and Stauble, 1967). The Elele 1 Well, located approximately 38 km north-northwest of Port Harcourt, serves as the designated type section for this formation (Short and Stauble, 1967). The top of the Benin Formation corresponds to the recent delta top surface, which is exposed above water, while its base reaches a depth of 4600 feet and is marked by the youngest marine shale layer. Within the shallow regions of the formation, non-marine sand dominates, indicating deposition in alluvial or upper coastal plain environments during delta progradation (Doust and Omatsola, 1989). Due to the absence of well-preserved fauna,

precise age dating is challenging, but the formation is estimated to range in age from the Oligocene epoch to the present (Short and Stauble, 1967). The thickness of the formation diminishes towards the basin and terminates near the shelf edge.

2.3 LOCAL GEOLOGY

The study area is located within the Benin Formation, which consists of three lithological units. These units include the Drift/Top soil, characterized by loose, light gray-dirty sands, silt, and mudflows. The Alluvium, found only along river banks, is composed of light gray-brown-dirty white sands, silts, clays, gravels, and pebbles. Lastly, the Benin Formation itself is comprised of reddish-brown clay sand at the top, followed by thick sequences of poorly bedded, friable loose sand, gravelly-pebbly sand, and pinkish-white clay stringers (Akujize and Irabor, 2014).

The Uwelu auto-shops and mechanic workshops are situated within the Drift/Top soil layer of the Benin Formation, as depicted in Figure 2.1.

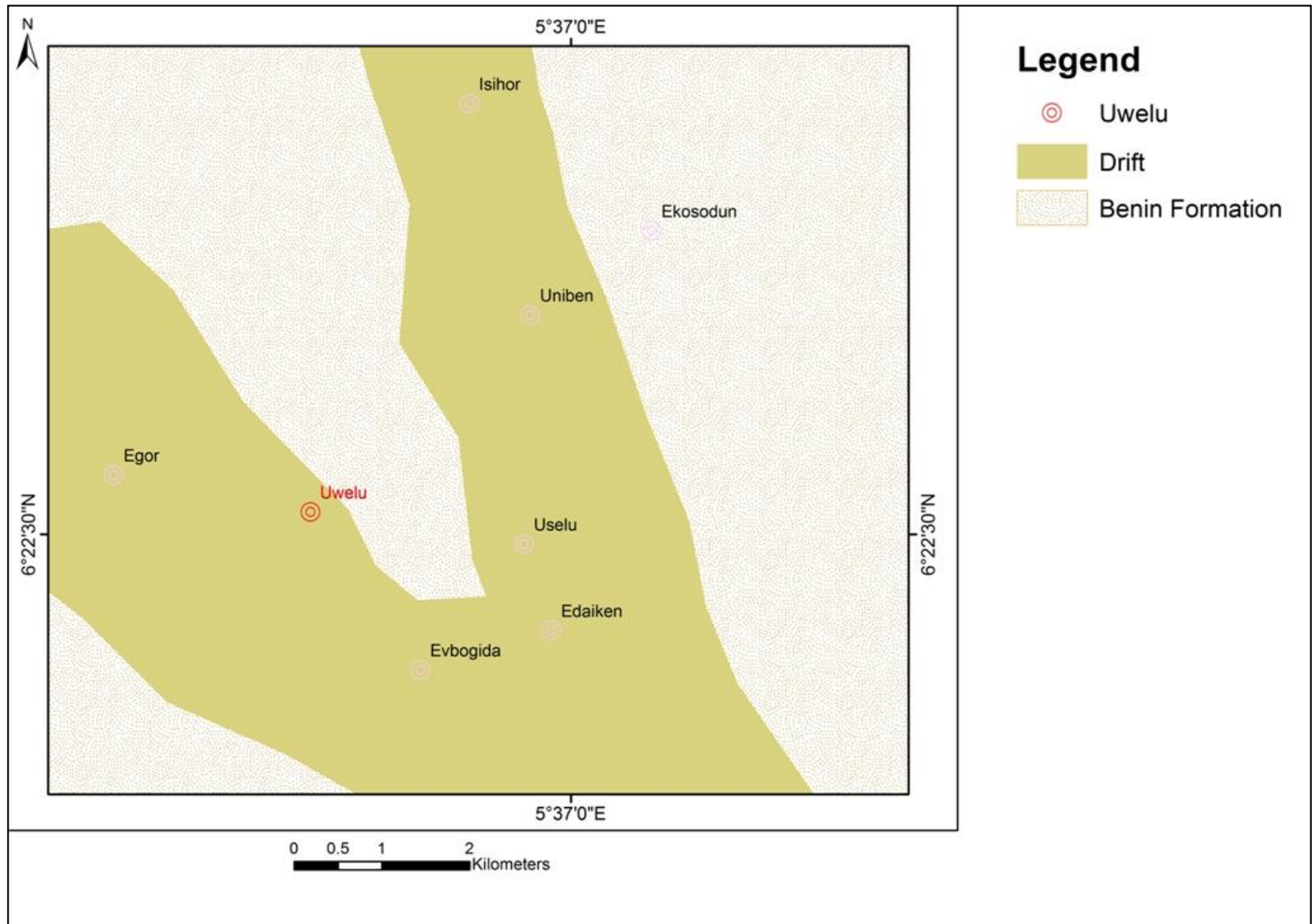


Figure 2.1: Geology of the study area (adapted from Akujieze, 2004)

CHAPTER THREE

METHODOLOGY

3.1 SAMPLE COLLECTION

Nine (9) sample points including control were profiled at 0-5 cm, 5-10 cm, 10-15cm and 15-30cm. The control site which was east of the study area was situated about 1km away. Instruments used for sample collection are hand auger, Global Positioning System (GPS), ruler, sample bags, marker, and masking tapes.

3.2 LABORATORY ANALYSIS

A dried fine soil sample weighing one gram was placed into a round-bottom flask that had been cleaned with acid. To this flask, 10 cm³ of concentrated nitric acid was added. The mixture was then slowly evaporated on a hot plate over a period of one hour. The resulting solid residue from each sample was digested using a mixture of concentrated nitric acid (HNO₃) and perchloric acid (HClO₄) in a ratio of 3:1. This digestion process was carried out at room temperature for 10 minutes before heating on a hot plate. The heating continued intermittently until a steady temperature of 150°C was reached and the fumes of HClO₄ completely evaporated (Jacob et al., 2009). After cooling to room temperature, the digested mixture was filtered using Whatman No.1 filter paper into a 50 cm³ volumetric flask. The flask was then filled to the mark with deionized water after rinsing the vessels to recover any remaining metal. The filtrate was stored in clean polyethylene bottles for subsequent analysis. Heavy metal concentrations were determined using an Atomic Absorption Spectrophotometer (AAS) with instrument settings and operational conditions following the manufacturer's specifications. The instrument was calibrated using standard metal solutions of known concentrations (1 mg/dm³) in replicates. In-situ measurements of physicochemical parameters such as electrical conductivity (EC) and pH were taken using a multi-parameter EC/pH meter.

3.3 EXPERIMENTAL PROCEDURES FOR SOIL

3.3.1 ELECTRICAL CONDUCTIVITY

Twenty (20) grams of the fresh soil sample was weighed into a 100 ml glass beaker. Twenty (20) milliliters of sterile distilled water was added and the suspension was stirred continuously for 30 minutes. The mixture was allowed to stand for another 30 minutes undisturbed. A Digital pH/EC Meter (Labtech) was used in determining soil conductivity by dipping the sensitive rod into the mixture and a steady reading taken.

3.3.2 DETERMINATION OF PH

The pH reading was obtained with the aid of a Labtech pH/EC multi-meter which was earlier standardized with buffer 4.0, 7.0 and 9.0. Twenty (20) grams of the fresh soil sample was weighed into a 100 ml glass beaker. Twenty (20) milliliters of sterile distilled water was added and the suspension was stirred continuously for 30 minutes. The mixture was allowed to stand for another 30 minutes undisturbed. A Labtech pH/EC meter probe was dipped into the solution and steady readings noted (Kalra and Maynard, 1991).

3.3.3 TOTAL DISSOLVED SOLIDS

Heat an evaporation dish for 1 hr to $600 \pm 25^{\circ}\text{C}$. Cool and store the evaporation dish in a desiccator. Precisely measure the volume (in mL) of the soil saturation extract needed to yield on evaporation a minimum of 25 mg of residue. Pass the measured volume of extract through a filter membrane, followed by three successive 15-mL volumes of DDI water. Weigh the evaporation dish. Transfer the complete filtered sample to an evaporation dish. Heat the evaporation dish to evaporate the filtered sample but do not bring it to a boil and don't heat to the point where the filtered sample is dry. When the filtered sample is nearly dry, transfer it to a 103°C drying oven and complete the evaporation. Dry the evaporation dish and residue for 1 hr at $180 \pm 2^{\circ}\text{C}$, cool in a desiccator, and weigh the evaporation dish and residue. Repeat the 1-h drying, cooling in the desiccator, and weighing cycle until a constant weight is attained (or until

the weight loss is <4% of the previous weight or 0.5 mg, whichever is less). Record the weight of the dried residue plus dish. The TDS (in mg L⁻¹) is calculated by

$$\text{TDS} = 1000 \frac{A - B}{V_{se}}$$

where A is the weight of the dried residue plus the evaporation dish (mg), B is the weight of the evaporation dish (mg), and V_{se} is the volume of soil saturation extract (mL) (Rhoades, 1996).

3.3.4 MINERAL (HEAVY METALS) ANALYSIS

The soil sample was spread on a clean plastic sheet placed on a flat surface and air dried under room condition for 72hrs. The soil was sieved and 5g sample was taken from the sieved soil and put in a beaker. Ten (10) ml of nitric perchloric acid, ratio 2:1 was added to the sample. The sample was digested at 105oC. 5ml of HCl was added to the digester again and digested for 30mins. The digest was then removed from the digester and allowed to cool to room temperature. The cooled digest was washed into a 100ml standard volumetric flask and was made up to 100ml mark with distilled water. Determination of Nickel (Ni), Chromium (Cr), Vanadium (V), Zinc (Zn), Lead (Pb) and Cadmium (Cd) were done by aspirating the solution for (analysed) each metal analysis into the Atomic Absorption Spectrometer (AAS) Solaar 969 Unicam Model (Adelekan and Abegunde, 2011).

3.4 STATISTICAL ANALYSIS

Statistical analysis is very useful in providing knowledge, and assists in interpretation of data. It is widely applied in recent times to investigate the heavy metal concentration, accumulation and distribution in soils (Qishlaqi and Moore, 2007). Statistical analyses of heavy metal contents in the soil samples from Auto mechanic shops and workshops in Uwelu were performed using Pearson Correlation analysis and ANOVA analysis by the software package SPSS version 21.0.

3.5 CONTAMINATION FACTOR (CF)

A common approach to estimate how much soil has been imparted anthropogenically with heavy metals is to calculate the Contamination Factor (CF) for metal concentrations above the un-

contaminated background levels (Pam *et al.*, 2013a). Pollution is measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material (Dasaram *et al.*, 2010; Fagbote *et al.*, 2010). The CF method normalizes the measured heavy metal content with respect to samples collected (Table 3.1). (Oguntimehin, and Ipinmoroti, 2008; Fagbote *et al.*, 2010; Huu *et al.*, 2010; Pam *et al.*, 2013). CF is calculated according to the following equation:

$$\text{Contamination Factor (CF)} = \frac{\text{Concentration of metal in sample from the study area}}{\text{Concentration of metal in control or reference}}$$

As the CF values increase, the contributions from the anthropogenic source increase.

Table 3.1: Categories of contamination factor (Dasaram *et al.*, 2010)

Contamination factor	Category
CF < 1	Low contamination factor
1 < CF < 3	Moderate contamination factor
3 < CF < 6	Considerable contamination factor
CF > 6	Very high contamination factor

3.6 GEOACCUMULATION INDEX

The extent of heavy metal contamination was assessed using geoaccumulation index (Igeo) and the Igeo values were calculated using equation described by Onder *et al.* (2007), Mediolla *et al.* (2008), Huu *et al.* (2010) and Okoro *et al.* (2013).

$$\text{Geoaccumulation index} = \text{Igeo} = \text{Log}_2 C_{\text{metal}}/1.5 C_{\text{ref. (control)}}$$

Where C_{metal} is the measured concentration of the heavy metal in the soil sample and

C_{ref} is the concentration of the metal in the reference or control sample.

The factor 1.5 is introduced to minimize the possible variations in the background or control values which may be attributed to lithogenic (natural factors affecting the spatial

distribution of topsoil mass magnetic susceptibility) variations in the soil. The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as indicated in table 3.2.

Table 3.2: Categories for Geo-accumulation index (Igeo) (Muller, 1969)

Igeo value	Igeo class	Value of soil quality
$I_{geo} < 0$	0	Unpolluted
$0 \leq I_{geo} < 1$	1	Unpolluted to moderately polluted
$1 \leq I_{geo} < 2$	2	Moderately polluted
$2 \leq I_{geo} < 3$	3	Moderately to strongly polluted
$3 \leq I_{geo} < 4$	4	Strongly polluted
$4 \leq I_{geo} < 5$	5	Strongly to very strongly polluted
$I_{geo} \geq 5$	6	Very strongly polluted

3.7 POLLUTION LOAD INDEX (PI)

The extent of heavy metal contamination of auto-mechanic workshops in Uwelu were evaluated by employing the method based on the pollution load index (PI) according to the equation:

$$PI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \times \dots \times CF_n)^{1/n}$$

Where n is the number of metals studied and CF is the contamination factor.

In this study, the contamination factor for each metal in the soil samples from the study area was calculated. The pollution load index was calculated based on the contamination factor for each metal in the sites. The PI provides simple but comparative means for assessing a site quality (Table 3.3).

Table 3.3: Categories of PI (Hakanson, 1980)

PI	Category
$PI < 1$	Low contamination factor indicating low contamination
$1 < PI < 3$	Moderate contamination factor
$3 < PI < 6$	Considerable contamination factor
$6 < PI$	Very high contamination factor

CHAPTER FOUR

4.0

RESULT AND DISCUSSION

Table 4.1: Physical and Heavy metal concentration of soil samples in the study area

	Ni (mg/kg)	Cr (mg/kg)	V (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	pH	EC (uS/cm)	TDS (mg/kg)
S1 0-5cm	81.67	26.59	43.69	0.22	0.29	9.12	4.97	78	39.78
S1 5-10cm	68.18	22.2	36.47	0.18	0.24	7.61	5.21	101	51
S1 10-15cm	64	20.84	34.23	0.17	0.23	7.14	5.31	55	28.05
S1 15-30cm	58.88	19.17	31.49	0.16	0.21	6.57	5.11	94	47.94
S2 0-5cm	109.07	35.51	58.34	0.29	0.39	12.18	5.26	92	46.92
S2 5-10cm	97.78	31.83	52.3	0.26	0.35	10.91	5.17	63	32.13
S2 10-15cm	93.8	30.54	50.17	0.25	0.33	10.47	4.99	78	39.78
S2 15-30cm	90.46	29.45	48.38	0.24	0.32	10.1	5.31	77	39.27
S3 0-5cm	29.4	9.57	15.73	0.08	0.1	3.28	4.89	68	34.68
S3 5-10cm	24.55	7.99	13.13	0.07	0.09	2.74	5.89	69	35.19
S3 10-15cm	23.04	7.5	12.32	0.06	0.08	2.57	5.32	85	43.35
S3 15-30cm	21.2	6.9	11.34	0.06	0.07	2.37	5.89	57	29.07
S4 0-5cm	39.27	12.78	21	0.11	0.14	4.38	5.27	89	45.39
S4 5-10cm	35.2	11.46	18.83	0.09	0.12	3.93	5.24	84	42.84
S4 10-15cm	16.26	5.3	8.7	0.04	0.06	1.82	5.34	64	32.64
S4 15-30cm	14.33	4.66	7.66	0.04	0.05	1.6	5.44	49	24.99
S5 0-5cm	79.73	28.62	49.77	0.26	0.32	9.89	5.09	92	41.78
S5 5-10cm	66.18	21.22	41.05	0.14	0.27	8.16	5.33	99	53.66
S5 10-15cm	61.5	19.51	37.02	0.11	0.24	6.76	5.49	65	23.08
S5 15-30cm	44.03	17.92	29.53	0.1	0.22	5.17	5.08	102	42.15
S6 0-5cm	98.54	32.41	51.34	0.31	0.38	11.94	5.28	100	49.11
S6 5-10cm	91.02	28.25	47.33	0.27	0.37	9.89	5.14	62	31.45
S6 10-15cm	86.26	26.78	44.49	0.26	0.35	9.34	5.05	81	37.29
S6 15-30cm	79.22	21.31	38.91	0.21	0.33	9.11	5.21	73	38.92
S7 0-5cm	38.23	10.15	14.78	0.11	0.13	3.94	4.94	72	44.92
S7 5-10cm	35.05	9.86	11.45	0.09	0.12	3.45	5.74	78	45.77
S7 10-15cm	32.11	9.15	10.28	0.08	0.09	2.86	5.63	92	52.41
S7 15-30cm	28.56	5.21	10.1	0.06	0.06	1.52	5.88	64	32.01
S8 0-5cm	36.04	29.92	23.55	0.21	0.19	6.12	5.39	92	51.59
S8 5-10cm	33.16	21.04	21.29	0.14	0.17	5.01	5.13	90	45.34
S8 10-15cm	21.98	15.25	18.41	0.09	0.11	3.33	5.56	75	36.82
S8 15-30cm	18.39	10.62	14.93	0.05	0.09	2.08	5.29	61	29.15

Table 4.2: Physical and Heavy metal concentration of soil control samples in the study area

	Ni (mg/kg)	Cr (mg/kg)	V (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	pH	EC (uS/cm)	TDS (mg/kg)
SC1 0-5cm	33.88	11.2	18.28	0.1	0.12	3.26	5.33	97	42.63
SC2 0-5cm	31.78	9.8	17.88	0.08	0.09	3.88	5.39	64	38.04
SC3 0-5cm	32.02	10.8	16.1	0.09	0.12	3.78	5.36	70	37.14
SC1 5-10cm	23.89	7.1	6.98	0.05	0.04	2.29	5.35	52	30.03
SC2 5-10cm	27.95	5.1	8.56	0.04	0.06	2.37	5.22	66	28.88
SC3 5-10cm	24.81	5.5	7.11	0.03	0.05	3.98	5.21	56	29.83
SC1 10-15cm	8.97	2.98	4.63	0.02	0.03	1.12	5.12	90	42.65
SC2 10-15cm	8.78	2.78	4.65	0.02	0.03	0.9	5.45	81	42.2
SC3 10-15cm	8.77	2.88	4.91	0.02	0.03	0.95	5.42	78	42.14
SC1 15-30cm	7.76	2.33	4.21	0.02	0.03	0.92	5.83	86	36.34
SC2 15-30cm	7.54	2.33	3.98	0.02	0.03	0.81	5.23	77	37.03
SC3 15-30cm	7.59	2.78	4.05	0.02	0.03	0.82	5.5	53	36.79

Table 4.3: Summary of physical and heavy metal concentration of soil samples in the study area

Profile	Statistics parameter	Ni (mg/kg)	Cr (mg/kg)	V (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	pH	EC (uS/cm)	TDS (mg/kg)
0-5cm	Mean	63.994	23.194	34.775	0.199	0.243	7.606	5.136	85.375	44.271
	S.E.	11.211	3.749	6.285	0.031	0.041	1.282	0.066	3.995	1.909
	Std. Dev.	31.710	10.604	17.778	0.089	0.117	3.625	0.188	11.300	5.399
	Min.	29.4	9.57	14.78	0.08	0.1	3.28	4.89	68	34.68
	Max.	109.07	35.51	58.34	0.31	0.39	12.18	5.39	100	51.59
5-10cm	Mean	56.390	19.231	30.231	0.155	0.216	6.463	5.356	80.750	42.173
	S.E.	10.005	3.078	5.654	0.027	0.038	1.095	0.104	5.431	2.982
	Std. Dev.	28.297	8.707	15.993	0.077	0.108	3.098	0.293	15.360	8.434
	Min.	24.55	7.99	11.45	0.07	0.09	2.74	5.13	62	31.45
	Max.	97.78	31.83	52.3	0.27	0.37	10.91	5.89	101	53.66
10-15cm	Mean	49.869	16.859	26.953	0.133	0.186	5.536	5.336	74.375	36.678
	S.E.	10.800	3.251	5.824	0.030	0.041	1.177	0.080	4.334	3.212
	Std. Dev.	30.547	9.194	16.471	0.085	0.116	3.328	0.228	12.258	9.084
	Min.	16.26	5.3	8.7	0.04	0.06	1.82	4.99	55	23.08
	Max.	93.8	30.54	50.17	0.26	0.35	10.47	5.63	92	52.41
15-30cm	Mean	44.384	14.405	24.043	0.115	0.169	4.815	5.401	72.125	35.438
	S.E.	10.276	3.160	5.355	0.028	0.041	1.226	0.113	6.476	2.768
	Std. Dev.	29.066	8.938	15.147	0.078	0.117	3.469	0.320	18.318	7.830
	Min.	14.33	4.66	7.66	0.04	0.05	1.52	5.08	49	24.99
	Max.	90.46	29.45	48.38	0.24	0.33	10.1	5.89	102	47.94
Control 0 - 5cm	Mean	32.56	10.6	17.42	0.09	0.11	3.64	5.36	77	39.27
	S.E.	0.664	0.416	0.670	0.006	0.010	0.192	0.017	10.149	1.700
	Std. Dev.	1.149	0.721	1.161	0.010	0.017	0.333	0.030	17.578	2.944
	Min.	31.78	9.8	16.1	0.08	0.09	3.26	5.33	64	37.14
	Max.	33.88	11.2	18.28	0.1	0.12	3.88	5.39	97	42.63
Control 5 - 10cm	Mean	25.55	5.9	7.55	0.04	0.05	2.88	5.26	58	29.58
	S.E.	1.229	0.611	0.506	0.006	0.006	0.550	0.045	4.163	0.355
	Std. Dev.	2.129	1.058	0.877	0.010	0.010	0.953	0.078	7.211	0.614
	Min.	23.89	5.1	6.98	0.03	0.04	2.29	5.21	52	28.88
	Max.	27.95	7.1	8.56	0.05	0.06	3.98	5.35	66	30.03
Control 10 - 15cm	Mean	8.84	2.88	4.73	0.02	0.03	0.99	5.33	83	42.33
	S.E.	0.065	0.058	0.090	0	0	0.067	0.105	3.606	0.161
	Std. Dev.	0.113	0.100	0.156	0	0	0.115	0.182	6.245	0.279
	Min.	8.77	2.78	4.63	0.02	0.03	0.9	5.12	78	42.14
	Max.	8.97	2.98	4.91	0.02	0.03	1.12	5.45	90	42.65
Control 15 - 30cm	Mean	7.63	2.48	4.08	0.02	0.03	0.85	5.52	72	36.72
	S.E.	0.067	0.150	0.068	0	0	0.035	0.173	9.849	0.202
	Std.Dev.	0.115	0.260	0.118	0	0	0.061	0.300	17.059	0.350
	Minimum	7.54	2.33	3.98	0.02	0.03	0.81	5.23	53	36.34
	Maximum	7.76	2.78	4.21	0.02	0.03	0.92	5.83	86	37.03

Table 4.4: Test of Difference between Control and soil samples

	SAMPLES	CONTROL	
	0-5cm	0-5cm	P-Value
Ni	63.99±11.21	32.56±0.66	p>0.05
Cr	23.19±3.75	10.6±0.42	p>0.05
V	34.78±6.29	17.42±0.67	p>0.05
Pb	0.199±0.031	0.09±0.01	p>0.05
Cd	0.24±0.041	0.11±0.01	p>0.05
Zn	7.61±1.28	3.64±0.19	p>0.05
pH	5.14±0.07	5.36±0.02	p>0.05
EC	85.38±3.995	77±10.15	p>0.05
TDS	44.27±1.91	39.27±1.7	p>0.05
	5-10cm	5-10cm	P-Value
Ni	56.39±10.01	25.55±1.23	p>0.05
Cr	19.23±3.08	5.9±0.61	p<0.05
V	30.23±5.65	7.55±0.51	p<0.05
Pb	0.16±0.027	0.04±0.01	p<0.05
Cd	0.22±0.038	0.05±0.01	p<0.05
Zn	6.46±1.1	2.88±0.56	p>0.05
pH	5.36±0.104	5.26±0.05	p>0.05
EC	80.75±5.43	58±4.16	p<0.05
TDS	42.17±2.98	29.58±0.36	p<0.05
	10-15cm	10-15cm	P-Value
Ni	49.87±10.8	8.84±0.07	p>0.05
Cr	16.86±3.25	2.88±0.06	p<0.05
V	26.95±5.82	4.73±0.09	p>0.05
Pb	0.13±0.03	0.02±0.0	p>0.05
Cd	0.19±0.04	0.03±0.0	p>0.05
Zn	5.54±1.18	0.99±0.07	p<0.05
pH	5.34±0.08	5.33±0.11	p>0.05
EC	74.38±4.33	83±3.61	p>0.05
TDS	36.68±3.21	42.33±0.16	p>0.05
	15-30cm	15-30cm	P-Value
Ni	44.38±10.28	7.63±0.07	p>0.05
Cr	14.41±3.16	2.48±0.15	p>0.05
V	24.043±5.36	4.08±0.07	p>0.05
Pb	0.12±0.028	0.02±0.0	p>0.05
Cd	0.17±0.041	0.03±0.0	p>0.05
Zn	4.82±1.23	0.85±0.04	p>0.05
Ph	5.4±0.11	5.52±0.17	p>0.05
EC	72.13±6.48	72±9.85	p>0.05
TDS	35.44±2.77	36.72±0.2	p>0.05

Table 4.5: Contamination factor (CF) of heavy metals from soil sample within the study area

Depth	Ni	Cr	V	Pb	Cd	Zn
S1 0-5cm	1.97±0.97	2.19±1	2.00±1.02	2.21±0.98	2.20±1.06	2.09±1
S1 5-10cm	2.30±1.15	3.26±1.48	4.00±2.12	3.88±1.91	4.33±2.16	2.24±1.08
S1 10-15cm	5.64±3.46	5.85±3.19	5.70±3.48	6.63±4.24	6.21±3.87	5.59±3.36
S1 15-30cm	5.82±3.81	5.81±3.6	5.89±3.71	5.75±3.91	5.63±3.89	5.66±4.08

Values are means of all samples collected ± standard deviation

Table 4.6: Geo accumulation Index (Igeo) of heavy metals of soils in the study area

Depth	Ni	Cr	V	Pb	Cd	Zn
S1 0-5cm	0.22±0.75	0.37±0.8	0.22±0.81	0.41±0.74	0.39±0.76	0.32±0.76
S1 5-10cm	0.45±0.75	0.97±0.74	1.21±0.85	1.21±0.72	1.36±0.77	0.42±0.75
S1 10-15cm	1.64±0.98	1.74±0.91	1.64±1.01	1.87±0.97	1.77±1.00	1.64±0.95
S1 15-30cm	1.66±1.00	1.67±1.01	1.69±1.00	1.64±1.00	1.55±1.12	1.55±1.13

Values are means of all samples collected ± standard deviation

Table 4.7: Pollution Load Index (PI) of heavy metals of soils from the study area

Depth	Ni	Cr	V	Pb	Cd	Zn
0 - 5cm	2.109853	2.426892	2.110563	2.498223	2.460886	2.298848
5 – 10cm	2.595925	4.20007	5.260723	5.271965	6.016523	2.532445
10 – 15cm	7.806658	8.550145	7.82501	9.679961	8.79549	7.818508
15 – 30cm	7.982446	8.033098	8.178996	7.812422	7.213364	7.187169

Table 4.8: Correlation matrix of heavy metal in soil (0-5cm) from the study area

	<i>Ni</i>	<i>Cr</i>	<i>V</i>	<i>Pb</i>	<i>Cd</i>	<i>Zn</i>
Ni	1					
Cr	0.80546	1				
V	<u>0.97727</u>	<u>0.866</u>	1			
Pb	<u>0.89392</u>	<u>0.9629</u>	<u>0.9287</u>	1		
Cd	<u>0.97716</u>	<u>0.9001</u>	<u>0.9859</u>	<u>0.97</u>	1	
Zn	<u>0.97437</u>	<u>0.9075</u>	<u>0.9846</u>	<u>0.97</u>	<u>0.9995</u>	1

$r(0.05)(\infty 2) \text{ df}(6) = 0.707$

$r(0.01)(\infty 2) \text{ df}(6) = 0.834$

Bold values = Significant ($P < 0.05$)

Bold values with underline = Highly Significant ($P < 0.01$)

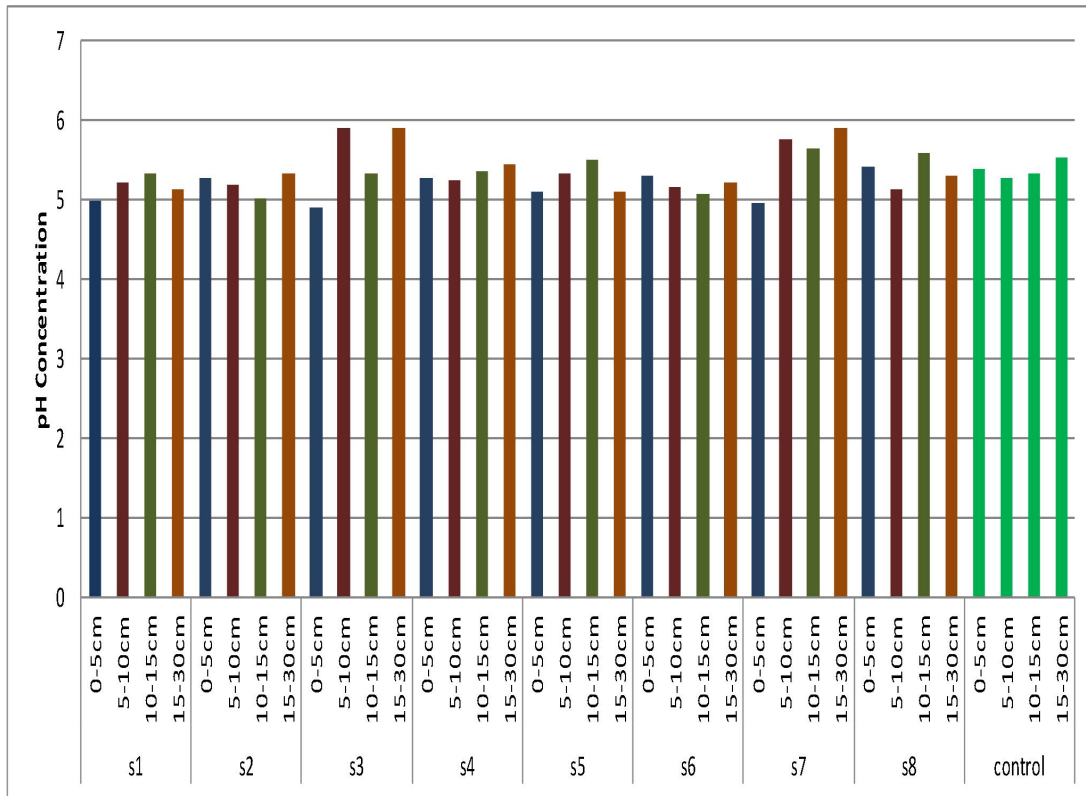


Figure 4.1: Comparative pH concentration and control of soil samples from the study area

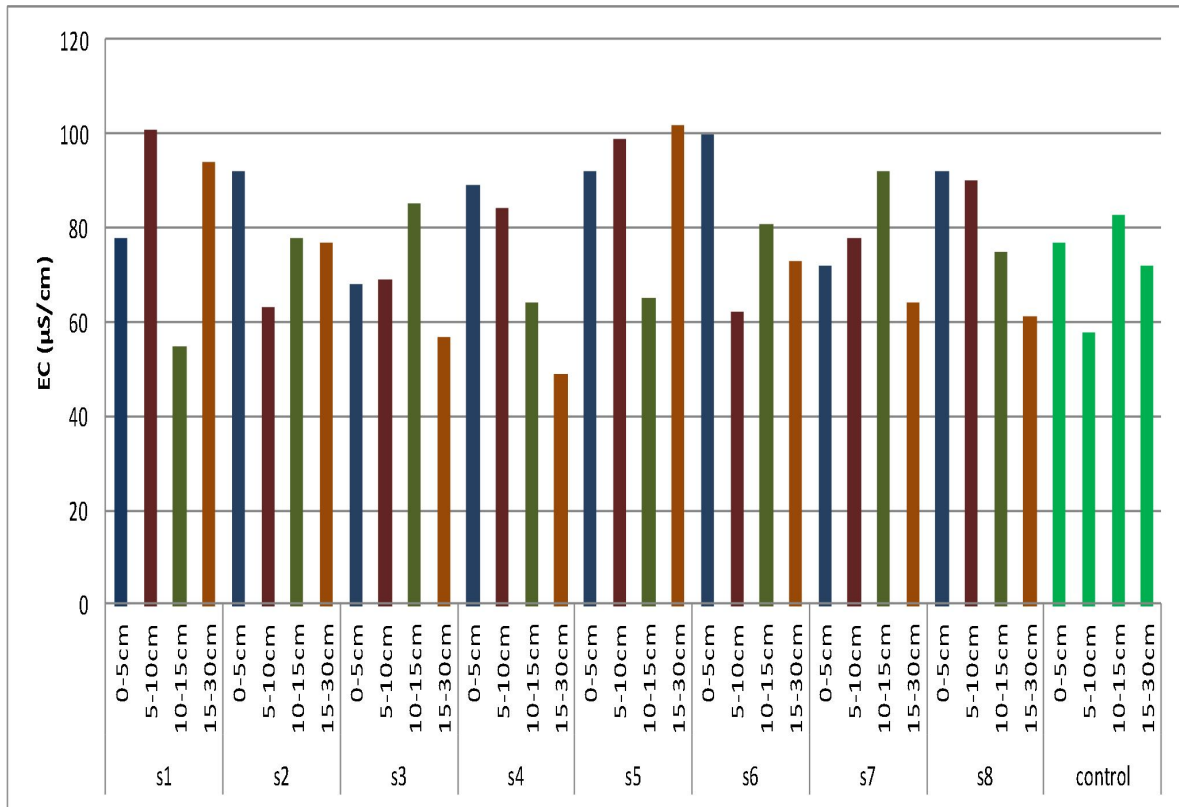


Figure 4.2: Comparative Electrical Conductivity concentration and control of soil samples from the study area

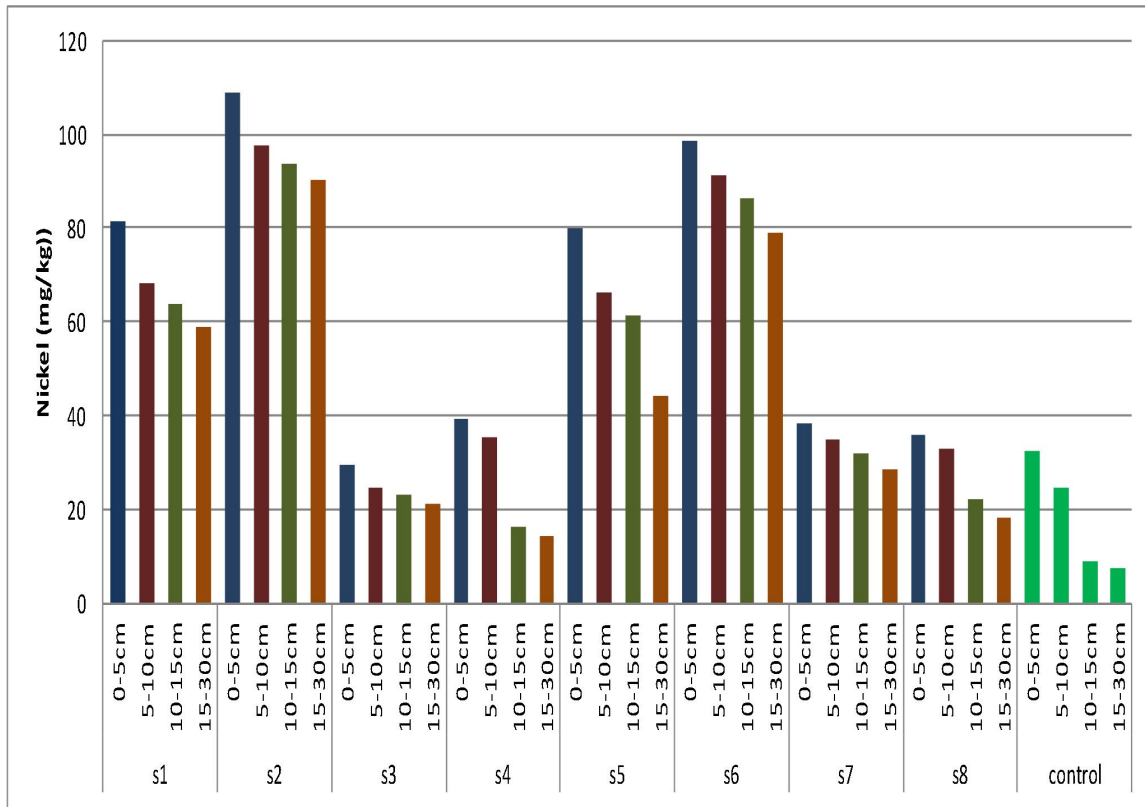


Figure 4.3: Comparative Nickel concentration and control of soil samples from the study area

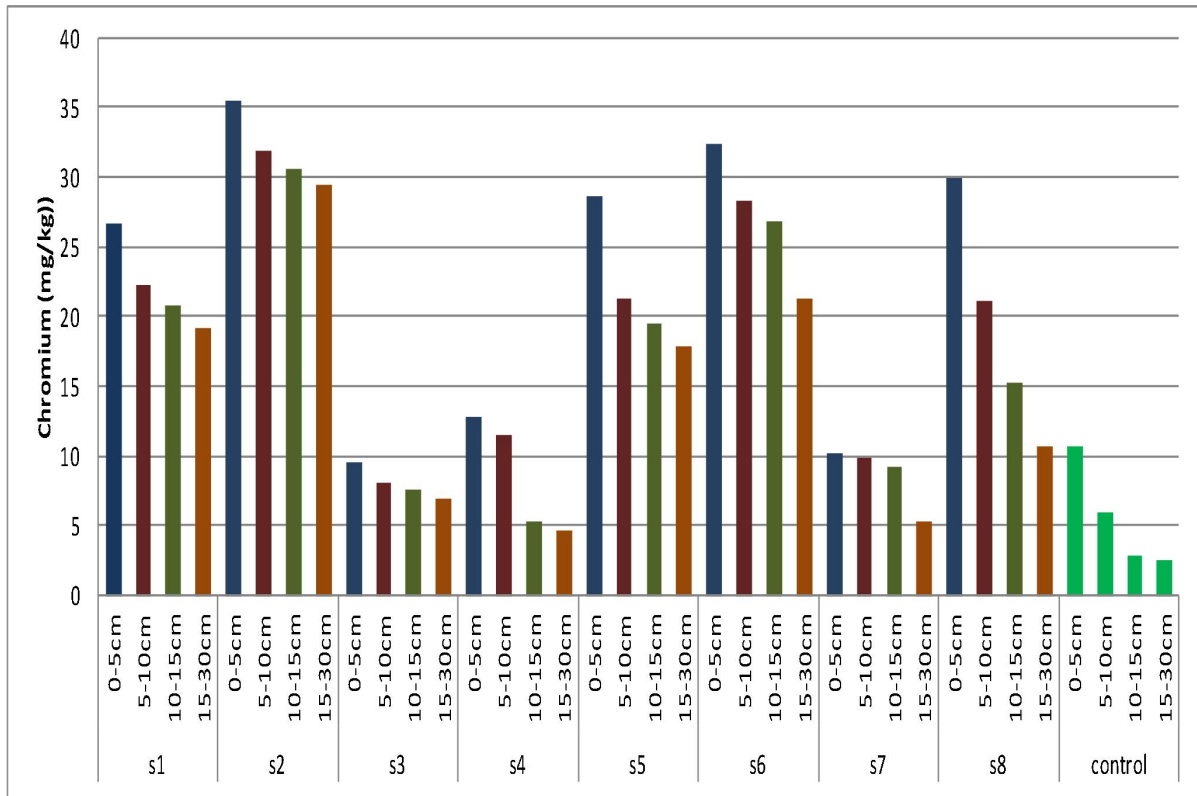


Figure 4.4: Comparative Chromium concentration and control of soil samples from the study area

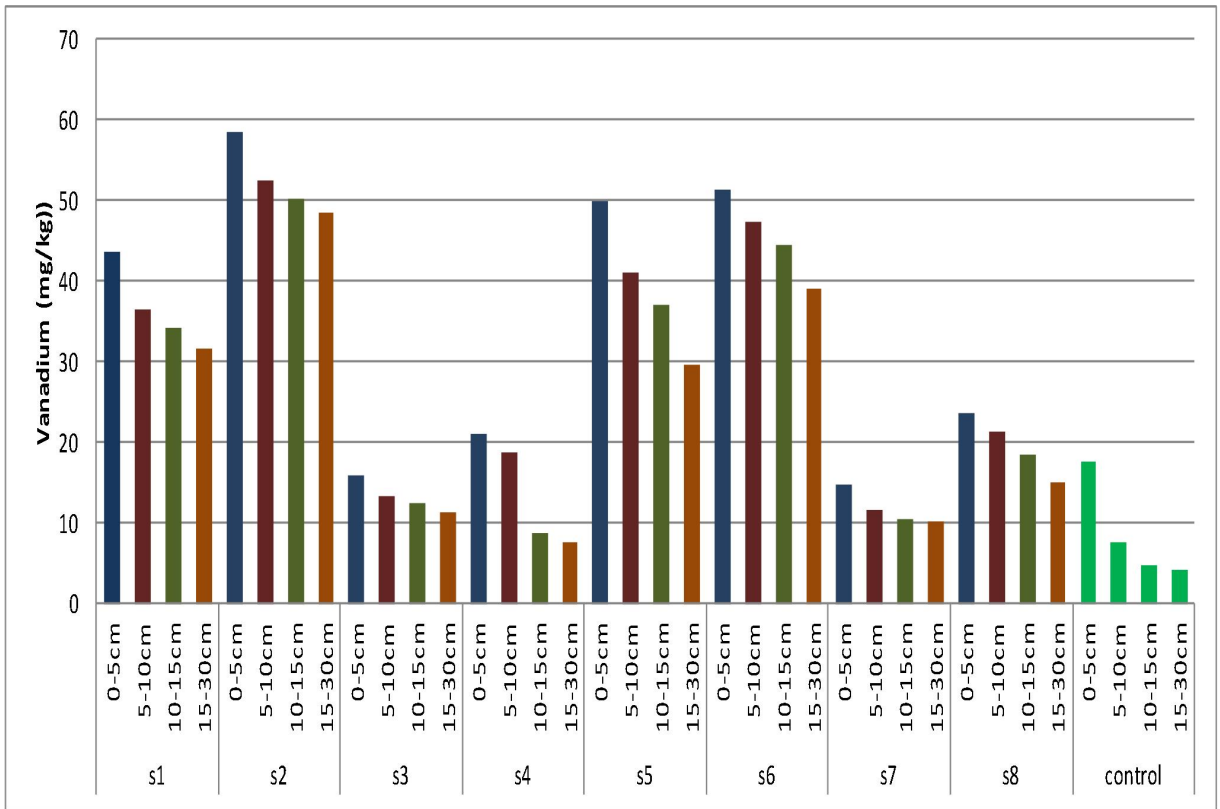


Figure 4.5: Comparative Vanadium concentration and control of soil samples from the study area

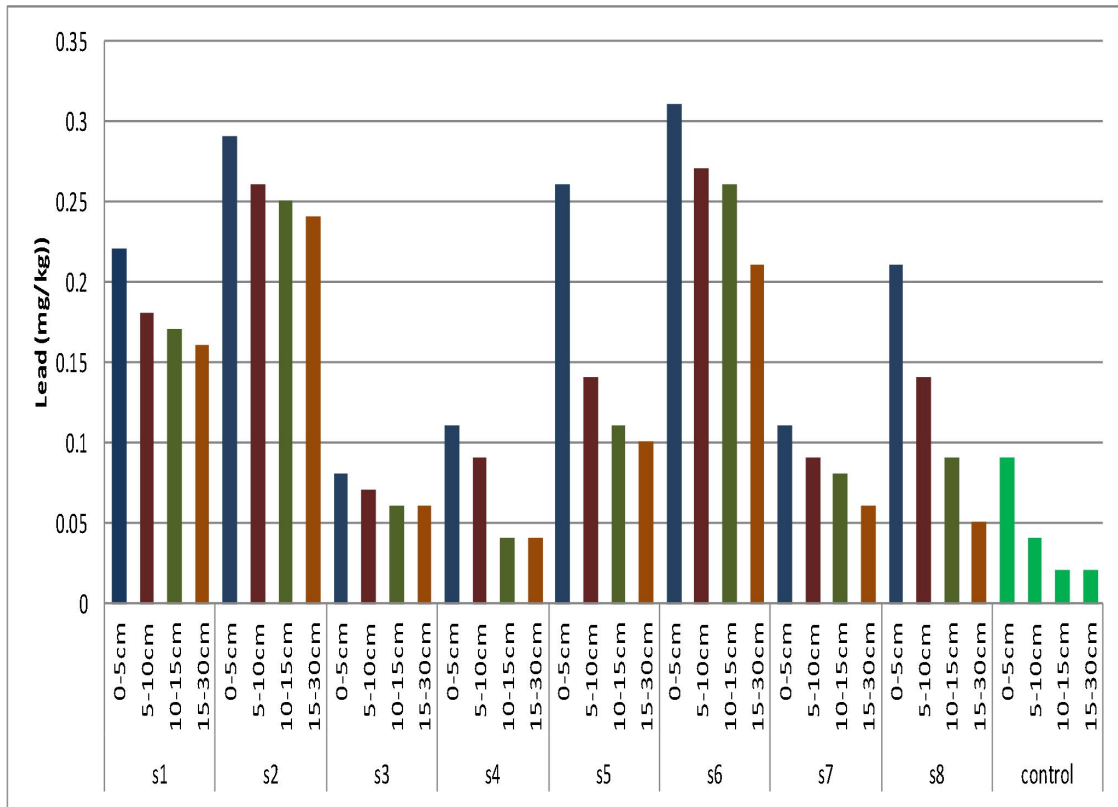


Figure 4.6: Comparative Lead concentration and control of soil samples from the study area

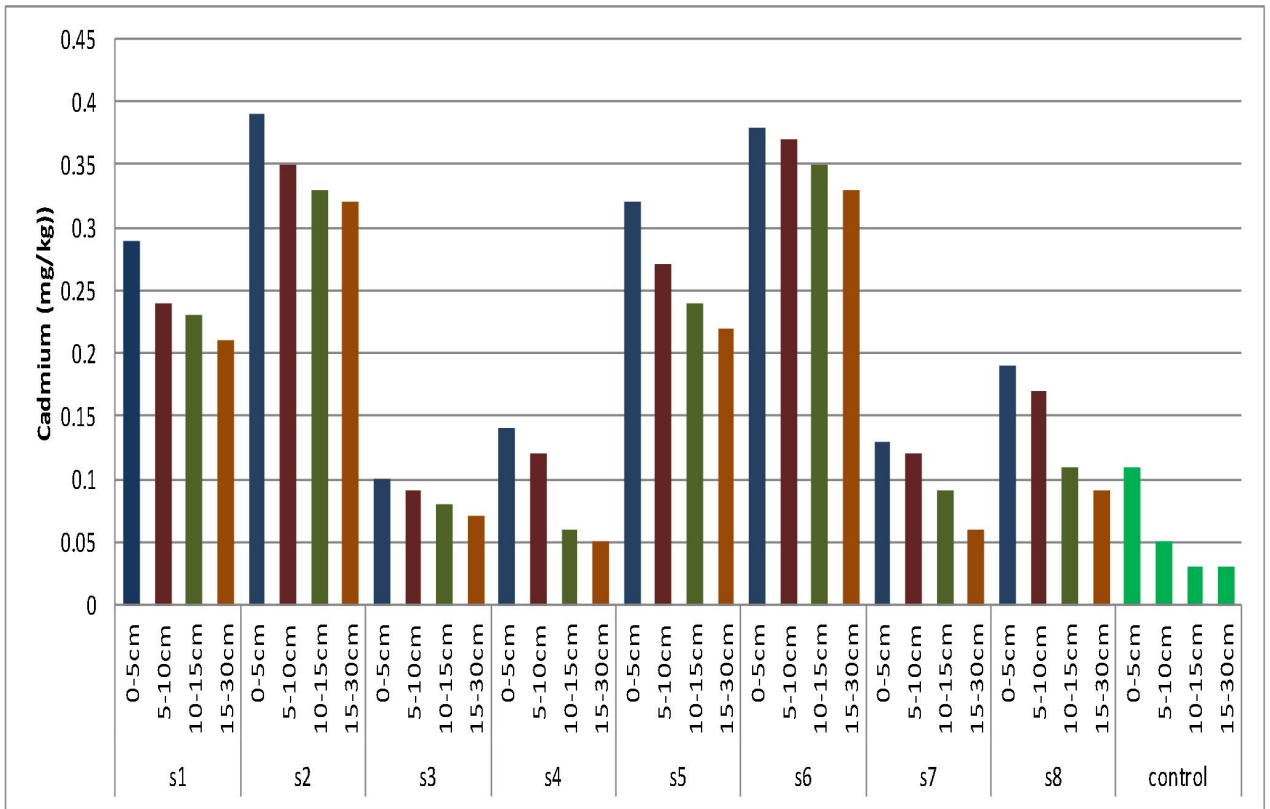


Figure 4.7: Comparative Cadmium concentration and control of soil samples from the study area

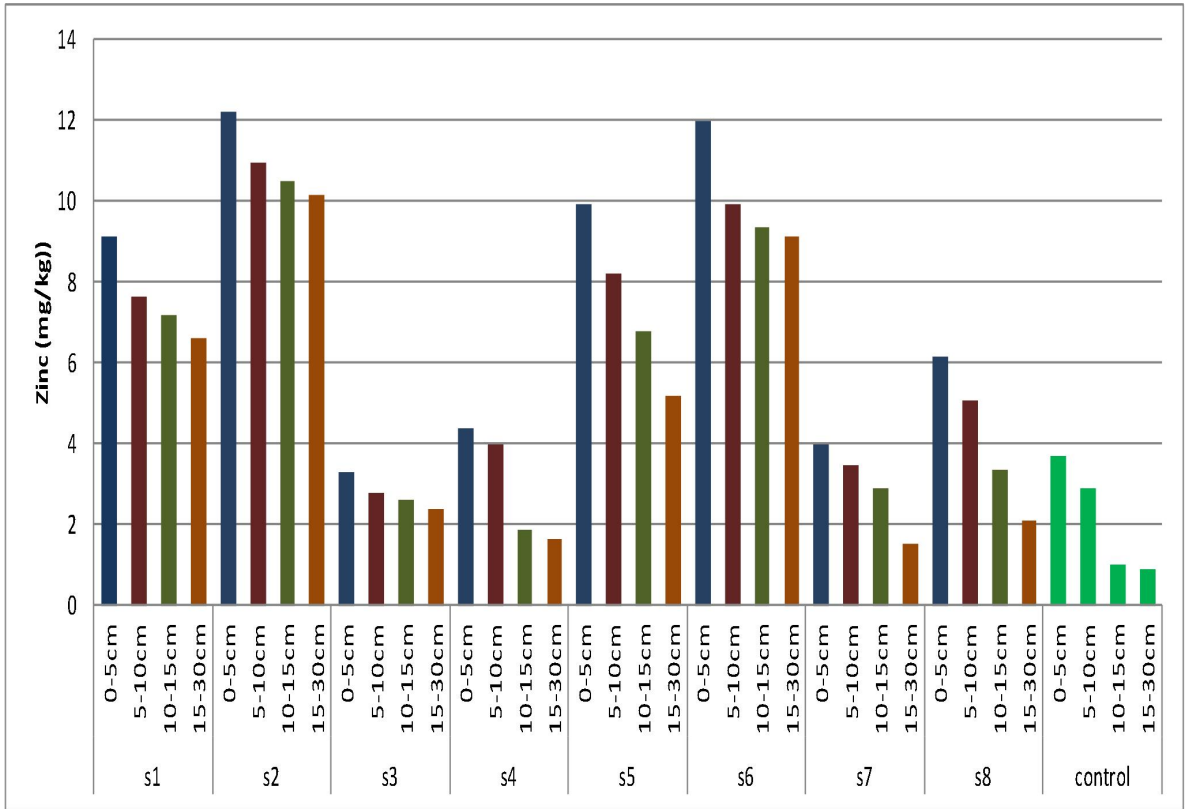


Figure 4.8: Comparative Zinc concentration and control of soil samples from the study area

4.1 DATA PRESENTATION

Heavy metal parameters analyzed for soil were Nickel, Chromium, Vanadium, Lead, Cadmium, and Zinc (Table 4.1). Physical parameters analyzed for soil were pH, Electrical conductivity and total dissolved solids (Table 4.1).

4.2 DESCRIPTIVE ANALYSIS

The summary of physical and heavy metal analysis which includes mean, standard error, standard deviation, minimum, maximum and control values for soil samples were presented in Table 4.3.

4.3 ANOVA

The comparison of soil samples from the study area with the control group was analyzed using analysis of variance, and the results are presented in Table 4.4.

For the topsoil depth of 0-5cm, there was no significant difference observed between the control group and the soil samples.

However, at a subsoil depth of 5-10cm, significant differences were found between the control group and the study area samples in terms of Chromium, Vanadium, Lead, Cadmium, Electrical Conductivity, and Total Dissolved Solids. Similarly, at a subsoil depth of 10-15cm, there were significant differences between the control group and the study area samples in terms of Chromium and Zinc. Lastly, at a subsoil depth of 15-30cm, there was no significant difference observed between the control group and the soil samples collected from the study area.

4.4 CORRELATION

The significant relationship between concentrations of heavy metals in the top soil (0–5cm) was established by performing correlation analysis (Table 4.8). There was positive high significant

correlation at $p < 0.01$ between all the heavy metals except Nickel and Chromium which has significant correlation at $p < 0.05$.

4.5 CONTAMINATION FACTOR

The contamination factor (Cf) was calculated by comparing the concentration of heavy metals in the study area with the background value represented by the control sample (see Table 4.5). Cf values ranging from 0.5 to 1.5 indicate that the metals are predominantly derived from natural sources, such as crust materials or natural processes. However, Cf values greater than 1.5 suggest that the sources are likely to be anthropogenic, such as auto-mechanic shops and workshops in this particular study.

The Cf values revealed that all heavy metals, including Cadmium and Lead with the highest Cf values, showed a range of contamination levels from no contamination to considerable contamination in the topsoil (0-5cm). In the subsoil at a depth of 5-10cm, Cadmium and Vanadium exhibited the highest Cf values, indicating a range of contamination from moderate to very high. Similarly, at a depth of 10-15cm, Lead and Cadmium had the highest Cf values, indicating contamination ranging from moderate to very high. In the subsoil at a depth of 15-30cm, Lead, Zinc, and Chromium showed the highest Cf values, indicating contamination ranging from moderate to very high. Furthermore, at profile depths of 10-15cm and 15-30cm, all heavy metals showed very high contamination values. This suggests that the subsoil at these depths is heavily contaminated due to heavy metal leaching from the topsoil as a result of anthropogenic activities.

4.6 GEO-ACCUMULATION INDEX (I-GEO)

Table 4.6 shows the geochemical index (I-geo) values for the soil samples. According to the I-geo data, the topsoil (0–5 cm) showed a variety of heavy metal contamination levels, from moderate contamination to uncontaminated. Vanadium, lead, and cadmium levels in the subsurface at a depth of 5 to 10 cm ranged from uncontaminated to moderately/highly contaminated. Lead showed contamination levels ranging from no contamination to substantial

contamination for the subsoil at a depth of 10–15 cm. Similarly, all heavy metals showed contamination levels ranging from no contamination to moderate/high contamination in the subsoil at a depth of 15–30 cm. Cadmium had the highest I-geo value of all the heavy metals, measured at a depth of 0–5 cm in the topsoil. In a similar vein, the greatest I-geo values were found in the subsurface at depths of 5–10 cm for cadmium, 10–15 cm for lead, and 15–30 cm for lead.

4.7 POLLUTION LOAD INDEX (PLI)

The PLI for the soil samples are presented in Table 4.7. The PLI revealed that the study area showed moderate contamination in top soil, 0-5cm, moderate to considerable contamination in sub soil, 5-10cm, very high contamination in sub soil 10-15cm and 15-30cm. The PLI increased with depth.

4.8 PHYSICAL CHARACTERISTICS

4.8.1 HYDROGEN POTENTIAL (pH)

pH, also known as hydrogen potential, plays a crucial role in determining soil activity. It is widely recognized that pH is an important soil characteristic that significantly influences solute concentration and the sorption/desorption of contaminants in the soil (Kadem et al., 2004). As indicated in Table 4.3, pH values vary across different depths within each location. In the topsoil (0-5cm), pH values ranged between 4.89 and 5.39, while in the subsoil at a depth of 5-10cm, pH values ranged from 5.13 to 5.89. Similarly, in the subsoil at depths of 10-15cm and 15-30cm, pH values varied between 4.99-5.63 and 5.08-5.89, respectively. Furthermore, the control pH values ranged from 5.33 to 5.39 in the topsoil (0-5cm), 5.21 to 5.35 in the subsoil at a depth of 5-10cm, 5.12 to 5.45 in the subsoil at a depth of 10-15cm, and 5.23 to 5.83 in the subsoil at a depth of 15-30cm.

No significant difference was observed between the control pH values and the pH values of the study area. Higher pH levels can potentially reduce the mobility of certain metal species in the soil, while lower pH values typically enhance the distribution and transport of metals. The distribution of pH values is illustrated in Figure 4.1.

4.8.2 ELECTRICAL CONDUCTIVITY (EC)

paraphrase: Soil electrical conductivity (EC) is a measurement that indicates the level of salt content or salinity in the soil. It serves as a significant indicator of soil health, influencing various factors such as crop yields, crop suitability, plant nutrient availability, and the activity of soil microorganisms. These factors, in turn, impact essential soil processes including the emission of greenhouse gases like nitrogen oxides, methane, and carbon dioxide.

The mean and standard deviation of soil electrical conductivity values for the study area are as follows: 85.38 ± 11.3 $\mu\text{S/cm}$ in the topsoil (0-5cm), 80.75 ± 15.36 $\mu\text{S/cm}$ in the subsoil at a depth of 5-10cm, 74.38 ± 12.26 $\mu\text{S/cm}$ in the subsoil at a depth of 10-15cm, and 72.13 ± 18.32 $\mu\text{S/cm}$ in the subsoil at a depth of 15-30cm. As for the control samples, the mean electrical conductivity values are 77 ± 17.58 $\mu\text{S/cm}$ in the topsoil (0-5cm), 58 ± 7.21 $\mu\text{S/cm}$ in the subsoil at a depth of 5-10cm, 83 ± 6.25 $\mu\text{S/cm}$ in the subsoil at a depth of 10-15cm, and 72 ± 17.06 $\mu\text{S/cm}$ in the subsoil at a depth of 15-30cm. The distribution of electrical conductivity values is visually represented in Figure 4.2.

4.9 HEAVY METAL

4.9.1 NICKEL (Ni^{2+})

Nickel is generally distributed uniformly throughout the soil profile, and the typical nickel content in soil varies widely depending on the parent rock. Elevated levels of nickel in surface soils are associated with soil formation processes and anthropogenic contamination, primarily attributed to agricultural and industrial activities.

In the topsoil (0-5cm), the mean, minimum, and maximum concentrations of nickel were recorded as 63.99 ± 31.71 mg/kg, 29.4 mg/kg, and 109.07 mg/kg, respectively. In the subsoil at a depth of 5-10cm, the corresponding values were 56.29 ± 28.3 mg/kg, 24.55 mg/kg, and 97.78 mg/kg. Similarly, in the subsoil at depths of 10-15cm and 15-30cm, the mean, minimum, and

maximum nickel concentrations were 49.87 ± 30.55 mg/kg, 16.26 mg/kg, 93.8 mg/kg, and 44.38 ± 29.07 mg/kg, 14.33 mg/kg, 90.46 mg/kg, respectively.

For the control samples, the mean nickel concentrations were 32.56 ± 1.15 mg/kg in the topsoil (0-5cm), 25.55 ± 2.13 mg/kg in the subsoil at a depth of 5-10cm, 8.84 ± 0.11 mg/kg in the subsoil at a depth of 10-15cm, and 7.63 ± 0.11 mg/kg in the subsoil at a depth of 15-30cm. There was no significant difference observed between nickel concentrations in the study area and the control samples across all depth profiles.

A strong positive correlation was found between nickel and all other heavy metals. It is worth noting that high levels of nickel can lead to various types of cancer in animals, affecting different parts of their bodies. The primary sources of nickel contamination in soil include metal plating industries, the combustion of fossil fuels, nickel mining, and electroplating. The distribution of nickel concentrations is depicted in Figure 4.3.

4.9.2 CHROMIUM (Cr⁶⁺)

Chromium (Cr) is a hard, gray metal that is commonly found in nature in its trivalent state. Small amounts of hexavalent chromium (Chromium (VI)) compounds are also present. Chromite (FeOCr₂O₃) is the sole ore that contains a significant amount of chromium. However, the ore is not found in its pure form, and the highest grade of chromite ore contains approximately 55% chromic oxide.

In the topsoil (0-5cm), the minimum and maximum chromium values were recorded as 9.57 mg/kg and 35.51 mg/kg, respectively. In the subsoil at a depth of 5-10cm, the corresponding values were 7.99 mg/kg and 31.83 mg/kg. Similarly, in the subsoil at depths of 10-15cm and 15-30cm, the minimum and maximum chromium concentrations were 5.3 mg/kg and 30.54 mg/kg, and 4.66 mg/kg and 29.45 mg/kg, respectively.

For the control samples, the mean chromium concentrations were 10.6 ± 0.72 mg/kg in the topsoil (0-5cm), 5.9 ± 1.06 mg/kg in the subsoil at a depth of 5-10cm, 2.88 ± 0.1 mg/kg in the subsoil at a

depth of 10-15cm, and 2.48 ± 0.26 mg/kg in the subsoil at a depth of 15-30cm. Generally, the chromium values from the study area were higher than those from the control samples.

Hexavalent chromium can be toxic, particularly when inhaled. It can cause damage to the lining of the nose, throat, and lungs. Studies of workers in chromium processing factories have classified hexavalent chromium as a known human carcinogen due to chronic inhalation exposure. Exposure to chromium can also have adverse effects on the gastrointestinal tract, liver, and kidneys.

Figure 4.4 displays the distribution of chromium concentrations in the study area.

4.9.3 VANADIUM (V^{2+})

Vanadium is a shiny, silvery-white metal with no odor. It can sometimes have a crystalline appearance. Vanadium readily reacts with various substances and forms a wide range of compounds that exhibit different colors. The primary sources of vanadium releases are likely to be oil refineries and the combustion of fossil fuels, as vanadium naturally occurs in these materials. Steelworks and other industries that utilize vanadium may also contribute to its release into the environment.

In the topsoil (0-5cm), the mean \pm standard deviation of vanadium concentration was recorded as 34.78 ± 17.78 mg/kg. In the subsoil at a depth of 5-10cm, the concentration was 30.23 ± 15.99 mg/kg. Similarly, in the subsoil at depths of 10-15cm and 15-30cm, the mean \pm standard deviation of vanadium concentration was 26.95 ± 16.47 mg/kg and 24.04 ± 15.15 mg/kg, respectively.

For the control samples, the mean vanadium concentrations were 17.42 ± 1.16 mg/kg in the topsoil (0-5cm), 7.55 ± 0.88 mg/kg in the subsoil at a depth of 5-10cm, 4.73 ± 0.16 mg/kg in the subsoil at a depth of 10-15cm, and 4.08 ± 0.12 mg/kg in the subsoil at a depth of 15-30cm. There was no significant difference observed between vanadium concentrations in the study area and the control samples, except in the subsoil at a depth of 5-10cm.

A strong positive correlation was found between vanadium and all other heavy metals. Vanadium can enter the body through inhalation of air containing vanadium, ingestion of food or water containing vanadium, or dermal contact with vanadium. Exposure to vanadium may affect the central nervous system, leading to symptoms such as headaches and tremors. The full effects of vanadium ingestion on human health are not well-documented, but some studies suggest that symptoms may include abdominal cramps, diarrhea, and a green coloration of the tongue. Dermal contact with vanadium compounds can cause skin irritation and dermatitis.

The distribution of vanadium in the study area is depicted in Figure 4.5.

4.9.4 LEAD (Pb²⁺)

Lead is a highly prevalent environmental contaminant found in soil, and its presence poses a significant threat to human health. It is especially dangerous for young children, as lead is a toxic element that can have severe effects on their well-being. Various forms of lead can be found in the environment, with a significant portion present in the soil. This increases the risk of lead exposure during human activities.

In the study area, soil samples were collected at different depths, and the concentrations of lead were measured. The mean concentration of lead in the topsoil (0-5cm) was recorded as 0.199 ± 0.09 mg/kg, with a minimum value of 0.08 mg/kg and a maximum value of 0.31 mg/kg. In the subsoil (5-10cm), the mean concentration was 0.155 ± 0.08 mg/kg, with a minimum value of 0.07 mg/kg and a maximum value of 0.27 mg/kg. Similar patterns were observed in the subsoil at depths of 10-15cm and 15-30cm, with mean concentrations of 0.133 ± 0.09 mg/kg and 0.115 ± 0.08 mg/kg, respectively.

Control samples, which represent values without contamination, showed lower lead concentrations compared to the study area. The mean concentration in the topsoil control sample was 0.09 ± 0.01 mg/kg, while in the subsoil at depths of 5-10cm, 10-15cm, and 15-30cm, the mean concentrations were 0.04 ± 0.01 mg/kg, 0.02 ± 0.0 mg/kg, and 0.02 ± 0.0 mg/kg, respectively.

Overall, there was no significant difference between the profile samples from the study area and the control samples, except at a depth of 5-10cm, where a difference was observed.

Lead is known to have a strong positive correlation with other heavy metals. Its poisoning can lead to various harmful effects, including neurological and developmental impairments. Exposure to lead primarily occurs through ingestion, inhalation, and contact with the skin. The extent of harm caused by lead depends on factors such as the dose of exposure, the frequency and duration of exposure, and other environmental conditions.

Children, particularly young ones, are more vulnerable to lead poisoning due to their smaller size, their tendency to put objects in their mouths, and their need for essential nutrients for growth and development. Children with poor nutrition, especially those lacking calcium, are at even higher risk, as their bodies may absorb lead as a substitute for the missing calcium. While lead poisoning in adults is less common, it is a significant concern for pregnant women, as trace amounts of consumed lead can be passed on to the fetus.

The distribution of lead in the study area is depicted in Figure 4.6.

4.9.5 CADMIUM (Cd²⁺)

Cadmium in soils originates from natural and human activities. Natural sources include underlying bedrock and transported materials like glacial till and alluvium. Human activities contribute to cadmium contamination through aerial deposition, sewage sludge, manure, and the application of phosphate fertilizers. Compared to its mobility in air and water, cadmium has limited mobility in soils.

The highest and lowest recorded values for cadmium in the topsoil (0-5cm) were found in soil samples S2 and S3, respectively. In the subsoil at depths of 5-10cm, the maximum and minimum values were observed in soil samples S6 and S3, respectively. Similarly, in the subsoil at depths of 10-15cm and 15-30cm, the highest and lowest values were recorded in soil samples S2 and S4, as well as S6 and S4, respectively.

Control samples, which represent uncontaminated values, showed mean concentrations of 0.11 ± 0.02 mg/kg in the topsoil (0-5cm), 0.05 ± 0.01 mg/kg in the subsoil (5-10cm), and 0.03 ± 0.0 mg/kg in both the subsoil at depths of 10-15cm and 15-30cm. Cadmium did not exhibit a significant difference compared to the control samples, except in the 5-10cm profile. Additionally, cadmium displayed a strong positive correlation with other heavy metals.

Extensive research has been conducted on the impact of cadmium exposure on human health since the 1950s, following the occurrence of Itai Itai disease in Japan. This disease affected post-menopausal women with low levels of iron and zinc who consumed cadmium-contaminated rice. In the human body, cadmium primarily accumulates in the kidneys and can lead to kidney failure if levels reach a critical threshold. Studies have shown that kidney effects may be reversible at low exposure levels once cadmium exposure is reduced or eliminated. However, at high exposure levels, cadmium can also affect bones, leading to Itai Itai disease. The distribution of cadmium concentrations across the study area is presented in Figure 4.7.

4.9.6 ZINC (Zn^{2+})

Zinc, a naturally occurring element, is vital for the biological processes of all living organisms. The mean \pm standard deviation concentrations of zinc were recorded as 7.61 ± 3.63 mg/kg in the topsoil (0-5cm), 6.46 ± 3.1 mg/kg in the subsoil (5-10cm), 5.54 ± 3.33 mg/kg in the subsoil (10-15cm), and 4.82 ± 3.47 mg/kg in the subsoil (15-30cm). The control samples had mean concentrations of 3.64 ± 0.33 mg/kg in the topsoil (0-5cm), 2.88 ± 0.95 mg/kg in the subsoil (5-10cm), 0.99 ± 0.12 mg/kg in the subsoil (10-15cm), and 0.85 ± 0.06 mg/kg in the subsoil (15-30cm). In all profile depths, the zinc concentrations from the study area were higher than the control values. There was no significant difference between the zinc concentrations and the control values, except in the 10-15cm profile. Zinc exhibited a strong positive correlation with all other heavy metals. Excessive amounts of zinc can have direct toxic effects, leading to gastrointestinal and immunologic problems. High levels of zinc can also interfere with copper

absorption, resulting in copper deficiency symptoms. Through the food chain, zinc accumulates, leading to higher levels in meat compared to vegetables and fruits.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This research was conducted in the urban area of Benin City to assess the pollution levels generated by several auto workshops in the city. The findings of the investigation indicate that the soil in the study area is generally moderately acidic, creating favorable conditions for the leaching of heavy metals.

At soil depths of 0-5 cm and 15-30 cm, no significant difference was observed compared to control values. However, at soil depths of 5-10 cm and 10-15 cm, there was a significant difference between the control values and the levels of Chromium, Vanadium, Lead, Cadmium, Zinc, and Electrical Conductivity.

Strong positive correlations were found between all the heavy metals, except for Nickel and Chromium, which exhibited only a significant correlation. Cadmium, Vanadium, Lead, Zinc, and Chromium demonstrated Contamination Factor values greater than 1.5 in all the soil samples, indicating contamination from anthropogenic sources. Cadmium and Lead showed high geo-accumulation index values, suggesting moderate to heavy contamination.

The Pollution Load Index of the soil profiles revealed that the subsoil at depths of 10-15 cm and 15-30 cm exhibited the highest contamination levels with the highest PLI values.

The soil in the study area can be described as heavily polluted with heavy metals due to the activities of automobile spare parts markets and workshops in the vicinity.

5.2 RECOMMENDATION

- It is recommended that further studies on metal speciation should be carried out in order to ascertain the form in which the various metals exist since it may have effect on its mobility in the soil.
- Study of different remediation schemes is necessary to ascertain the most effective approach to remove metals from the soil.
- Refining techniques used for engine oil could be employed in order to conserve resources and also preserve our environment.
- It is recommended that government should provide appropriate places that will serve as automobile village where auto repairs are kept at safe distances from human habitation.
- Education and legislation on management of wastes in place such as auto-mechanic workshops should be intensified to forestall the effects of heavy metal related wastes on the environment, particularly on groundwater.
- Also, modern waste disposal facilities should be acquired by relevant authorities and appropriate waste disposal sites be chosen to avoid the injurious effects of indiscriminate disposal of used oils/lubricants, scrap metals etc.
- In addition, continuous monitoring and further studies on the level of these heavy metals should be carried out in the near future and at intervals to ascertain long-term effects of this anthropogenic impact.

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