GEOCHEMICAL CHARACTERISATION OF LEAD IN SOILS, SEDIMENTS AND DUSTS OF IBADAN AND LAGOS, SOUTHWESTERN NIGERIA

BY

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ABSTRACT

The presence of Heavy Metals (HM) in soils, sediments and dusts are good indicators of contaminations of urban environment. Lead (Pb) is of grave concern amongst other HM because of its toxic impact on the environment and human health. Previous studies on HM have focused on the determination of concentrations and spatial distribution in various Nigerian cities. However, the geochemical fate and nature of Pb in Nigeria's environmental media is relatively unknown. This study was therefore designed to quantify and characterize Pb in soils, sediments and dusts from Ibadan and Lagos, Southwestern Nigeria.

A total of seventy-three composite soils, 56 sediments, 17 road dusts and 10 representative rock samples were collected randomly from the cities of Ibadan and Lagos. Soil, sediment and dust samples were air-dried, screened, pulverised and sieved through 63µm nylon mesh. The sieved fractions and pulverised rock samples were digested using standard methods and analyzed for elemental components using Inductively Coupled Plasma-Mass Spectrometer, (ICP-MS). The chemical fractionations of Pb in the samples were determined by sequential analysis. Lead isotopes compositions of the samples were determined using quadrupole-based ICP-MS. Petrological and mineralogical analyses of rocks and other samples were determined using X-Ray Diffraction. The geochemical data were subjected to statistical analyses using Pearson correlation and R-mode factor analyses. Lead Isotopic Ratios (LIRs) and geo-accumulation indexes were used in evaluating and discriminating Pb sources.

The concentration (ppm) of Pb in soils, sediments and dusts for Lagos were: 21.0-1963.0; 23.0-830.0 and 22.0-830.0; while in Ibadan soils and sediments were: 13.0 - 470.0 and 17.0-3288.0; respectively. For rock samples from Ibadan and Lagos, the values were: 2.9-20.3 and 2.8-7.2 ppm. Chemical fractionation (%) of Pb were: organic-sulphide (42.78-82.45); reducible (8.23-27.20); carbonate (9.00-43.60) and exchangeable (0.01-0.23) phases, respectively. Lead isotopes (ppm) showed that ^{204}Pb ranged 1.72-47.41; ^{206}Pb, 30.69-779.68; ^{207}Pb, 27.00-664.46 and ^{208}Pb, 65.67-1642.27 in Ibadan samples while that of Lagos were: ^{204}Pb, 1.43 - 31.00; ^{206}Pb, 25.26 - 509.74; ^{207}Pb, 21.96-446.22 and ^{208}Pb, 52.61-1089.93. Ibadan and Lagos rocks Pb isotopes (ppm) were: ^{204}Pb, (0.02-0.07 and

0.03-0.06); ^{206}Pb, (0.56-2.33 and 0.56-1.21); ^{207}Pb, (0.38-1.56 and 0.47-1.01) and ^{208}Pb, (1.19-4.13 and 1.22-2.57), respectively. Quartz, microcline, k-feldspar, plagioclase and kaolinite were the preponderant minerals in powdered rocks, soils and sediments. An enrichment of radiogenic Pb (^{206}Pb, ^{207}Pb and ^{208}Pb) were observed in soils, sediments and dusts relative to their local background values, an indication of anthropogenic origin of Pb. The plots (^{208}Pb/^{207}Pb)/(^{206}Pb/^{207}Pb) revealed that over 80% of Pb in the environmental media was derived from anthropogenic sources. The LIRs of soils, sediments and dusts were characterised by lower ^{208}Pb/^{206}Pb ratios while the bedrocks had higher ^{208}Pb/^{206}Pb.

Lead contents of the soils, dusts and sediments in most parts of the two cities were significantly higher than the natural background levels and held in chemically active geochemical phases. The lead types are more of the radiogenic types and this portend great risk to the environment and public health.

Keywords: Anthropogenic influence, Lead isotopes, Radiogenic lead, Geochemical fractionation, Sequential analyses

Word count: 480

CERTIFICATION

I certify that this work was carried out by Olubukola O. AFOLABI (SI: 140519) in the Department of Geology, Faculty of Science, University of Ibadan, Nigeria.

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DEDICATION

This Research work is dedicated to **ALMIGHTY GOD THE BEGINNING AND THE END IN WHOM THERE IS NO VARIABLE.**

To my mother **Mrs. Beatrice Gbonjubola AFOLABI** who brought me into this world and laid the foundation for this research while toiling under the sun and in the rain.

In memory of my late supervisor **Prof. Akinlolu F. ABIMBOLA**

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A journey of a thousand miles begins in a day and ends in a day. Indeed, I am a creation of God Almighty; I give thanks to God who single-handedly saw me through thick and dark period of my life right from my conception up till this very moment. Now unto Him Who is able to do exceedingly, abundantly above all that we ask or imagine, Who has brought out the treasure out of an earthen vessel that the excellence of His power may be of Him alone and not of any man. God the Father, God the Son and God the Holy Spirit; Trinity, I pledge allegiance with all my heart. Thank You Haba Father!!!

I will like to express my heartiest and most sincere appreciations and thanks to my God sent respected and honorable supervisor Dr Akinade S. OLATUNJI, whose keen interest, guidance and encouragement has been a source of great help and inspiration throughout this research work. Sir, you have played a significant role in my academic pursuit in life. You started the mentoring right from my undergraduate through the master's level up till this very moment. I remember I came to you immediately after my masters for Ph.D. supervision and you told me you were not ripe for Ph.D. supervision but as nature will have it you ended up being my supervisor for the program. This is just to show that I am not an abandon project in your life and there is a need for you to complete the project you started in 2004. Thank you so much sir, I pray for you and your family that you will never become an abandon vessel in the hands of your creator. Thank you and God bless sir!

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Finally, while acknowledging my debts and gratitude to all these persons and sources, I humbly accept responsibility for any shortcomings of this work.

Above all, unto Him who has chosen the foolish things of this world to confound the wise and the weak things of the world to confound the mighty, I return all thanks and adoration to His Name for His divine provision, protection and promotion. May HIS NAME ALONE FOREVER BE GLORIFIED IN MY LIFE. HALLELUYAH!!!

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CHAPTER ONE

INTRODUCTION

1.1 General Statement

Toxic metals like Pb, As, Cd, e.tc, are carcinogenic with serious health implications such as induced tumor promotion, behavioral disorder, respiratory difficulties such as asthma and genetical disorder (mutation). This has resulted in the growing consciousness about health risks aspect of environmental chemicals and hence, brought about a major paradigm shift in global concern towards assessing and preventing heavy metals accumulation in soils, sediments, water and dusts (Ahmed et al., 2009). The long biological half-lives and non-biodegradability nature of heavy and trace metals have also made heavy metal toxicity a thing of global concern.

Lead (Pb) is an extremely stable metal found naturally in the environment as well as in manufactured products. The average concentration of Pb in the Earth's crust is around 13µg/g-1 but there is considerable variability in its natural concentrations in the environment because of the inputs from mineralized deposits of Pb. The major sources of lead emissions have historically been from fuels in on-road motor vehicles (such as cars and trucks) and industrial sources. Lead is a non-degradable metal, once a medium is contaminated with Pb, it remains a long-term source of Pb exposure. As a result of the Environmental Protection Agency (EPA's) regulatory efforts to remove lead from on-road motor vehicle gasoline, emissions of lead from the transportation sector dramatically declined by 95 percent between 1980 and 1999 and levels of lead in the air decreased by 94 percent between these periods in US. Today, the highest levels of lead in the environment are usually found near lead smelters. The major sources of lead emissions to the environmental media today are ore and metals processing and piston-engine aircraft operating on leaded aviation gasoline (USEPA, 1996; Komarek et al., 2008; Bird, 2011). Lead is a biologically non-essential heavy metal, it is teratogenic, carcinogenic, toxic at low concentrations and bioaccumulative in organisms. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders (Nriagu, 1992; Hu et al., 1994; 1996). Lead poisoning symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death (Figure 1.1).

Routes of exposure to lead include contaminated air, water, soil, food and consumer products. Occupational exposure is a common cause of lead poisoning in adults. One of the largest threats to children is lead in-paint that exists in many homes, especially older ones; thus children in older housing with chipping paints are at greater risk. Several public health professionals claim that Pb-based paints alone determine the footprint for Pb and consequently the childhood exposure to Pb. However, in contrast, there is a body of literature suggesting that Pb accumulates in soils and sediments from multiple sources and particularly from two main sources, paint and gasoline, determine the foot print and ultimately childhood Pb exposure (Fillippeli et al., 2005; Liadlaw et al., 2005; Brown and Jaccobs, 2006; Mielke et al., 2008). Metallic lead (Pb) is not itself toxic to humans but bioavailable forms of Pb are toxic because they are easily taken into the body and cause plumbism (i.e. acute lead poisoning). Prevention of lead exposure can range from individual efforts (e.g. removing lead-containing items such as piping or blinds from the home) to nationwide policies (e.g. laws that ban lead in products or reduce allowable levels in water or soil).

Human beings have been mining and using this heavy metal for thousands of years, thereby poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the

20th century. No safe threshold for lead exposure has been discovered—that is, there is no known amount of lead that is too small to cause harm (NSC, 2009; CDC, 2002). In March 2010, an unusually high number of deaths, primarily among children under the age 5 in Zamfara, northwestern part of Nigeria was reported (MSF-Holland, 2011). Critical investigation of blood samples revealed that the increased mortality was as a result of acute lead poisoning, determined to be caused by massive environmental contamination from artisanal mining and processing of gold found in lead rich ore. Similarly, in May 2015, Pb poisoning was reported from the Nigerian dailies in Shikira/Tungan Kawo communities in Niger State, North central Nigeria that a total of 30 children under age three years reportedly died of lead poisoning while several others were critically ill. The children developed same symptoms such as high fever, restlessness, excessive crying, convulsion and death. The cause of this usual death was as a result of lead poisoning.

Classically, "lead poisoning or intoxication" has been defined as exposure to high levels of lead typically associated with severe health effects. Poisoning is a pattern of symptoms that occur with toxic effects from mid to high levels of exposure; toxicity is a wider spectrum of effects, including subclinical ones (i.e. those that do not cause symptoms) (Fig.1.1). The amount of lead in the blood and tissues, as well as the time of exposure, determines its toxicity. Lead poisoning may be acute or chronic, but the latter is much more common. Lead forms a variety of compounds and exists in the environment in various forms. Features of poisoning differ depending on whether the agent is an organic or inorganic one. Organic lead poisoning is now very rare, because countries across the world have phased out the use of organic lead compounds as gasoline additives but such compounds are still used in industrial settings. Organic lead compounds, which cross the skin and respiratory tract easily, affect the central nervous system predominantly. This thus make the study of Pb concentration in environmental media a necessity.

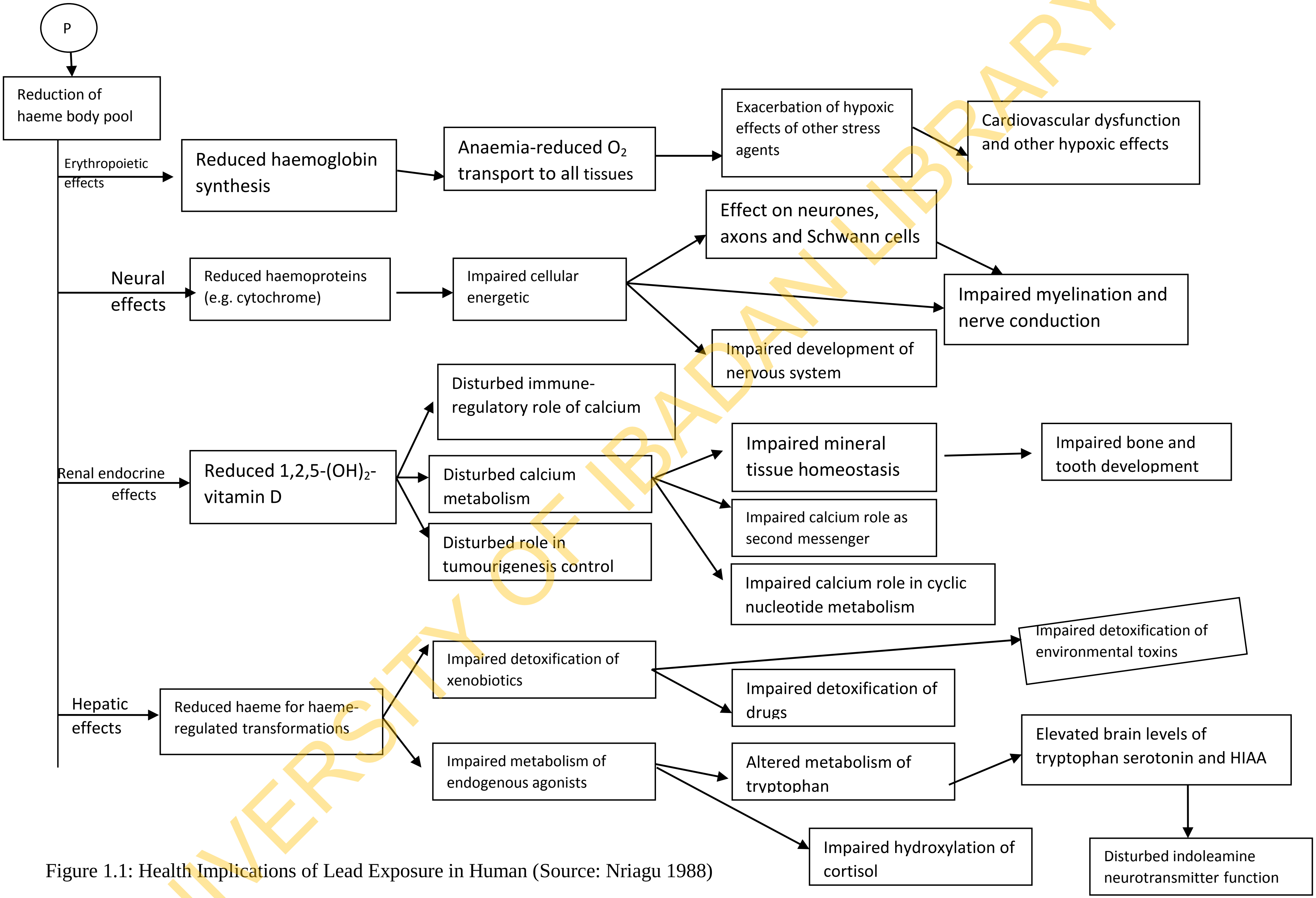


Figure 1.1: Health Implications of Lead Exposure in Human (Source: Nriagu 1988)

1.2 Justification of the Research

Heavy metal concentration in soils, sediments or aerosols has been reported to be an indicator of urban environmental quality. However, the severity of pollution depends not only on heavy metal contents of different environmental media but also on the proportion of their bioavailable and labile forms (Lu et al., 2003; Santos et al., 2005; Watmough et al., 2005). The biochemical and ecotoxicological significance of an element is associated with its specific form and the prevailing local environmental factors such as climate, temperature, pH and Eh. Measurements of total element concentrations do not provide enough information to estimate the bio-accessible proportion of an element to humans and other forms of life. However, partial chemical extraction methods have been used in order to determine the bio- accessible fractions of environmental elements. Over the years, metal speciation has been an important tool in applied geochemistry not only for environmental studies but also for mineral exploration (Thurms et al., 2008; Demetriades et al., 2010).

Cities are known to have been in existence for several thousand years though their sizes were relatively small however, evolution of cities is synonymous to the process of urbanisation (Oyesiku, 2002). According to the UNPD (2001) report on World Urbanization Prospect's, approximately one-half of the world's population now lives in urbanized areas. Urbanization and the accompanying industrial activities result in the release and subsequent deposition of pollutants and other persistent toxic substances, thereby leading to degradation of environmental conditions. The emergence of great factories and consumption of immense quantities of coal and other fossil fuels as a result of the industrial revolution gave rise to unprecedented air, soil, sediment and water pollution from the large volume of industrial and chemical discharges coupled with the growing load of untreated human wastes (Afolabi, 2010).

In Nigeria, ineffective planning and rapid industrialisation has led to unplanned housing structures, (Figure 1.2) traffic congestion and eventually environmental degradation. High degree of industrialisation and urbanisation has led to a strong risk of heavy metal contamination in most urban environments. The increase in human population and the high urbanisation and industrial growth rate in Nigerian cities has made it one of the most densely populated black countries in the world with an estimated population of 182.2 million (NPC, 2016).

The process of urbanization had escalated, as southwestern Nigeria continues to expand progressively as a result of increasing population and urbanization which now stands at about 90,000,000 inhabitants (NPC, 2016). These processes of urbanization have led to the generation of increased wastes in the cities leading to indiscriminate disposals of urban effluents as well as high traffic congestions that pose serious threats to the environment and ultimately to human health. Despite the fact that leaded gasoline has been phased out in several countries of the world notably US, Canada, China, Japan but there has not been officially announced banned in most African countries including Nigeria as the gasoline sold in many African countries contains about 0.5 - 0.8 g/L of Pb, which is the highest levels in the world (Ogunseitan and Smith, 2007). Although, Nigeria depends largely on importation of fuel. Lead pollution is still a major challenge in Nigeria.

A great number of studies have been carried out to quantify and assess metal concentrations in soils, sediments, road dusts, particulate matter, water and even vegetation within the major cities in southwestern Nigeria. Most of these studies have reported very high concentrations of metals most especially Pb which call for very urgent attention (Onianwa, 2001; Abimbola et al., 2006, 2007; Odewande and Abimbola, 2008; Olatunji et al., 2009; Olatunji and Abimbola, 2010; Afolabi, 2010; Ajibade, 2013; Oladiran, 2012; Odunmbaku, 2012). However, none of these studies was able to differentiate and ascertain the sources of Pb and did not report any occurrence of lead/zinc mineralisation in any part of western Nigeria. It is thus imperative to have the source(s) of these metals investigated.

In an attempt to document the dispersal and deposition of Pb, a reliable tracer is required to identify the provenance of the metal. Pb isotopes have been used as geochemical tracers in many environmental studies (Hopper et al.,1991). Their use is facilitated by the fact that Pb in the environment retains the isotopic signature of the ore it originated from (Hopper et al.,1991) and as a result, naturally and anthropogenically sourced Pb often have different isotopic compositions (Marcantonio et al., 1999).

Figure 1.2: Unplanned Housing Structures in the city of Ibadan (Sourcee: this study)

A key aspect of their usefulness as tracers is the fact that Pb isotopic fractionation does not occur in industrial and environmental processes. The Pb isotopic composition of an ore body or anthropogenic source does not change during the transition to a secondary weathering environment unless there is mixing with secondary Pb sources (Ault et al., 1970, Cheng and Hu, 2010).

Knowledge about the concentration and spatial distribution of naturally and anthropogenically occurring chemical elements in soils and sediments in Nigeria is remarkably limited. Presently, there is neither a common soil or sediments geochemical database for Nigeria nor a sound understanding of the processes that may control the variability of chemical elements such as Pb, Cd, As, Zn in the country. It has become increasingly apparent that identifying the origin of these metals most especially Pb contaminants and the environmental media to which they are incorporated is required to facilitate effective environmental management of these cities at large. Similarly, the knowledge of their transport system and migration pattern is of crucial importance. Up till now, no lead isotopic data are available for both soils and stream sediments in the south western Nigeria. Hence, tracing the contamination sources of heavy metals by lead isotopes could be useful in designing sound environmental management approach to minimize pollution.

1.3 Aim and Objectives of the study

The aim of this study is to characterise and differentiate Pb contamination in the urban soils, sediments and dusts of Lagos and Ibadan metropolises with the following objectives: To

i. assess the Pb contamination of the urban soils, sediments and dusts in the study areas
ii. examine the isotopic composition of Pb in various chemical forms in the media
iii. identify other possible sources of metal contaminant in the media
iv. differentiate the Pb in these media
v. study the chemical partitioning of Pb using a five step sequential chemical extraction method

vi. understand the processes causing the observed variations.

vii. to ascertain the operationally defined phase partitioning of Pb and selected metals in the study areas

1.4 Scope of the study

In order to achieve the afore-mentioned objectives, this research work is divided into four phases which are carried out systematically and harmonized in order to arrive at the set goals. The desk study and review of existing geochemical data. These will subsequently follow by field reconnaissance and samples collections which basically involve randomly modified systematic geological and geochemical mapping of the study areas. This includes sampling of the bedrocks, topsoil, stream sediments, drain sediments and road dusts. The laboratory analyses of samples will involve samples preparations and chemical analyses of the samples.

The results of chemical analyses and field data will be subjected to statistical analysis, data collection and interpretation using Excel, SPSS 22.0 Window, Surfer 12.0 window, Arc GIS and Arc View for thesis writing. Graphs and tables are used in data presentation. Ultimate conclusions will be drawn from Pb content with regards to the degree of contamination and isotope signatures of Pb in the study areas.

1.5 The Physiographical Settings

The physiographical settings of the study areas will be discussed under the sections below;

1.5.1 Climate and Vegetation

The study areas are situated within the tropical rainforest belt with a climate characterized by alternation of dry and wet seasons. The wet season runs from April through October when the effect of the south-west monsoon wind overwhelms that of the north-east trade wind which usually causes dry seasons from November to April. The wet season is characterized by heavy rainfall with corresponding low temperatures while the dry season comes with high temperatures and little or no rainfall. Annual rainfall varies between 100 to 1884 mm with mean annual rainfall of about 1200 mm and 1300 mm in both cities. The annual mean temperature ranges from 20.20 ^{o}C and 35 ^{o}C while the relative humidity varies between 27.5 % and 98.2 % (Ajibade, 2013; Odunmbaku, 2012).

Two main vegetation types have been identified in the study areas, the swamp forest of the coastal belt and the dry lowland rain forest (Iloeje, 1987). Very little or no vegetation remained in their natural virgin state with the exceptions of some areas in Ibadan. The swamp forests are combinations of mangrove forest and coastal vegetation developed under the brackish conditions of the coastal areas and the swamp of the fresh water lagoons and estuaries. Red mangrove as well as mangrove shrubs, silt rooted trees with dense undergrowth, raffia and climbing palms are characteristics of these zones, while in the sea ward side of the zones are characterized by stretches of sands and beaches (Olatunji, 2006).

1.5.2 Relief and Drainage

The relief of the entire southwestern Nigeria can be divided into two major units, the undulating lowland terrain and the hills and dome shaped inselbergs. The undulating terrains consist of Pedi plains and dissected complex plains while the hills and inselbergs consist of undifferentiated metamorphic and igneous rocks. Several drainage patterns thought to be controlled by the underlying lithology and geological structures are observable throughout the areas. The most prominent drainage pattern in southwestern Nigeria is dendritic (Ajibade, 2013). Most rivers in the study areas are seasonal and flow NE-SW directions along fractures, faults and joints trend. The land areas within the region are drained by some major rivers, streams and some isolated marshy depressions.

1.5.3 Location and Accessibility

This study was carried out within two cities in southwestern Nigeria cutting across two geological terrains. These two study areas fall within latitudes 07° 15' - 07° 30'(Ibadan); N 06° 28' - 06° 40' (Lagos) and longitudes 003° 45' - 004° 00'E (Ibadan); 003° 14' - 003° 25' (Lagos) located at the western coast of Africa (Figs 1.3a and 1.3b). The areas are bordered by Ogun, Ondo and Osun States and to the west by the Republic of Benin and to the south by Gulf of Guinea. Lagos as megacity has its population as at the last census stood at over 10 million inhabitants with an average population density of over 5 persons

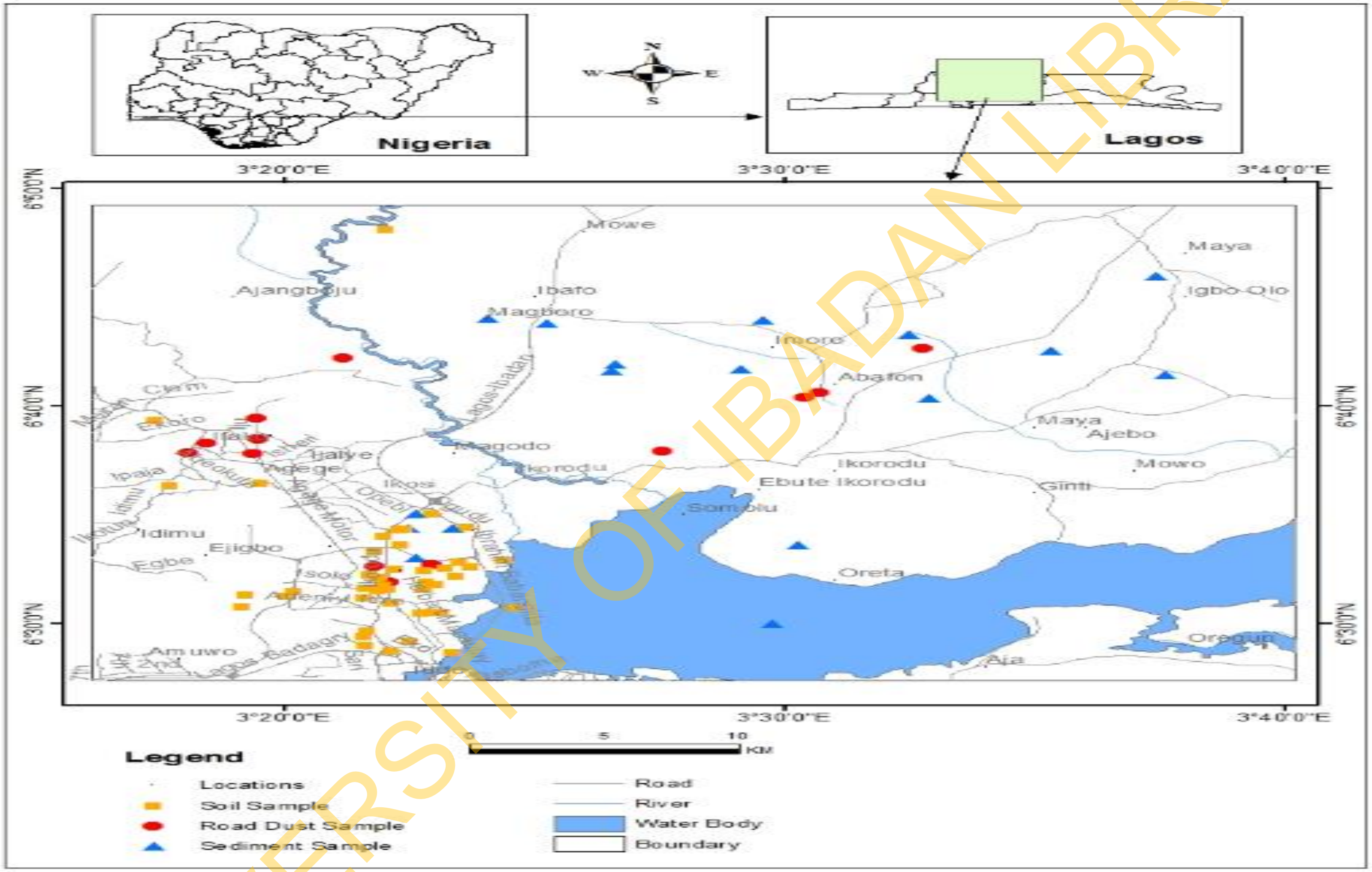


Figure 1.3a. Sampling location map of Lagos area

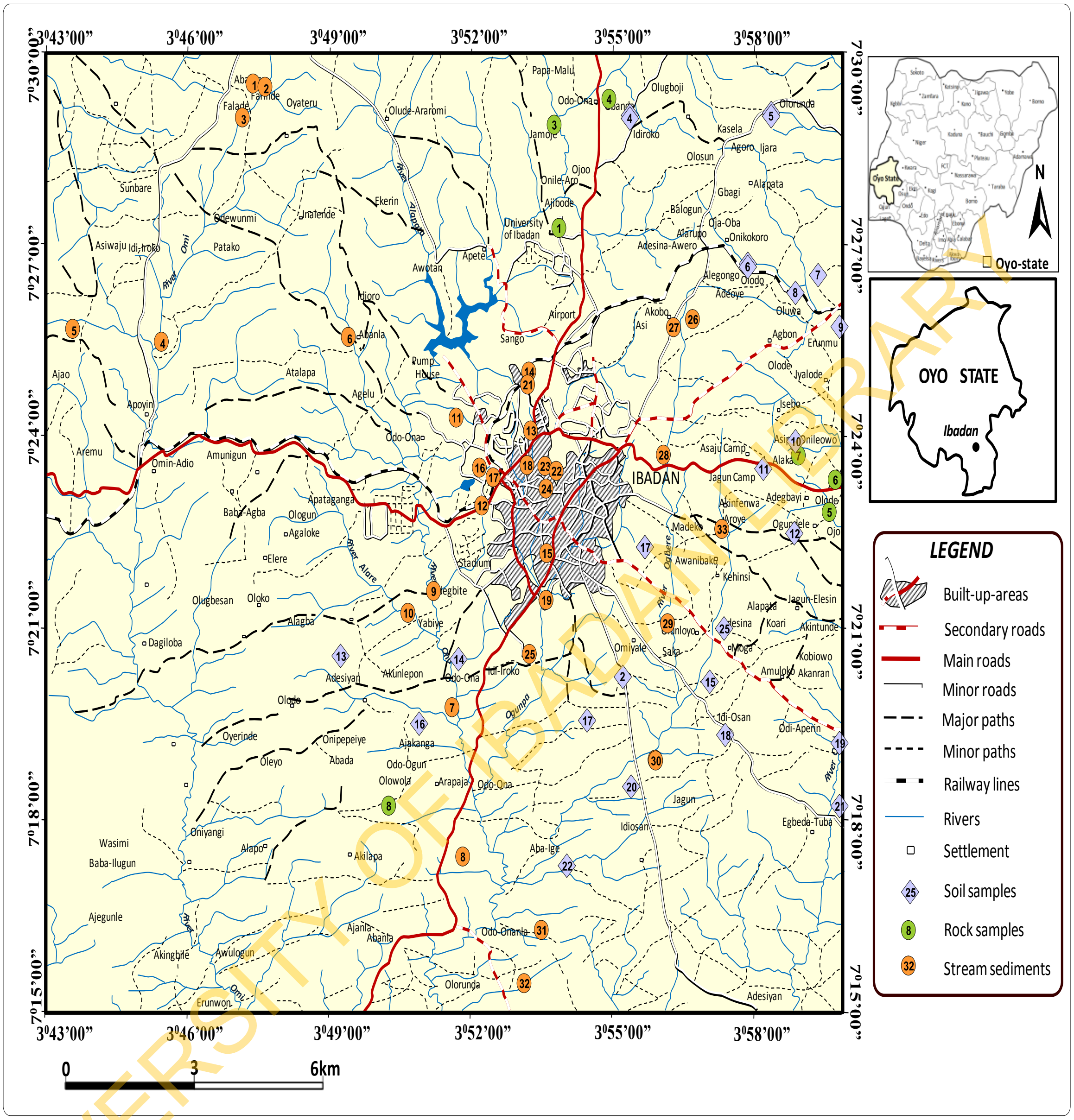


Figure 1.3b. Sampling location map of Ibadan area

per square kilometer while Ibadan on the other hand had a population in excess of 3 million inhabitants with population density of 3 persons per square kilometer (FRN, 2007). Accessibilities within the study areas are highly enhanced by a number of well-connected road networks, sea and air networks as well as inter-connected railway lines which characterized the areas.

1.6 Definition of Terms

Anthropogenic-Pb refers to Pb that are introduced into the environments after the ore deposits have been extracted, processed and/ or used (Erel et al., 1997). These anthropogenic Pb can be derived from mining, smelting, coal combustion, battery processing waste incineration and old paints (Bird et al., 2005; Hudson- Edward, 2003; Adamo et al., 1996; Gulec et al., 2001; Erel et al., 2004; Carignan et al., 2005). Anthropogenic Pb contamination of soils and sediments constitute a very serious environmental issue especially in industrial and urban areas. However, isotopic studies have proved increased Pb concentrations can originate from natural processes.

Several models for assessing and distinguishing between separate Pb sources have been proposed by Semlali et al., (2001, 2004); Prohaska et al., (2005); Monna et al., (1997, 2000) but the most commonly used model is the simple binary model proposed by Komarek et al., (2008) that allows calculating the approximate contribution of two end members. Another mixing model which takes into consideration Pb concentration was introduced by Monna et al., 2000.

$$\%A = \frac{({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb})_{\mathrm{sample}} - ({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb})_{\mathrm{Background}}}{({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb}) - ({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb})_{\mathrm{Background\ A}}}$$

Where A% is the contribution of anthropogenic Pb in the analyzed sample and $^{206}Pb/^{207}Pb_{sample}$ *is the isotopic composition of Pb in the sample;* $^{206}Pb/^{207}Pb_{Anthropogenic}$ *is the isotopic composition of the contaminant and* $^{206}Pb/^{207}Pb_{Background}$ *is the isotopic composition of background Pb.*

1.6.1 Pb isotopes as geochemical tracers

The developments in isotope geochemistry have led to significant advances in the ability to undertake source determinations at contaminated sites; unravel commingled plumes of contaminants and monitor natural attenuation at contaminated sites (Komarek et al., 2008; Bird et al., 2010). A very important aspect in application of Pb isotopes as a tracer is that ore derived lead (Pb) present within the environment generally has a very different isotopic signature to background (geogenic) Pb present within the older country rock (Hopper et al., 1991). Anthropogenic Pb generally displays more radiogenic isotopes ratios than geogenic Pb (Xu et al., 2009). Detection of pollution in soils and sediments by Pb isotopic means is based on the existence of significant Pb isotopic differences between natural background materials and most pollutants containing Pb of industrial origin. Pb deposits are geochemical anomalies characterized by very high Pb/U and Pb/Th compared to ordinary rocks. The usefulness of Pb isotopes as geochemical tracers is that factors such as atomic weight and oxidation behavior that generally controlled partitioning of isotopes does not play a significant role in case of Pb (Keinonen, 1992). Hence, fractionation of Pb isotopes does not occur during mining or smelting operation and other industrial processes (Flegal and Smith, 1995). However, apparent Pb isotopes fractionation can occur over geological time as a consequence of parent isotope disequilibrium between Th and U rather than daughter Pb isotopes fractionation (Amelin and Neymark, 1998). Pb subsequently released into the environment retains the isotopic signature of the original ore deposit from which it was sourced.

The isotopic ratios of Pb is commonly employed when use as geochemical tracers, the radiogenic ^{206}Pb/^{207}Pb and ^{208}Pb/ ^{207}Pb ratios are often preferred and this has been calculated by Sangster *et al.*, 2000 that 86% of the discriminative power of Pb isotope signatures is due to the ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes. However, because of inconsistency in the isotopic ratios used in most published works, Cheng and Hu, (2010) in their review work on Pb isotopic fingerprinting and its applications in lead pollution studies in China suggested the use of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios in environmental studies and ^{207}Pb/^{206}Pb ratios in geochronology studies.

A characteristic nature of a tracer is that it must be conservative over a wide range of environmental conditions (Yeager et al., 2005). Pb is generally characterized as insoluble and having a conservative behavior in the secondary environments (Bindler et al., 2004). It is easy to analyse and can be derived from varieties of sources through anthropogenic activities and natural processes. Pb has four isotopes which include the stable isotope ^{204}Pb with relative abundance of 1.4%; and the long-lived radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb with relative abundance of 24.1%, 22.1% and 52.4% which are the daughter cells of the decay of ^{238}U, ^{235}U and ^{132}Th respectively (Table 1.1) while ^{204}Pb has no radiogenic precursors and it is commonly referred to as primeval Pb (Doe, 1970; Ault et al., 1970). The natural Pb isotope composition of rocks depends on the age of the lithogenic system (Bird, 2011), the U/Pb and Th/Pb ratios of the system and the mixing during remobilization and metamorphism (Keinonen, 1992).

In the formation of Pb deposits, Pb is separated from the parent Uranium and Thorium isotopes, with the Pb isotopic composition of the hydrothermal fluids being frozen into Pb-bearing minerals (Church et al., 1993). The isotopic composition of a given ore deposit is a function of the decay rate of the parent isotopes (Table 1.1); the initial ratio of the abundance of the parent to the abundance Pb (^{238}U/^{204}Pb), (^{232}Th/^{204}Pb) in the reservoir; the initial isotopic composition of reservoir Pb and the duration of reservoir evolution prior to separation of Pb by geological processes. The Pb isotopic signature of Pb deposit depends on the age of mineralization and the proportion of radiogenic ^{206}Pb, ^{207}Pb and ^{208}Pb relative to stable ^{204}Pb which are higher in the younger ores therefore giving higher ratios to ^{204}Pb (Chillrud et al., 2003). As a result of difference in magmatic composition and the timing of mineralization over the past 3Ga; Pb isotope signatures of ore deposits will vary significantly. It is crucial to note that Pb isotope signatures within a single ore deposit or mining district may vary as a result of spatial differences in the mixing of Pb from differing geological sources (Haest et al., 2010) or due to successive phases of ore formation leading to age related variations in isotope signatures (Bird, 2011; Kouzmanov et al., 2002; Moritz et al., 2005). The isotopic composition of Pb in soils always reflects the mixing sources and source apportionment can be quantified where all sources of Pb are characterised and have specific ratios (Komarek et al., 2008).

Table 1.1. Lead Isotopes and their Parent Cells

Parent Isotope	Pb Isotope	Decay half-time of the parent isotope (years)	Decay constant of the parent isotope (years^{-1})
-	^{204}Pb	-	-
^{238}U	^{206}Pb	$4.466*10^{9}$	λ_{238U}: $1.552*10^{-10}$
^{235}U	^{207}Pb	$0.704*10^{9}$	λ_{235U}: $9.850*10^{-10}$
^{232}Th	^{208}Pb	$1.401*10^{9}$	λ_{232Th} :$4.948*10^{-11}$

(Source: Komarek et.al., 2008)

1.7 Sources of Heavy Metals in the Environments

Heavy metals occur naturally in the soil and stream environments from the pedogenetic processes of weathering of bedrock materials at levels that are regarded as trace (<0.1%) and rarely toxic (Kabata-Pendias and Pendias, 2001). Due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media (D'Amore, 2005). The heavy metals essentially become contaminants in the soil environments because (i) their rates of generation via man-made cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (D'Amore, 2005). A simple mass balance of the heavy metals in the soil can be expressed as follows (Alloway, 1995; Lombi and Gerzabek, 1998):

$$M_{total} = (M_p + M_a M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_l) \text{ ----------------------- } \textit{Equation 1}$$

Where "M" is the heavy metal, "p" is the parent material, "a" is the atmospheric deposition, "f" is the fertilizer sources, "ag" are the agrochemical sources, "ow" are the organic waste sources, "ip" are other inorganic pollutants, "cr" is crop removal, and "l" is the losses by leaching, volatilization etc.

It is projected that the anthropogenic emission into the atmosphere, for several heavy metals, is one-to-three orders of magnitude higher than natural fluxes (Sposito and Page, 1984). Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than lithogenic ones (Kaasalainen and Yli-Halla, 2003). Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of mine tailings, leachates from improperly protected landfills, leaded gasoline and lead-based paints, fertilizer and pesticides, animal manures, coal combustion residues, petrochemicals and atmospheric deposition (Khan et al., 2008; Zhang et al., 2010).

1.7.1 Anthropogenic sources of Heavy Metals in Soils

1. Fertilizers

Certain metals are essential components for plants growth, however, some soils are deficient in these metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth. Crops may be supplied with these metals as an additive to the soil or as a foliar spray. Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for optimum growth. These compounds contain trace amounts of heavy metals such as Hg, Cd and Pb as impurities, which may significantly enrich over time in the soil.

2. Pesticides

Several common pesticides contain substantial concentrations of metals. For instance, in the recent past, about 10% of the chemicals approved for use as insecticides and fungicides in the UK were based on compounds which contain Cu, Hg, Mn, Pb, As or Zn (McLaughlin et al., 2000). Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Arsenic-containing compounds were also used extensively to control cattle ticks and pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr, and As, and there are now many derelict sites where soil concentrations of these elements greatly exceed background concentrations (McLaughlin et al., 2000). Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or nonagricultural purposes such as recreational center.

3. Biosolids and Manures

The application of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb, and so forth, in the environments (Basta et al., 2005). Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries (Sumner, 2000). Although most manure are seen as valuable fertilizers, in the pig and poultry industry, Cu and Zn are added to diets as growth promoters and Arsenic contained in poultry health products may also have the potential to cause metal contamination of the soil (Sumner, 2000; Chaney and Oliver, 1996). The manures produced from animals on such diets contain high concentrations of As, Cu, and Zn, and if repeatedly applied to restricted areas of land, can cause considerable build-up of these metals in soil and run-off in the long run. Biosolids (sewage sludge) are primarily organic solid products, produced by wastewater treatment processes that can be beneficially recycled (USEPA, 1994). Land application of biosolids materials is a common practice in many countries that allow the reuse of biosolids produced by urban populations (Weggler et al., 2004). The term sewage sludge is used in many references because of its wide recognition and its regulatory definition.

However, the term biosolids is becoming more common as a replacement for sewage sludge because it is thought to reflect more accurately the beneficial characteristics inherent to sewage sludge (Silveira et al., 2003). It is estimated that in the United States, more than half of approximately 5.6 million dry tons of sewage sludge used or disposed of annually is land applied, and agricultural utilization of biosolids occurs in every region of the country. In the European community, over 30% of the sewage sludge is used as fertilizer in agriculture (Silveira et al., 2003). In Australia over 175 000 tons of dry biosolids are produced each year by the major metropolitan authorities, and currently most biosolids applied to agricultural land are used in arable cropping situations where they can be incorporated into the soil (McLaughlin et al., 2000).

There is also considerable interest in the potential for composting biosolids with other organic materials such as sawdust, straw, or garden waste. If this trend continues, there will be implications for metal contamination of soils. The potential of biosolids for contaminating soils with heavy metals has caused great concern about their application in agricultural practices (Canet et al., 1998). Heavy metals most commonly found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment. Under certain conditions, metals added to soils in applications of biosolids can be leached downwards through the soil profile and contaminate groundwater.

4. Wastewater

The application of municipal and industrial wastewater and related effluents to land dates back to about 400 years and now is a common practice in many parts of the world (Reed et al., 1995). Worldwide, it is estimated that 20 million hectares of arable land are irrigated with wastewater. In several Asian and African cities, studies suggest that agriculture based on wastewater irrigation accounts for 50 percent of the vegetable supply to urban areas (Bjuhr, 2007). Although the metal concentrations in wastewater are usually relatively low, long-term irrigation of land with such wastewater can eventually result in heavy metal accumulation in the soil.

Soil heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways include the ingestion of plant material grown in (food chain), or the direct ingestion (oral bioavailability) of contaminated soil (Basta and Gradwohl, 1998). Other materials are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition. Although some are disposed of on land, few have benefits to agriculture or forestry. In addition, many are potentially hazardous because of their contents of heavy metals (Cr, Pb, and Zn) or toxic organic compounds and are seldom, if ever, applied to land (Sumner, 2000).

5. Air-Borne Sources

Airborne sources of metals include stack or duct emissions of air, gas, or vapour streams, and fugitive emissions such as dust from storage areas or waste piles. Metals from airborne sources are generally released as particulates contained in the gas stream. Some metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will convert to oxides and condense as fine particulates unless a reducing atmosphere is maintained (Smith et al., 1995). Stack emissions can be distributed over a wide area by natural air currents until dry and/or wet precipitation mechanisms remove them from the gas stream. Fugitive emissions are often distributed over a much smaller area because emissions are made near the ground. In general, contaminant concentrations are lower in fugitive emissions compared to stack emissions. The type and concentrations of metals emitted from both types of sources will depend on site-specific conditions. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on land or sea; most forms of fossil fuels contain some heavy metals and this is, therefore, a form of contamination which has been continuing on a large scale since the industrial revolution began. For example, very high concentration of Cd, Pb, and Zn has been found in plants and soils adjacent to smelting works. Another major source of soil contamination is the aerial emission of Pb from the combustion of fossil fuel containing tetraethyl lead. This contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Zn and Cd may also be added to soils adjacent to roads, the sources being tires, and lubricant oils (USEPA, 1996c).

1.7.2 Sources of Heavy Metals in Drainage Basins

Sources of heavy metal pollution in water and sediment can be natural and anthropogenic. However, the most common source of pollution in drainage basins according to (Wong et al., 2007; Wong et al., 2006; Bjuhr, 2007**)** is the anthropogenic activities including:

1. Agriculture runoff carrying fertilizers, pesticides/insecticides/herbicides and other pollutants into water bodies such as lakes, rivers, ponds can lead to increase in nitrates and phosphates in water that could be harmful to human health.
2. Storm water runoff carrying various petroleum products and other contaminants from urban and rural areas (ditches). These usually form sheens on the water surface.
3. Leaking sewer lines may add tri-halo-methane (such as chloroform) as well as other contaminants into groundwater and surface water. Discharges of chlorinated solvents from dry cleaners to sewer lines are also a recognized source of water pollution with these persistent and harmful solvents.

4. Mining activities involve crushing of rocks, that usually contain many trace metals and sulphides. The left over may easily generate sulphuric acid in the presence of precipitation water.
5. Foundries have direct emissions of metals (including Hg, Pb, Mn, Fe, Cr and other metals) and particulate matters into the air.
6. Industrial discharges may add significant pollution to water bodies, but are usually regulated today.
7. Accidental leaks and spills associated with handling and storage of chemicals may happen anytime and, although they are usually contained soon after they occur, the risk of polluting surface and groundwater is possible
8. Intended/illegal discharges of wastes – while such occurrences are less common today, they may still happen due to the high cost of proper waste disposal. Illegal waste discharges into water bodies have been recorded all over the world.
9. Burning of fossil fuels – the emitted ash particles usually contain toxic metals (such as As or Pb). Burning will also add a series of oxides including carbon dioxide to air and water bodies.
10. Transportation – even though Pb has been banned in gasoline in the U.S. and many other countries, vehicular emissions with other tailpipe compounds (including sulfur and nitrogen compounds, as well as carbon oxides) that may end up in water bodies via atmospheric fallout or deposition with precipitation water still constitute a great problem.
11. Domestic or household wastes in contact with water may degrade slowly releasing harmful compounds that can affect both human health and ecosystem.
12. Disposal of personal care products and household chemicals (including detergents and various cleaning solutions) – this is a serious problem since the releases to water are unpredictable and hard if not impossible to control. It is up to each of us to minimize this contribution to water pollution by controlling our consumption and disposal of such products as well as trying to recycle them.

1.7.3 Heavy Metal Chemistry, Potential Risks and Health Implications

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu and Hg (USEPA, 1996). Knowledge of the basic chemistry, environmental and associated health implications of these heavy metals is necessary in understanding their speciation, bioavailability and remedial options. The fate and transport of heavy metals in soils and sediments depend largely on the chemical form and speciation of the metal, once in the soil or sediment, heavy metals are adsorbed by initial fast reaction, followed by slow adsorption reaction and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility and toxicity (Shiowatana et al., 2001; Buekers, 2007). This distribution is believed to be governed by chemical reactions such as mineral precipitation and dissolution, ion exchange, adsorption and desorption, aqueous complex, biological immobilization and mobilization and plant uptake in soils.

Lead is a group IV metal with atomic number 82, atomic mass 207.2, density 11.4 g /cm^3, melting point 327.4°C and boiling point 1725°C. It is a naturally occurring bluish-gray metal usually found as a mineral combined with other elements, such as Sulphur (i.e., PbS, $PbSO_4$), or oxygen ($PbCO_3$) and ranges from 10 to 30 mg kg^{-1} in the earth's crust (USDHHS, 1999). Globally, the average concentration of Pb in surface soils is about 32 mg kg^{-1} and this varies from 10 to 67 mg kg^{-1}. Lead ranks fifth behind Fe, Cu, Al and Zn in industrial production of metals. About half of the Pb used in the world goes for the manufacture of Pb storage batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments and caulking. Metals commonly alloyed with Pb include antimony (Sb), calcium (Ca) and tin (Sn), silver (Ag), strontium (Sr) and tellurium (Te) (Manahan, 2003).

Ionic lead, Pb (II), lead oxides and hydroxides and lead-metal oxyanion complexes are the general forms of Pb that are released into the soils, sediments, groundwater and surface waters. The most stable forms of lead are Pb (II) and lead-hydroxyl complexes. Lead (II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997). The predominant insoluble Pb compounds are lead phosphates, lead carbonates (form when the pH is above 6) and lead (hydro) oxides (Raskin and Ensley, 2000). Lead sulphide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions. Under anaerobic conditions, a volatile organo-lead (tetra-methyl lead) can be formed as a result of microbial alkylation (GWRTAC, 1997). Lead (II) compounds are predominantly ionic (e.g., Pb^{2+} $SO_4{}^{2-}$) whereas Pb (IV) compounds are covalent (e.g. tetraethyl lead, $Pb(C_2H_5)_4$).

Lead forms several basic salts (such as $Pb(OH)_2$ and $2PbCO_3$) which were once used as white paint pigment and considered as source of chronic lead poisoning to children who ate house-paints peelings. Many compounds of Pb (II) and a few Pb (IV) are useful. The two most common of these are lead (IV) oxide and lead sulphate, which are participants in the reversible reaction that occurs during the charge and discharge of lead storage battery. In addition to the inorganic compounds of lead, there are a number of organic lead compounds such as tetraethyl lead.

The toxicities and the environmental effects of organic lead compounds are particularly noteworthy because of the former widespread use and distribution of tetra ethyl lead (TEL) as additive in gasoline. Although over 1000 organic lead compounds have been synthesized but the commercial importance and toxicological effects are largely limited to the alkyl (methyl and ethyl) lead compounds and their salts (e.g. di-methyl di-ethyl lead; tri-methyl lead chloride and diethyl lead dichloride). Inhalation and ingestion are the two routes of Pb exposure and the effects are similar. Pb accumulates in the body organs (i.e., brain) which may lead to poisoning or even death. The gastrointestinal tract, kidneys and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration, with children under the age of six being at a greater risk.

Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia and weakness of the joints when exposed to lead (NSC, 2009). It is well known to be toxic and its effects have attracted more attention than any other heavy metals. Lead can cause serious injury to the brain, nervous system, red blood cells and kidneys (Baldwin and Marshall, 1999). Lead is a particularly dangerous chemical, as it can accumulate in individual organisms and also in entire food chains. The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust. In general, plants do not absorb or accumulate lead. However, in soils testing high in lead, it is possible for some lead to be taken up. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops. Higher concentrations are more likely to be found in leafy vegetables and on the surface of root crops. Since plants do not take up large quantities of soil lead, the lead levels in soil considered safe for plants will be much higher than soil lead levels where eating of soil is a concern (geophagia). The risk of lead poisoning through the food chain increases as the soil lead level rises above 300 ppm (Rosen, 2002).

CHAPTER TWO

THE REVIEW OF REGIONAL GEOLOGIC SETTINGS AND RELATED WORKS ON LEAD ISOTOPES

2.1 General Statement

This chapter is divided into two sections;

1. The review of regional geological settings of southwestern Nigeria which comprises of the Eastern Dahomey Basin and the Basement Complex of southwestern Nigeria.
2. The review of related works on lead (Pb) and lead isotopes as well as other potentially harmful metals.

2.2 Regional Geological Settings of Southwestern Nigeria

The geological set up of Nigeria broadly comprises sedimentary basins and crystalline basement complex, which occur more or less in equal proportion (Fig.2.1). The sedimentary terrains of Nigeria consist of seven basins which are widely distributed from north to south and east to west. These basins are the Benue Trough, Dahomey Basin, Anambra Basin, Sokoto Basin, Borno Basin, Mid-Niger (Nupe) Basin and the Niger-Delta Basin. The sediments in all these basins are mainly Upper Cretaceous to Recent in age while the Basement Complex rocks are mainly Precambrian (Dada, 1989).

2.2.1 Geology of the Eastern Dahomey Basin

Dahomey Basin is an extensive sedimentary basin stretching from the eastern Ghana, Togo and the Republic of Benin to the Western parts of Nigeria up to the Benin hinge line (Fig.2.2a). The basin is one of the sedimentary basins of Nigeria. However, it is the eastern portion of the Dahomey Basin that is exposed in the south-western part of Nigeria (Fig.2.2b). The Eastern Dahomey Basin is bounded in the North by Precambrian Basement Complex of South-western Nigeria, the Gulf of Guinea to the South and eastward by the Okitipupa Ridge (Adegoke, 1969).

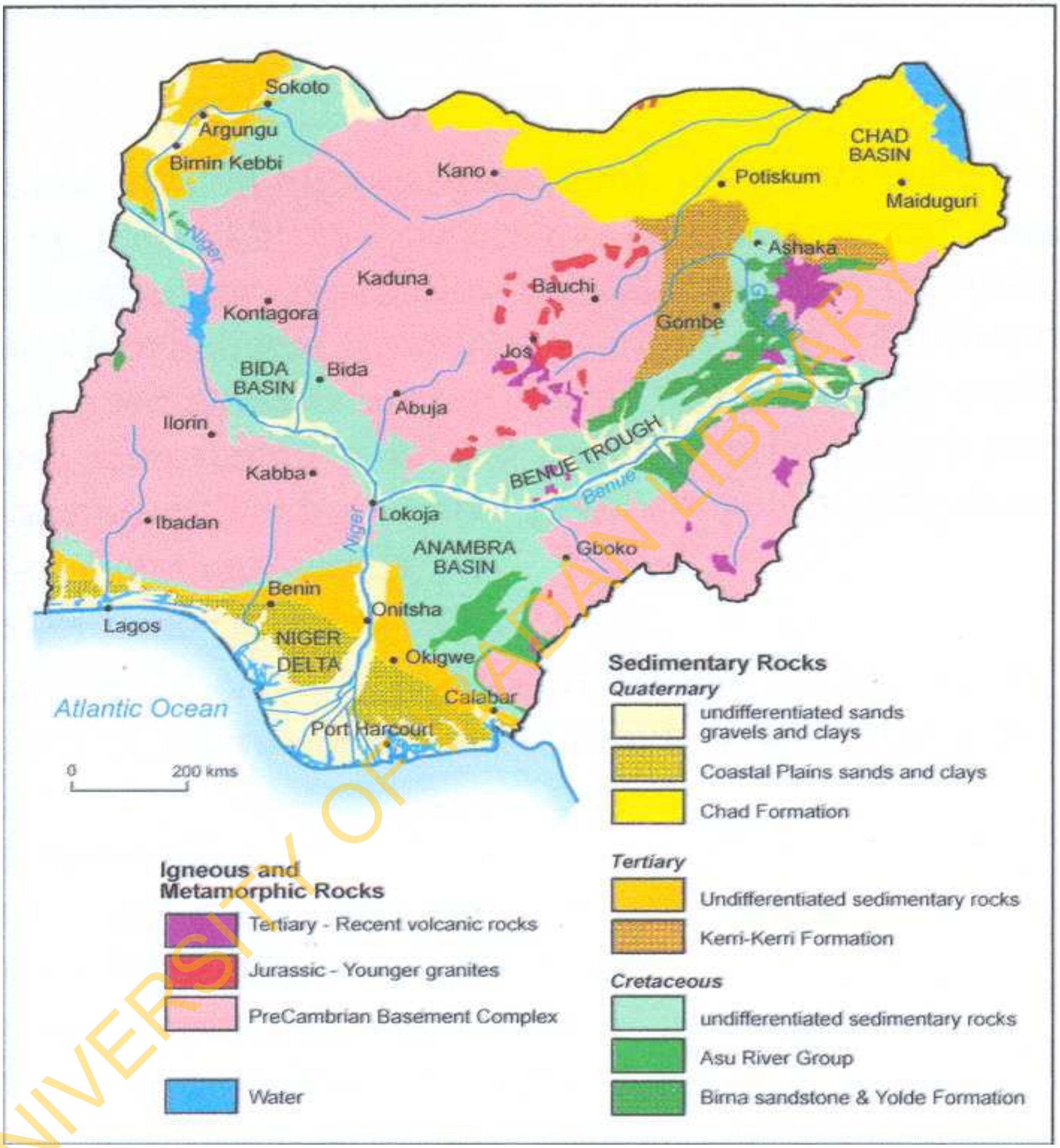


Figure 2.1. The Geological map of Nigeria

(Source: Obaje, 2009)

2.2.1.1 Tectonic Setting and Evolution

The Dahomey Basin was initiated during the Early Cretaceous separation of the Gondwanaland (Burke and Dewey 1971; Whiteman, 1982). The Benin Flank marks the zone of constriction in the basin and the thinning of the sediments and this separates the Dahomey Basin from Niger Delta Basin. Structurally, the basin is bounded in the west by faults and the other tectonic structures associated with landward extension of Romanche fracture zone. The Okitipupa Ridge and the Benin Hinge line have been described as landward extension of the chain fracture zone (Omatsola and Adegoke, 1981). The Dahomey Basin has also been described as a cratonic margin with the lower opened to the ocean. The basement rocks which under lie the basin are tilted toward the South Atlantic and have been faulted into horsts and graben structures (Omatsola and Adegoke, 1981; Fig. 2.2a).

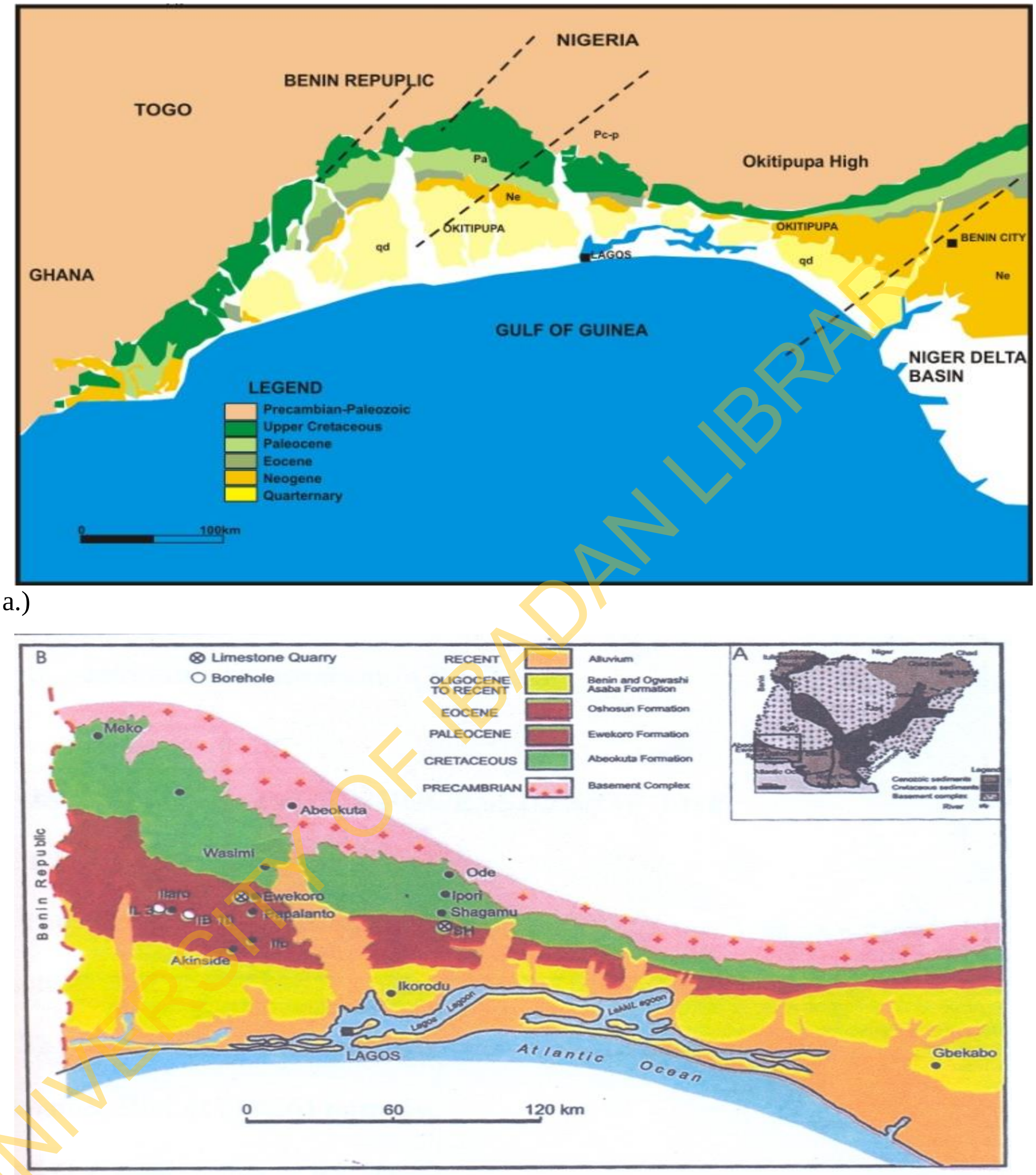
2.2.1.2 Litho-stratigrahy of the Eastern Dahomey Basin

The sediments of the eastern Dahomey Basin are Early Cretaceous to Holocene (Agagu, 1985) in age and dominantly clastic with occurrence of shale and limestone. The lithostratigraghy of the basin has been grouped in the following order (Fig. 2.2b and Table 2.1):

i. The Abeokuta Group – Oldest
ii. The Ewekoro Formation
iii. The Akinbo Formation
iv. The Oshosun Formation
v. The Ilaro Formation
vi. The Coastal Plains Sands and Alluvium

2.2.1.2.1 The Abeokuta Group

This is the oldest unit in the Eastern Dahomey Basin (Jones and Hockey, 1964). It unconformably overlies the Basement Complex. It used to be referred to as Abeokuta Formation but later upgraded to a group status with the age ranging from Neocomian to Paleocene (Omatsola and Adegoke, 1981). The group consists of conglomerate, sandstones, clays, shale and thin limestone.



a.)

b.)

Figure 2.2. a.) Generalised geological map of Dahomey Basin; **b.)** Generalised Geological setting of Eastern Dahomey Basin

(Source: Billman, 1976)

The exposure of the Abeokuta Group can be seen around kilometer 18 along the Ago Iwoye to Ijesa - Ijebu road where the conglomerate Ise Formation unconformably overlies the basement rocks (Olatunji, 2006). The sediments of the group are deposited in partly marine, partly brackish water and partly freshwater and have been described as the equivalent of the Nsukka Formation (Kogbe, 1976). The Abeokuta Group is subdivided into three formations and these are:

i. Ise Formation
ii. Afowo Formation
iii. Araromi Formation

1. Ise Formation

This consists essentially of highly indurate massive continental sandstone, grit and siltstone overlying the basement rocks (Omatsola and Adegoke, 1981; Agagu, 1985). The basal unit of the formation is predominantly conglomeratic and it is succeeded by gritty, coarse to medium grained loose sands inter-bedding (Omatsola and Adegoke, 1981, Agagu, 1985).

The basal conglomerates are sub angular to sub-rounded, poorly sorted and positively skewed, a reflection of the closeness of the provenance of the sediments to the depositional basin. The grain size distribution is leptokurtic and near symmetrical (Lawson, 1986). Clays form the major matrix and poor cementation makes the rock friable. It is Neocomian in age (Agagu, 1985).

2. Afowo Formation

This consists of medium to fine grained sandstones interbedded with relatively thick siltstones and shale rich in organic matter. It overlies the Ise Formation conformably (Omatsola and Adegoke, 1981). The sediments were deposited in a transitional to marginal marine environment and are bituminous in both surface and subsurface sections (Fayose, 1970). The age of the formation is from Turonian to Maastrichtian (Billman, 1992). It outcrops at the northern part of the basin and along the Okitipupa Ridge. The Afowo sandstones are texturally similar to the Ise sandstones and are moderately sorted, leptokurtic with skewness varying from fine skewed to near symmetrical (Lawson, 1986).

3. Araromi Formation

This is the upper most unit of Abeokuta Group that overlies the Afowo Formation. It is made up of medium grained sands, siltstones and shale at the base with intercalations of limestone, sands and lignite towards the top. The shale is mostly light to dark grey and is rich in organic matter. It ranges from Maastrichtian to Early Paleocene in age.

2.2.1.2.2 Ewekoro Formation

This conformably overlies the Abeokuta Group. It is a lensoid shaped unit, which pinches out towards the east and the south. The formation comprises limestone and marl that are rich in fossils particularly mollusks (Agagu, 1985). The formation is best exposed for study at Ewekoro and Shagamu quarries of Lafarge Company. The limestone is sandy towards the base and varies in thickness between 13 m and 35 m. This formation has been subdivided into three units by Adegoke, 1970 while Ogbe, 1970 proposed a fourth unit. The units are:

- The Red Phosphate Biomicrite (top)
- Algal Biospharite
- Shally Biomicrite
- Sandy Biomicrosparite (bottom)

The sandy Biomicrosparite which forms the base of the formation consists of light brown sandy limestone with stratification accentuated by variations in the quantity and the grain size of the interbedded quartz and glauconite. The Shally Biomicrite consists of pure limestone and constitutes the bulk of Ewekoro limestone. Little ferruginous materials appeared in the limestone, which has a light brown grey color. The Algal Biosparite limestone overlies the Shally Biomicrite unit with the top of the unit eroded, water worn, scoured and potholed. The red phosphatic biomicrite occurs in patches on algal biosparite. The age of the formation has been put at Paleocene (Kogbe, 1970).

Table 2.1. Stratigraphy of Eastern Dahomey Basin

Era	Jones and Hockey (1964)		Omatsola and Adegoke (1981)		Agagu (1985)	
	Age	Formation	Age	Formation	Age	Formation
Quaternary	Recent	Alluvium			Recent	Alluvium
Tertiary	Pleistocene to Oligocene	Coastal Plain Sands	Pleistocene to Oligocene	Coastal Plain Sands	Pleistocene to Oligocene	Coastal Plain Sands
	Eocene	Ilaro	Eocene	Ilaro Oshoshun	Eocene	Ilaro /Oshoshun
	Paleocene	Ewekoro	Paleocene	Akinbo Formation	Paleocene	Akinbo Formation
Late Cretaceous	Late Santonian	Abeokuta	Maastrichtian to Neocomian	Araromi Afowo	Maastrichtian to Neocomian	Araromi Member Afowo Member Ise Member

2.2.1.2.3 Akinbo Formation

This formation is about 10m thick grey laminated fossiliferous shale with the base defined by glauconitic rock band occurring above the Ewekoro Formation. The shale loses its laminations becoming more arenaceous and passes gradually into massive mud at the top. It is Paleocene in age (Agagu, 1985).

2.2.1.2.4 Oshosun Formation

This is made up of light greyish to purple clay with red mottling and occasionally pockets of grits, greenish clay and light to grey, fine laminated phosphate marl. The Oshosun fauna include mollusks, corals, crinoids, crustaceans, pelagic and planktonic foraminifera, fishes and sea snakes all suggesting a marine depositional setting. The age of the formation is Eocene (Agagu, 1985).

2.2.1.2.5 Ilaro Formation

This consists of fine grain sands, clays and shale. Textural analysis of the sand from the formation indicates beach, shoreline and near shore environments of deposition. The formation is poor in fossils but some benthic foraminifera have been described. The age of the formation is put at Eocene (Agagu, 1985).

2.2.1.2.6 Coastal Plain Sands and Alluvium

The Coastal Plain sands together with the Recent Alluvium constitute the Youngest sedimentary unit of the Dahomey Basin (Figs. 2.3 - 2.5). The Coastal Plain sand overlies the Ilaro Formation but evidence of this is lacking in surface exposure (Jones and Hockey, 1964). The Coastal Plain sands are made up of soft, very poorly sorted clayey sands, pebbly sands, sandy clays and rare thin lignite (Figs. 2.3 - 2.5). The age of the unit has been put at Oligocene to Pleistocene (Agagu, 1985). The Alluvium represents the modern sediments deposited along the main river channels that empty their contents into the lagoons. A combination of the Coastal Plain Sand and Recent Alluvium underlie the megacity of Lagos.

2.2.1.3 Geology of Lagos Area

One of the earliest published works related to the geology of Lagos was by Russ (1922) who described the underlying geology of the over 30 km wide strip of country along the

Lagos – Abeokuta railway. Due to the very poor exposures of the sedimentary succession within Lagos area, it has been very difficult to know the subsurface strata and subsequently reconstruct its geology. Generally, the Coastal Plain Sand and Recent Alluvium of the eastern Dahomey Basin, South western Nigeria, underlie the Lagos area. The name Coastal Plain sands was introduced by Tattam, (1944) to indicate extensive red earths and loose ill – sorted sands underlying the Recent deposits of the Niger Delta and overlying the Eocene Bende – Ameki Group. The Coastal Plain Sands consist of soft, very poorly sorted, clayey sands and rare thin lignite. The geology of Lagos is described using borehole logs obtained from the study area (Olatunji, 2006).

2.2.2 Basement Geology of Southwestern Nigeria

The Proterozoic sediments have been classified into the Older Meta-sediments of Early Proterozoic age and the Younger Meta-sediments of the Pan African age (Dada, 1989). Reactivated Archaean Basement often referred to as the Migmatite-Gneiss Complex, occupies nearly half of the surface area of Nigeria. It includes the Migmatite-gneisses of the Zinder in-lier in Niger-Republic in the northeast; those of Obudu and Oban-massif (Ekwueme and Schlag, 1989) in southeast Nigeria; the Migmatite-Gneiss Complex in neighbouring Cameroon Republic. The Migmatite-Gneiss Complex is dominated by quartzo-feldspathic biotite-hornblende bearing gneiss, schist and migmatite in which minerals such as garnet, silimanite, kyanite and staurolite suggest high-amphibolite facies (Oyawoye, 1972).

The evolution of the basement rocks in Nigeria is associated with the overall evolution of the African continent. It is believed that radiometric dating was used to unravel the evolution of the basement rocks in Nigeria which took place during five main orogenic events which correspond to five major ages that punctuated the Precambrian history of Africa. These are according to Rahaman, (1988) include viz:

Leonian Orogeny	3500 – 2900ma
Liberian Orogeny	2900 – 2400ma
Eburnean Orogeny	2400 – 1600ma
Kiberian Orogeny	1600 – 900ma
Pan African Orogeny	600 – 450ma

Figure 2.3. Lateritic Coastal Plain sands of eastern Dahomey Basin as exposed in Ojota area

Figure 2.4. Reddish Coastal Plain sands of eastern Dahomey Basin as exposed along Lagos-Abeokuta Road

Figure 2.5. Coastal Plain sands of eastern Dahomey Basin as exposed at Oke-Ira, Ogba area

The Pan African Orogeny is the most significant of all the Orogenies since it brought about evolution of the Older Granites and the subsequent reactivations, folding, deformation and metamorphism of the basement. Rahaman (1976) gave a more modified description of the basement complex and these are:

The Migmatite – Gneiss Complex
The Schists belts
The Older Granites and Related rocks

2.2.2.1 The Migmatite-Gneiss Complex of Southwestern Nigeria

The Migmatite-Gneiss Complex is the most widespread of the main rock units in the Basement Complex of Nigeria. It is a heterogeneous assemblage including migmatites, orthogneisses, paragneisses and a series of basic and ultra-basic metamorphosed rocks (Rahaman, 1988). Petrographic evidence indicates that the Pan African reworking has led to re-crystallization of many of the constituents' minerals of the Migmatite-Gneiss Complex by partial melting, with most displayed medium to upper amphibolite facies metamorphism (Rahaman, 1988). The supercrustal reflects in the Nigerian Basement are either intercalated within reworked Archaean gneiss as afore-mentioned or are unconformably disposed in synclinorial schist belts. The former category belongs to the so-called Older Metasediments, which are best known in the much-studied Ibadan-Ife region of southwestern Nigeria (Rahaman, 1988).

2.2.2.2 The Schist Belts (Younger Metasediments)

These are the Late Proterozoic pelites (represented by phyllite muscovite-schist and biotite-schist) with quartzite forming prominent strike ridges in several belts. Some belts contain ferruginous and banded quartzite, spessarite-bearing quartzite, conglomeratic horizons and marbles and calc-silicates. These Younger Metasediments occur in northwest to southwestern Nigeria (Annor, 1983). A major belt of the Younger Metasediments extends from Igarra in the southwestern Nigeria through Kabba and Okene to Lokoja (Annor, 1983). They occur as schist and meta-quartzite within the banded gneisses and extend for about 75km northward into the Iseyin area and eastward into the Ife area (Rahaman, 1976). In the later area, the Older Metasediments appear to be bounded by the Ifewara fault system which seems to separate this Older Iseyin-Ibadan-Ilesha Schist Belt from the presumably Late Proterozoic Igarra-Kabba-Lokoja schist belt to the east (Ajibade et al., 1987; Carby, 1989).

2.2.2.3 The Older Granites and Related Rocks (the Granitoids)

One of the implications of the widely-accepted Pan-African tectonic model of eastward subduction and continent – continent collision in the southern part of the trans-Sahara mobile belt is that it generated abundant granitoids in the Nigerian province (Burke and Dewey, 1972, Wright et al., 1985). Syntectonic to Late tectonic granitoids, diorites and syenites were intruded into both the Migmatite-Gneiss Complexes and overlying supercrustals. The intrusions are termed the Older granites to distinguish them from the Jurassic Younger Granites. In southwestern Nigeria, charmokites also occur among the Older Granites. The Older Granites range in size from small sub-circular cross-cutting stocks to large elongate concordant predominantly granodioritic batholiths (Olarewaju, 1998).

2.2.2.4 Geology of Ibadan

Ibadan metropolis falls within the Basement Complex areas of Nigeria. The rock units belong to the subdivision of the Migmatite-Gneiss Complex (Rahaman, 1976). The major rock units in Ibadan areas are generally referred to as the undifferentiated meta-sediments. They consist essentially of quartzite belonging to the metasediment series and the migmatite gneiss complex consisting of grey gneiss, banded gneiss, augen gneiss, amphibolite and amphibole schists and migmatites (Fig 2.6). These rock units are well-exposed in different parts of Ibadan metropolis with lots of pegmatite, dolerites, aplite and quartz veins as intrusions. The geology of Ibadan has been widely reported by various authors who were of the opinion that the rock suites comprise of meta-sedimentary series with associated minor igneous rocks which are variably altered by different metamorphic, magmatic and granitic processes (Rahman, 1988; Ajibade, 2013; Odewande, 2006 and Okunlola et al., 2009). These authors have identified the rock units in Ibadan to consist mainly of migmatite gneiss, gneisses of various types, granite, quartzite, amphibolite and schistose-quartz. Some of the rock types encountered in various parts of Ibadan metropolis are presented in Figures 2.7 - 2.11.

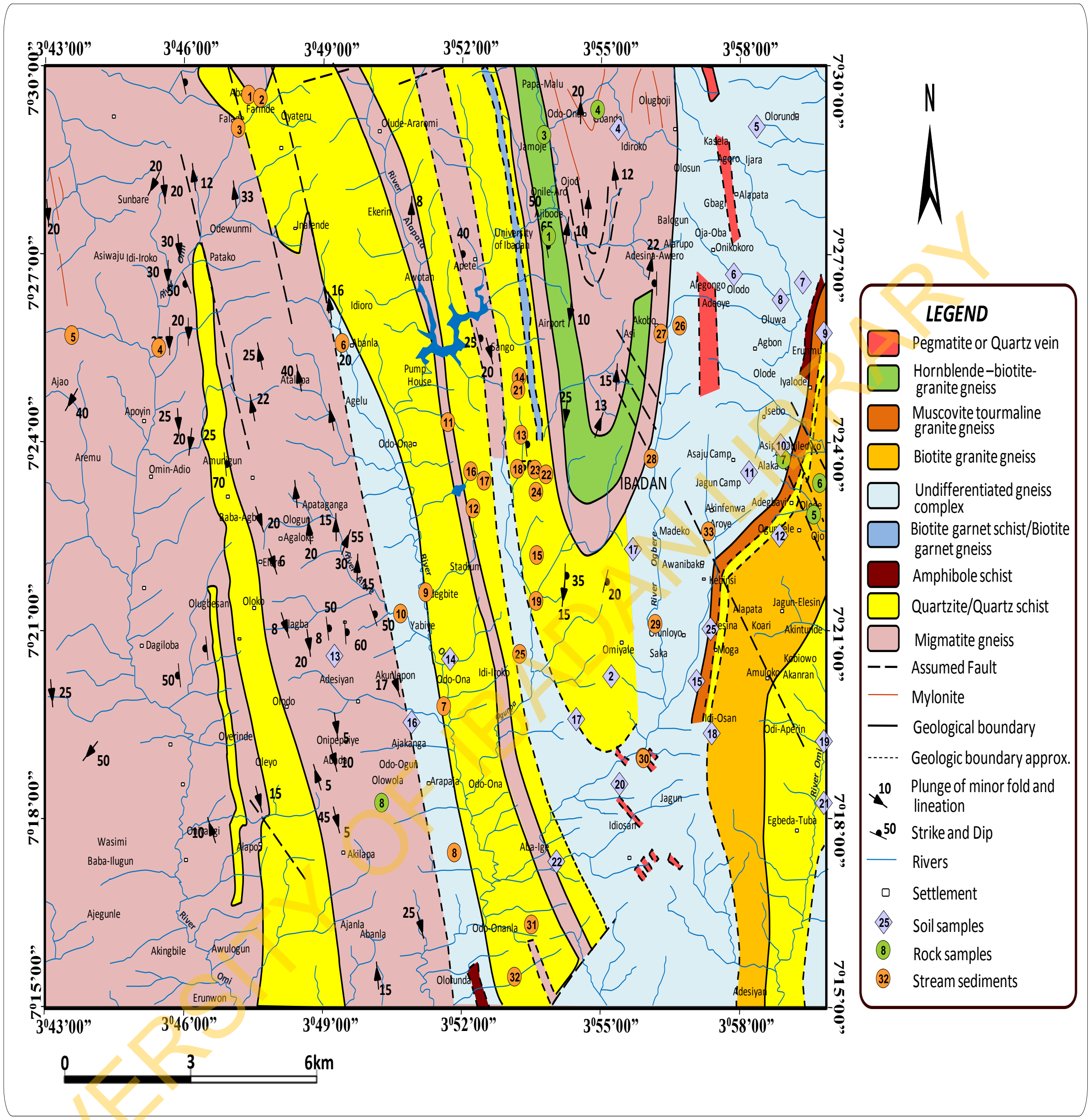


Figure 2.6. Geological map of Ibadan and its Environs

(Source: NGSA, 2004)

Figure 2.7. Quartzite exposure at Apata in Ibadan

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Figure 2.8. Biotite-Hornblende Gneiss from Moniya area of Ibadan metropolis

Figure 2.9. Biotite Gneiss in PW Quarry at Ojoo in Ibadan metropolis

Figure 2.10. Banded gneiss behind the IITA, Ibadan

Figure 2.11. Grey gneiss at Iyana Agbala area of Ibadan metropolis

2.3 Review of Related Works on Lead (Pb) Isotopes and Heavy Metals

The isotopic study of Pb was initially used as a geochronology tool; however, a second practical application is to trace the source of Pb in environmental materials. The natural variations in Pb-isotopic ratios (IRs) are useful to elucidate the origin of Pb; since the isotopic composition is characteristic of different sources. Pb isotopic signatures of unpolluted soils/sediments are generally higher ($^{206}Pb/^{204}Pb$ =18.5 - 19.5) than polluted soils. This is as a result that they may be derived/sourced from weathered rocks, where the Pb-Isotopic Ratios has evolved with time, reflecting the initial U/Pb and Th/Pb content of the parent materials (Hansmann and Koppel, 2000). In polluted soils/sediments, the polluting element has the isotopic signature of its source. Regarding the abundance of the radiogenic isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb and the analytical instrumentation to measure them, the combination among them to get IR values have proved to be a useful environmental tool in tracing Pb sources.

Lead (Pb) isotopic analysis has been widely used in environmental studies of Pb contaminations of soils, sediments and air as well as plants around the world (Flament et al., 2002; Wong et al., 2002; Wong and Li, 2004; Erel et al., 2001; Marcantonio et al., 1998). Environmental Pb has four isotopic forms which include ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is regarded as non-radiogenic and therefore remains stable.

Since the mid-sixties, Pb isotopes have been acknowledged as having the capability to identify the source of Pb present within a variety of the environment (Ault et al., 1970; Chow and Johnstone, 1965; Chow and Patterson, 1962; Chow et al., 1975). Spatial variability in soil, sediments and dusts Pb levels has been observed with greater levels of atmospheric lead emissions (Banin et al., 1987; Foner, 1990). It has been proposed by Swanson and Johnson, (1980) that lead remains in soil or sediment for varying lengths of time depending on the mobility of the organic matter and sesquioxides in the soil (Shirahata et al., 1980, Erel et al., 1997). Saether et al., (2011) while working on lead isotope distribution in podzolic soil profiles on different bedrocks in the Oslo area mapped an accumulated content of anthropogenic Pb and how deep in the soil profile the atmospherically deposited Pb has penetrated applying three different methods. They concluded that the amount of anthropogenically deposited Pb in the uppermost 20 cm (top-soil) of the podzolic soils in the region is 1-6t/km^2. Patterson in 1965 drew attention to the increase in levels of Pb from industrial sources in the environment and food. This work led to abolishing of tetra ethyl lead as an additive in petrol in the USA in 1986 and later in the use of Pb in food cans. This banning resulted in a fall of up to 80% in blood Pb levels. Pb in petrol and food cans is now completely banned in the developed countries but still a problem in most of the developing countries.

Researchers (Hopper et al., 1991; Grousset et al., 1999 and Maring et al., 1987) have used Pb isotopes to trace lead migration and pollution in both Europe and in the Mediterranean regions and concluded that the isotopic composition of anthropogenic Pb emitted to the environment is largely controlled by the isotopic values of the original ore bodies (Sturges and Barrie, 1987). The isotopic composition of lead in aerosols and soils in Israel has been used to characterize the sources of anthropogenic lead in the region, to ascertain the isotopic composition of natural, rock-derived lead in specific areas, and to determine rates of anthropogenic lead migration in soils (Erel et al., 1997).

Lee et al., (2008) concluded that the Pb isotopes in some China Lakes reflect the mining history of China while most researches carried out in China focused more on the isotopic composition of Pb within the airborne particulate matters within the urban centers (Chen et al., 2008; Duzgoren-Aydin, 2007; Li et al., 2009; Mukai et al., 1993, 2001). This has also been confirmed by Zhao et al., (2011), which concluded that the Pb isotopes of lake sediments can record the history of atmospheric Pb pollution triggered by regional industrial development. A review by Miller and Orbock-Miller (2007) identified fluvial environments as principal route for the dispersal of trace metals as well as an important sink.

Trace metals dispersal are mainly dominated by particulate-associated transport (Carter et al., 2006) giving rise to spatially extensive dispersal of contaminants from both points and diffuse sources (Bird et al., 2003; Hudson-Edwards et al., 2001). The importance of sediments and soils as transport mechanism of contaminants and as well as potential sources of contaminants (Hudson-Edwards et al., 1998) has increased in conjunction with greater focus on integrated environmental management (Macklin et al., 2006; Bird, 2011).

Gelinas and Schmit (1997) indicated that Pb isotopic signatures are generally preserved during trophic transfer of Pb between the phyton and nekton in minows while Miller et al., (2005) discovered a significantly lower ^{206}Pb/ ^{207}Pb ratios lower in muscle and liver compared to bone in soft tissues and bone of rainbow trout. The toxicity and the effects of environmental implication of lead on human health have been widely documented (NSC, 2009; Baldwin and Marshall, 1999; Nriagu, 1988). According to the World Health Organization, lead is absolutely non-essential to the human body and its most profound effects are seen in children (Nriagu, 1988). Surface soils provide a potential medium of exposure and are well correlated source of blood lead in urban children (Mielke and Reagan, 1998). A strong significant correlation has been established between lead concentrations in blood and IQ.

This was further confirmed by NSC (2009) in their summit that lead concentrations in blood have no apparent lower bound threshold as regards neuro-developmental effects. Lead in the bone has significantly been related to declines in hematocrit and hemoglobin among moderately lead exposed construction workers (Hu et al., 1994); among middle-aged to elderly men. It has also been related with the increased odds of clinically relevant hypertension (Hu et al., 1996), also with decreased in birth weight among mothers in Mexico City and among teenagers in Pittsburgh. It relates well with increased risk for antisocial delinquent behavior while other effects of lead toxicity in bone include cognitive performance and growth in children and cognitive performance, kidney function, gout, blood pressure, reproductive toxicity, and adverse cardiovascular events in adults (Gonzalez-Cossio et al., 1997). Stable lead isotopic studies have been used in distinguishing circulatory lead derived from current environmental exposures from older skeletal lead (Pb) that was assimilated into bone over the past, years. This was facilitated by long residence time of lead in human skeleton, which greatly exceed those in soft tissues and by the temporal changes in isotopic compositions of industrial lead emissions to human environment.

In the work of Hamilton and Clifton (1984) carried out on the Briston Channel, UK, where higher concentrations of Pb were found to be an indicative of lower ^{206}Pb/ ^{204}Pb and ^{206}Pb/ ^{207}Pb in the Briston Channel sediments. This was also observed by Petit et al., (1984) and Xu et al.., (2009) that strong relationship exists between the concentration of Pb and their isotopic ratios where lower ^{206}Pb/^{207}Pb ratios (i.e. an indicative of anthropogenic Pb) were demonstrated in association with higher Pb concentrations.

The first mass spectrometric demonstration of the variation in lead isotope abundances in minerals was performed by Nier (1938). The more recent growth in the use of Pb isotopes as geochemical tracers has been facilitated by developments in analytical approaches for determining reliable isotopic data. Recently, mass spectrometry either with thermal ionization or inductively coupled plasma as the ion source has been successfully applied in Pb isotopic studies. Thermal Ionisation Mass Spectrometry (TIMS) is a reliable analytical technique for precise and accurate determination of Pb isotope ratio in environmental samples (Weiss et al., 1999). Extensive chemical treatment and optimization of vaporization and ionization of samples prolong the analytical procedure but permit the determination of Pb isotopes with relative standard deviation (RSD) of 0.005 to 0.01% (Thirlwall, 2000).

It has been established that trace metals concentrations exhibit a strong relationship with particle size with preference to the silt and clay fractions (Miller, 1997). It may be expected that lead isotope signatures may display heterogeneity between the size fractions and also that the anthropogenic Pb may preferentially associated with the chemically active silt and clay although Pb may exist in sediments as coarser fragment from erosion from mines (Bird, 2011). It has been concluded that concentrations alone cannot clearly prove anthropogenic pollution since high metal concentrations may also come from natural processes. Hence, differences in Pb isotopic ratios combined with the variations of Pb concentrations have been used to identify the possible sources of anthropogenic Pb in both soils and sediments (Graney et al., 1995; Hansmann and Koppel, 2000; Reimann et al., 2011; Morton-Bermea et al., 2011).

Most of the studies in southwestern Nigeria suggested vehicle emissions, industrial wastes, unplanned urban setting and indiscriminate discharge of urban wastes (both liquid and solid) as possible sources of the heavy metals pollution. (Tijani et al., 2004; Olatunji et al., 2009; 2010).

Ingestion of soils and inhalation of dust particles are widely accepted as the major pathway for childhood exposure to lead based paints, leaded gasoline and other metals derived from vehicular traffic and other industrial sources (Rasmussen et al., 2001). The potential for exposure to contaminants via this source is greater for children because they are more likely to ingest more soils than adult as a result of behavioral present during childhood. Inadvertent soil ingestion among children may occur during mouthing of objects or hands. The toxicological effects are further aggravated by the unique physiology of children, the sensitivity of their developing vital organs and different chemical forms of metals involved (Nriagu, 1988; Hrudey et al., 1996). Soils are far more important dietary contributors because the concentrations of potentially harmful substances in soils are much greater than in water or any other media. Soil particles directly or indirectly transform into house dusts and road dusts can be ingested by adults and children through unintentional hand to mouth contact or dust inhalation (White et al., 1998).

Studies in Nigeria have shown that about 70% of children aged 6 to 35 months had blood lead levels greater than 10 g/dl and that flaking house paints are important culprits of this (Pfitzer et al., 2006; Wright et al., 2005). Similar study by Adebamowo et al., (2006) has been revealed that emulsion and gloss paints locally manufactured in Nigeria contained substantial levels of lead while Ward (1990) confirmed that vehicular emission accounted for the prevailing elevated levels of lead and other heavy metals in roadside dusts, soils, particulate matters, vegetation and streams. Lead released from vehicle exhaust has been linked to the addition of tetra-ethyl-lead as an additive to gasoline in order to increase its efficiency. As at 1987, the average content of lead (Pb) in Nigerian super grade gasoline is about 0.74 g/L and this put the Nigerian super gasoline as one of the highest leaded gasoline in the world (Arah and Nwankwo, 1987). Other constituents in gasoline include Cd, V and As, which are released into the environments via combustion of fossil fuel while metals such as Ni, Cr, Zn, Fe and Sb are essential components of vehicle parts which can be also released as a result of wearing and tearing.

CHAPTER THREE

MATERIALS AND METHODS

3.1 General Statement

The study involves field activities, laboratory activities as well as data interpretation using various geo-statistical tools and GIS methods.

3.2 Field Activities

Soils, stream surface sediments and roadside dusts were collected within Lagos and Ibadan metropolises. Samplings were concentrated at areas where elevated Pb concentrations have been reported in previous studies. The GPS was used to locate exact positions and elevations of sampling points. All information was recorded in field notebook. Hand auger was used in collecting soil samples from the respective depth, in this study the depth of interest was between 0-30 cm. Plastic sieves were used in sieving out dirt and stones from soils, sediments and roadside dusts after sampling. Stainless steel hand trowel was used in scooping out sediments along drainage channels.

Samples were collected during dry stable weather conditions using topographic maps of 1:100,000 as base maps for study areas (Federal Survey of Nigeria, 1964). Soil samples were collected from predetermined designations, within each grid using hand auger; five sub-samples were collected within each grid and thoroughly mixed together to form a composite sample. Samples were bagged in well-labelled sample bag before being transported to laboratory for onward preparations. Surface stream sediment samples were collected within the drains and the canals in Lagos metropolis using stainless steel hand trowel after removal of any extraneous materials such as debris. Four sub-samples were collected within 500 m along a drainage channel or canal. Samples were screened through 2 mm nylon sieve in order to remove coarser particles, debris and organic materials. A total of forty-eight soils, twenty-one stream sediments and seventeen road side dusts samples were collected within Lagos metropolis while a total of twenty-five soil samples and thirty-five stream sediments were collected within Ibadan metropolis.

In Ibadan, the surface stream sediments (0 – 20 cm) were collected randomly based on the previous studies (Ajibade, 2013). The surface sediments were chosen because this layer controls the exchange of metals between sediments and water (El Nemr et al., 2006). Four river channels draining Ibadan metropolis were chosen for this study and these are Rivers Omin, Ona, Ogbere and Ogunpa. At each sampling location, 5 sub-samples were collected within 500 m and mixed properly to give a composite sample. Twenty-five composite soil samples were collected randomly within Ibadan metropolis. Five sub-samples were collected at depths of 0 – 30 cm within 15m^2 and mixed properly to form a composite sample. Road side dusts were also collected with the aid of plastic brush and stainless steel trowel by the two extreme edges of the selected roads and the dividers.

All samples were air-dried under ambient room temperature. The samples were screened and homogenized and then pulverized in a ceramic mortar with a pestle then sieved through 63µm to obtain silt/clay fractions for chemical analyses. 1.0 g of the sieved fractions of the samples were weighed into a well labelled bags for chemical analyses. In order to study the relationship between the heavy metals and the lead isotope signatures in urban soils, sediments and dusts and their respective concentrations in the underlying materials, ten representative rock samples representing eight major rock types underlying Ibadan metropolis were collected during random geological mapping while core samples were also collected from boreholes within Lagos main land for geochemical analyses. Portion of the ten rock samples were cut into thin sections for their petrological studies at the Thin Section Laboratory while the petrological studies were carried out at the Petrology Laboratory all in the Department of Geology, University of Ibadan. Other portion of the rock- and core- samples were crushed, pulverized and then sieved to less than 63 µm using plastic sieve. 10 g of the sieved portions were weighed and prepared for whole rock chemical analysis. Also 10 g of the core samples were disaggregated, pulverized and then sieved to less than 63 µm and subsequently prepared for whole rock analysis.

3.3 Analytical Methods

3.3.1 Whole Rock Analysis

Ten fresh rock samples from the study areas and two Pb ores (galena) sourced from Kogi and Zamfara States (Nigeria) were crushed and pulverized and then sieved through 63 µm mesh sieve to obtain finely ground material for analyses. These samples were subjected to total digestion using HCl, HNO_3, $HClO_4$ and HF. These finely ground materials were analyzed for major, trace and rare earth elements on a combination of simultaneous/sequential thermos Jarrel-Ash ENVIRO 11 ICP at the Bureau Veritas Commodities Ltd, Vancouver, Canada. Calibrations were carried out with thirteen prepared USGS and Camnet certified reference materials. The detection limits for major oxides vary from 0.002 to 0.04 % while that of trace and rare earth elements vary from 0.01 to 20.0 ppm. Accuracy of analyses was controlled with the aid of certified geological reference materials such as STD GS311-1, STD GS910-4, STD SO-18, STD DS10, STD OREAS45EA, STD NIST-981-1Y and STD NIST 983-1Y supplied by the commercial laboratories were used as checks on the accuracy of the analyses while analysis of certified samples, randomly selected rock samples and blank samples were continuously run for seven times to determine the precision of the analyses.

3.3.2 Trace Elements and Lead Isotopes Analyses

3.3.2.1 Trace Elements Analyses

To determine the total Pb and other metals concentrations in soils, sediments and dusts, the dried, powdered and sieved fractions of the samples were dissolved using a combination of concentrated nitric acid (HNO_3) and per chloric acid ($HClO_4$). Metal concentrations of the digested solutions were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV) at Acme Laboratories, Canada. Samples with Pb contents greater than 100 ppm were identified and further analysed.

About 0.5 g of the clay fractions of these samples were digested with concentrated HNO_3 and $HClO_4$ (4:1 by volume). The mixtures were heated continuously in an aluminum block until they were nearly dry. 10.0 ml of 5 % (v/v) HNO_3 was then added to the test tubes and heated at 70 ^oC for 1hour. The solution was allowed to cool, then decanted into polythene tubes and centrifuged at 3500 rpm for 10 minutes. Pb and other heavy metals concentrations in the solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry. For quality control, blanks were repeatedly run seven times, replicates and standard reference materials were inserted into the samples batch, representing 20 and 10 % of the samples, respectively. Reference materials such as STD DS10, STD OREAS45EA, STD NIST-981-1Y and STD NIST-983-1Y supplied by the commercial laboratory were repeatedly analyzed at least four times for quality control and consistency.

3.3.2.2 Lead Isotopes measurements

In addition to the measurements metal concentration with ICP-MS, preliminary isotopic measurements from instrumental scans of all stable lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) were made. Fractionation corrections were derived from concurrent analyses of SRM 981 supplied by Acme Laboratories. Corrections for $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ averaged +0.006, +0.001, and +0.003, respectively. For Pb-isotope ratio determination, the extracted solution from 4-acid digestion were further digested with 7 M HNO_3 in transparent polypropylene tubes with caps in an autoclave at about 200 kPa (120 ^oC) for 3 minutes and analyzed for Pb isotopic composition. The isotopic ratios were corrected for mass spectrometric fractionation effects on the basis of repeated measurements of STD NIST-981-1Y and STD NIST-983-1Y (NIST; common lead standard reference material). Although partial leaching is generally used in environmental exposure assessment, often in accordance with USEPA Method 3050 (USEPA, 1996) because it enhances the anthropogenic signal but this signal might be otherwise swamped by geogenic Pb bound in insoluble minerals (Renberg et al., 2002). The digested samples were then analyzed for elemental content using Sector-based or sector field Inductively Coupled Plasma Mass Spectrometry method (ICP-SFMS). Control samples were analyzed to check analytical precision and consistency.

The ICP-MS instruments include those with quadrupole-based (ICP-QMS), sector-based or sector field (ICP-SFMS) and time-off sector-based (ICP-TOF-MS) techniques can be equipped with single or multiple collector (MC) detectors. ICP-QMS has lower accuracy and precision when compared to TIMS. This limitation is due to the unstable nature of the plasma ion source and analyzer parameters. Other drawback is that the masses are not detected simultaneously therefore, the precision during isotope ratio measurements obtained using single collector configuration is generally lower (Komarek et al., 2007). While ICP-SFMS has advantages of simplified sample preparation procedures with high sample through put with reduced measurement time (Quetel et al., 1997). Krachler (2007) concluded that ICP-SFMS has higher sensitivity, less electronic noise and ability to separate spectral interferences in high resolution mode while in low resolution modes it yields isotope ratio precision of <0.05% (Table 3.1).

3.3.3 Sequential Extractions

Selective extraction of some selected samples were carried out in order to investigate the mobility of Pb and other metals, and therefore determine their possible release into the environment and their toxicity. The chemical partitioning of Pb and other elements in selected samples (soil, sediments and road dust) was carried out using a modified Tessier's et al., (1979) five - step sequential chemical extraction method (Li et al., 1995). The chemical fractions and reagents used in the sequential extraction procedures are summarized below:

Readily soluble and Exchangeable fraction (F1): exchangeable, 1 M $MgCl_2$ at pH 7 for 1 hour;

Carbonate fraction (F2); bound to carbonate minerals specifically adsorbed to weak organic and inorganic complexes' 1 M sodium acetate adjusted to pH 5.0 with acetic acid for 5 hours at room temperature;

Reducible fractions (F3): 'bound to amorphous Fe and Mn hydroxides' 0.04 M hydroxylamine hydrochloric acid in 25% (v/v) acetic acid at 96 ^{o}C for 6 hours.

Organic and sulfide fractions (F4): 'bound to stable complexes of organic matter and sulfide minerals' 30 % H_2O_2 and 0.02M nitric acid at 85^{o}C for 5hours;

Residual fraction (F5) containing primary and secondary minerals held within their crystal structure respectively: 'residual' 5:1 mixture of HNO_3 and $HClO_3$ acids, followed by evaporation to dryness and dissolution of the residue in 6 M HCl.

It has been generally accepted that the reactivity and the potential bioavailability of heavy metals increases with increasing solubility (Li and Thornton, 2001). The exchangeable and carbonate fractions are the two most mobile forms of metals in soils and sediments are considered to be potentially bioavailable (Wong and Li, 2004). Heavy metals in the Fe-Mn hydroxides and organic fractions are usually relatively immobile and stable but may sometimes become mobile and bioavailable with time or upon changes of soils and sediments conditions such as decrease in pH and Eh. Heavy metals in the residual fraction were regarded as the most stable and least bioavailable form. The Pb and other elements concentrations of the extracted solutions were measured by ICP-MS (Fig. 3.1). The Pb concentrations of the procedure blanks were generally 0.5% of those of the analytical samples. The recovery rates calculated from the sum of the five fractions over the total metal concentrations determined independently ranged between 10 - 5%.

3.3.4 XRD Analysis

X-ray diffraction (Fig.3.2) was used to determine the mineralogical composition of some selected rock, soil, road-side dust and sediment samples from the study areas. The samples were air dried, disaggregated/pulverized and sieved to obtained the fine fractions (<75µm). A mixture of compounds gives a pattern that is made up of the patterns of all the individual compounds and this allowed the identification of phases in the sample by the Rietveld method (Bob, 2009).

The X-ray on passing through the sample gives peaks that are typical of each type of the minerals that make up the samples. The X-ray beams are diffracted along a group of planes and the way they are diffracted is characteristics of the arrangement of the atoms within the mineral. The XRD method is fast and non-destructive. For the purpose of this work, the X-ray Diffractions analysis was carried out at the Department of Earth, Ocean and Atmospheric Sciences; University of British Columbia, Vancouver, Canada.

Table 3.1. Summary data for analytical precision for Pb isotope determinations using a range of analytical methods

Analytical Technique	%RSD	References
TIMS	0.001-0.01	Cheng and Hu (2010)
	>0.005	Balcaen et al., (2010)
ICP-QMS	0.1-0.5	Cheng and Hu (2010)
	0.01-0.98	Hudson-Edwards et al., (1999)
HR/MS-ICP-MS	0.04-0.1	Walder et al., (1993)
	0.05-0.2	Heumann et al., (1998)
	<0.05	Cheng and Hu (2010)
MC-ICP-MS	0.01-0.02	Walder et al., (1993)
	≥0.002	Balcaen et al., (2010)
GDMS[a]	<0.03[b]	Riciputi et al., (1995)

a Glow Discharge Mass Spectrometry; b Determined for analysis of pure solid sample

(Source: *Bird, 2011)*

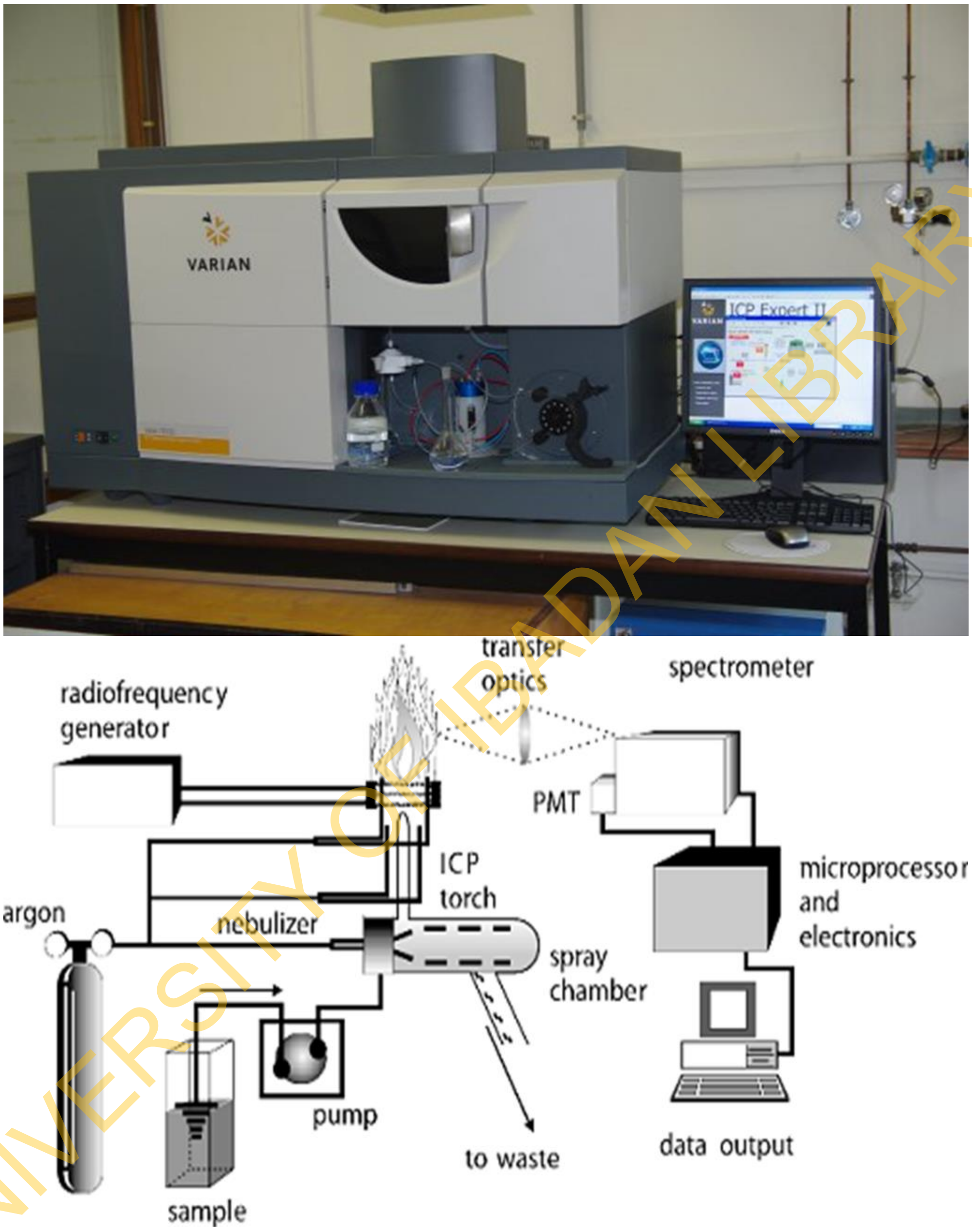


Figure 3.1. Image of an Inductively Coupled Plasma Emission Spectroscopy Used in Tessier Extraction

The principles of quantifying XRD phases are theoretical while the limitations on accuracy are experimental. There are single-peak methods, multiple-peaks methods and whole-pattern methods which include Rietveld but the whole - pattern methods are more preferable because of its accuracies of ± 2%. This procedure was adopted for the quantification and interpretation analyzed data. The Rietveld analysis is a mathematical method using analytical profile functions and least-squares algorithms to fit a theoretical to a measured pattern. In order to perform a Rietveld refinement structure, data for all phases present in the samples are needed. The determination of amorphous content of a sample with Rietveld refinement is possible by addition of a crystalline standard phase. An internal standard is mixed with the sample after the grinding. The interpretation and quantification analysis of the collected data were carried out by means of Search-March software by Bruker High Score + software using the ICSD PDF 4+ database version:2013 and ICSD (Inorganic Crystal Structure Database) database version:2007.

The samples were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronising Mill for 10 minutes. Step-scan X-ray powder-diffraction data were collected over a range 3-80° 2 θ with CoK α radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a Lynx Eye-XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

3.4 Data Treatment and Evaluation

The results of the chemical analyses were subjected to statistical analyses such as descriptive, Pearson correlation, Coefficient of variation and R-mode factor analyses using Excels, SPSS Window 22.0, Origin Window 10.0 and surfer 8. Results were interpreted using tables and figures such as scattered plots, bar charts and line graphs. Arc GIS and Arc-View were used in the production of geochemical and geologic maps while contamination indices such as Enrichment factor (EF), Degree of contamination and geo-accumulation Indices were also used in evaluating and assessing the environmental implications of the heavy metal contents and total lead contents. In order to assess the degree of contamination and distinguished between natural and anthropogenic pollution sources of Pb, the index of geo-accumulation used in many studies (Teng et al., 2003) was employed. The results of some major oxides were plotted against their corresponding SiO_2 contents, comparisons were made between some elements and their respective background values derived from underlying bedrocks. The results of the Pb isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb were normalized using the non-radiogenic primordial ^{204}Pb in order to eliminate the effect of natural variation in Pb content of the sampling media. The Pb Isotopic ratios used were ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb. The lead isotopic ratios (IRs) in soils, sediments and road side dusts from the study areas were calculated and plotted. Isotopic Ratios (IRs) of ^{206}Pb/^{207}Pb were plotted against the Pb concentrations in all the analyzed media. Ultimate conclusions were drawn from various inferences.

Figure 3.2. Image of XRD Machine

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Petrological Studies of Ibadan Migmatite-Gneiss-Quartzite Complex (MGQC)

The result of the petrological study revealed abundance of quartz, biotite, plagioclase feldspars and alkali feldspars (microcline) with some hornblende in virtually all the studied representative rock samples from the Migmatite-Gneiss-Quartzite Complex of Ibadan metropolis (Figs. 4.1 to 4.12). The following rock units were encountered in different parts of Ibadan metropolis:

1. The migmatite gneiss

This rock type constitutes about 30% of the rock types in Ibadan metropolis (Ajibade, 2013). The rock units are more predominant in the northern part of the metropolis extending from east to west. However, it is more prominent and well exposed in the north eastern part. Representative samples were collected from PW Quarry site at Ojoo, Moniya and Adegbayi areas of Ibadan metropolis. The rocks are composed essentially of quartz, feldspars, microcline, plagioclase and biotite. Abundance of Alkali feldspar grains were observed (Microcline crystals as evident with tartan twinning). Grain boundaries of the microcline (Mic) crystals with closely formed subhedral to euhedral flakes of biotite (Bt) also describes subhedral grain shape for the alkali feldspars. Minute flakes of muscovite (Mc) were also observed. Similarly, high relief garnets with trapezohedron habit were observed to distinctly set along the foliation plane defined by biotite flakes which was better observed under the plane polar (Figs. 4.1a-c- 4.2a-b).

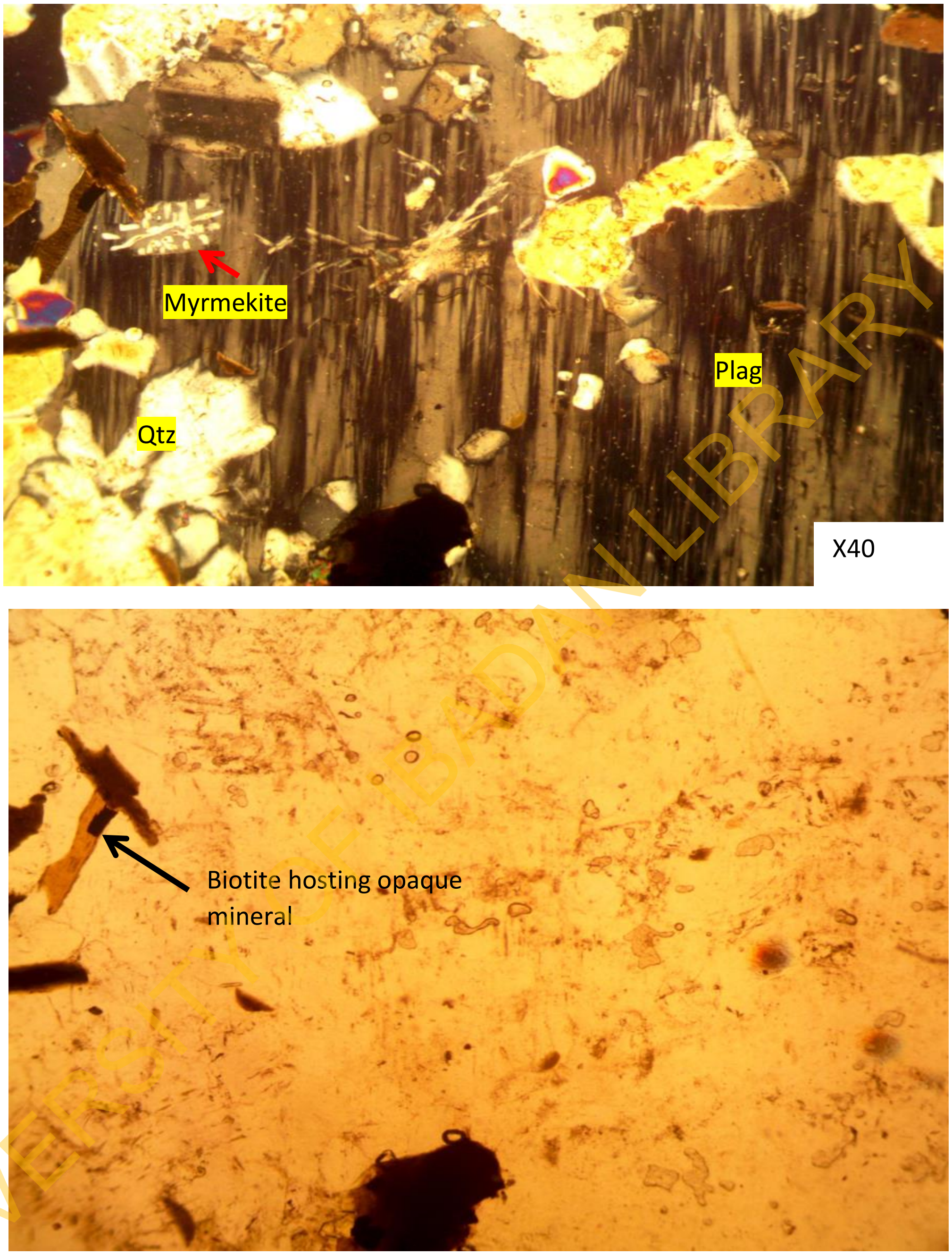


Figure 4.1a. Photomicrographs of migmatite gneiss @ Iyana Agbala

Plagioclase (Plag) mineral occurring as oikocryst exhibits deformation lamellae. Smaller grains of biotite occur as secondary biotite grains and host opaque minerals presumed to be magnetite. K-metasomatism may be linked with deformation as plagioclase crystal shows deformation lamellae. Myrmekite, quartz (Qtz) and plagioclase (Plag) are the dominant minerals

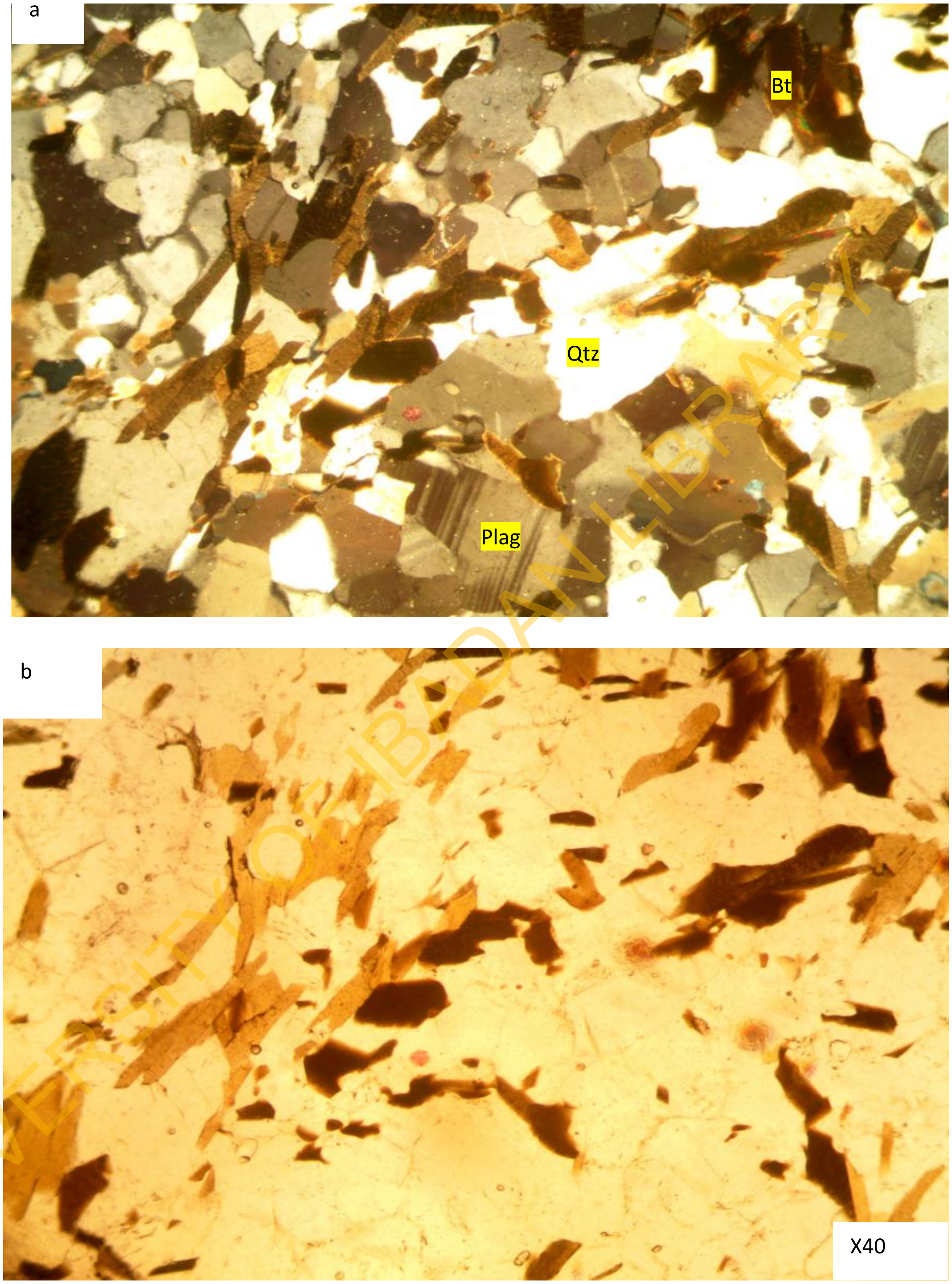


Figure 4.1b. Photomicrographs of biotite-hornblende gneiss behind IITA Moniya. *Plagioclase shows compositional variation by the range of tapering of twinning according to albite law (lower part of a). Biotite showing interference colours along its grain boundary from yellow to red.*

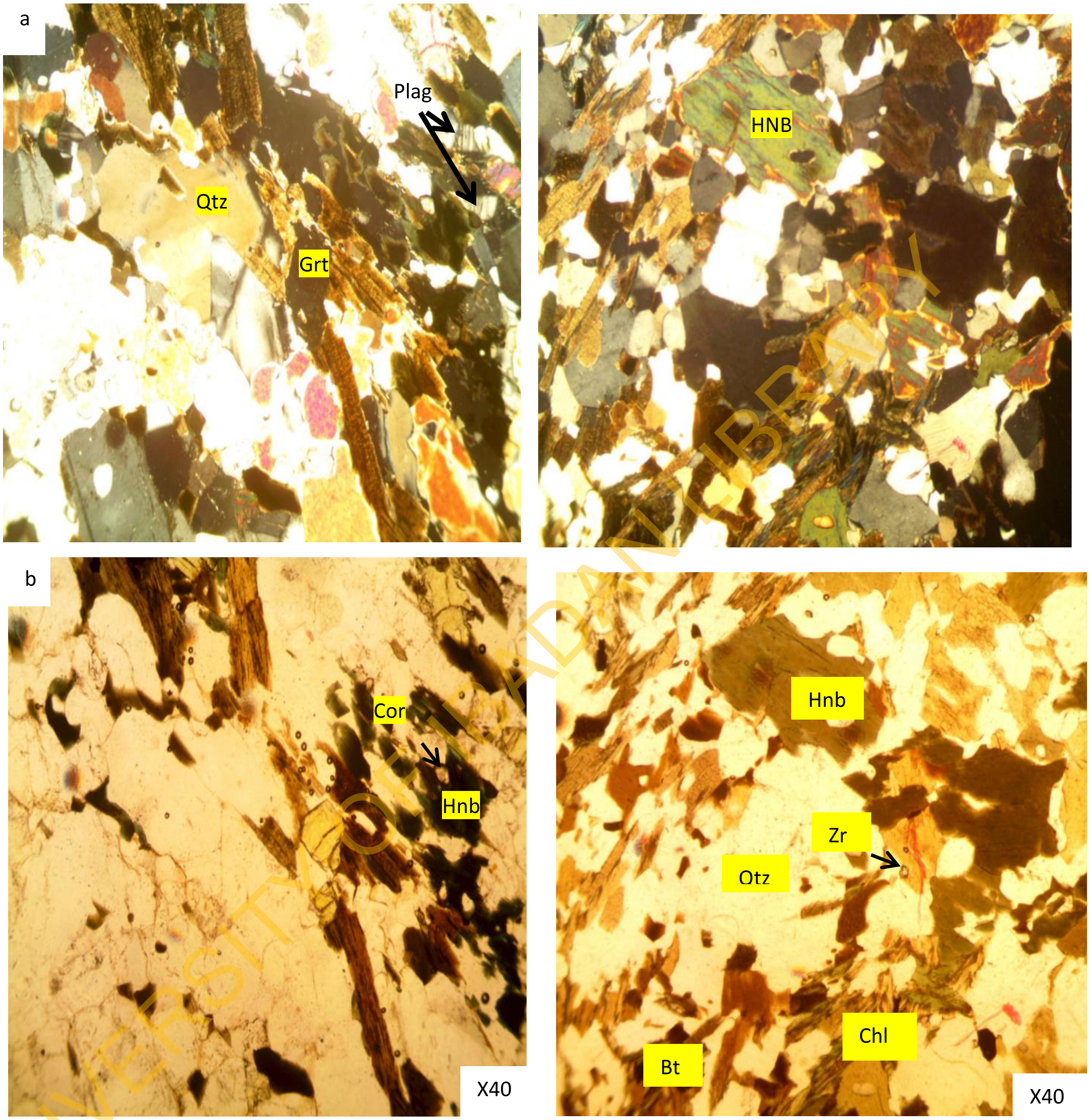


Figure 4.1c. Photomicrographs of banded hornblende biotite gneiss at Ojoo.

Right-Hand, Biotite (Bt), hornblende (Hnb), quartz (Qtz), plagioclase (Plag) and garnet (Grt). Garnet (Grt), corundum (Cor) and hornblende (Hnb) closely associate with large grains of biotite. Left-Hand, Chlorite (Chl) – biotite (Bt) alteration reaction is observed in the lower part of the plane polarised photomicrograph. Mineral composition is composed of quartz (Qtz), plagioclase (Plag), biotite (Bt) and hornblende (Hnb). Zircon occurs as an accessory mineral.

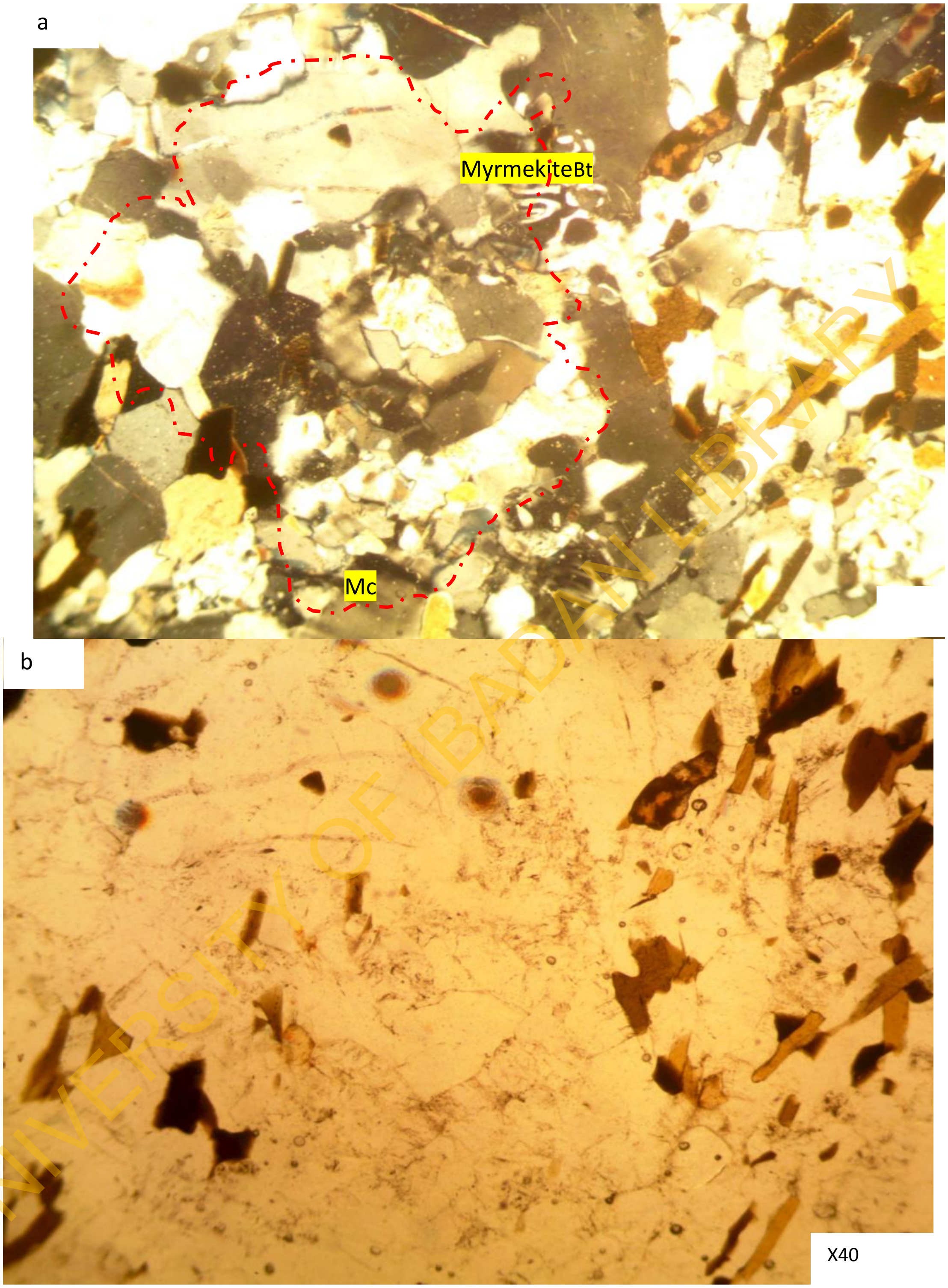


Figure 4.2a. Photomicrographs of biotite gneiss at Ojoo.

Evidence for K-metasomatism during the formation of myrmekite is shown. Oikocryst of fragmented quartz grain host grains of biotite and microcline (red outline) describes poikilitic texture.

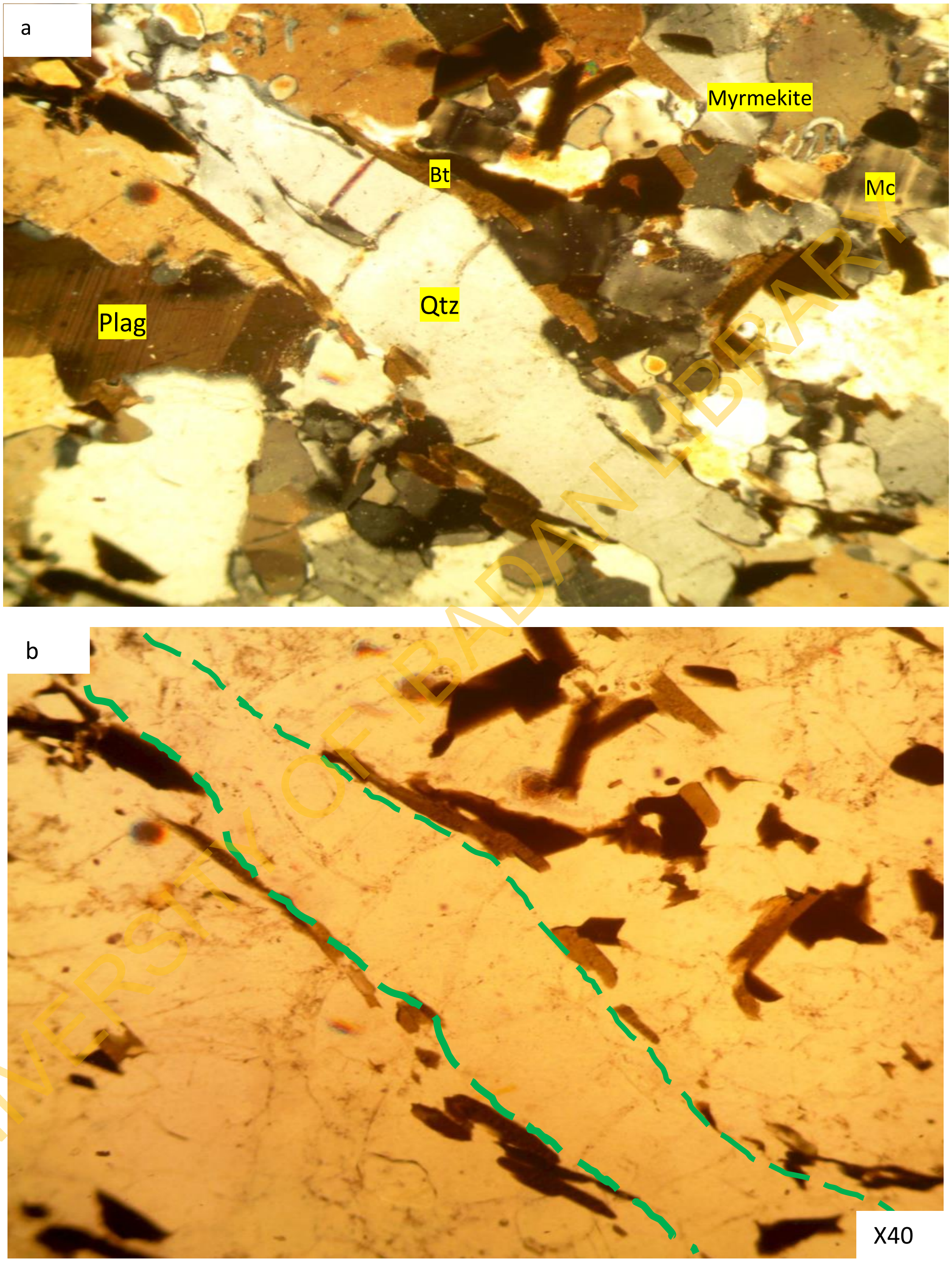


Figure 4.2b. Photomicrographs of biotite gneiss at Ojoo *Strained quartz (Qtz) mantled by biotite (Bt) grains exhibits cracks propagated perpendicularly to the boundary face with the foliation plane. Strained quartz and biotite grains define both lineation and foliation respectively*

2. Biotite gneiss

Typical examples of this rock unit were encountered within University Ibadan, Abadina and Ajibode areas of the metropolis. This rock unit contained lots of large stretched phenocrysts of feldspars in fine ground mass of mafic minerals. The rock was composed essentially of biotite, quartz grains that showed evidence of deformation as a result, exhibiting undulose extinction and lots of feldspars. Other minerals include microcline (Mc) and biotite (Bt). Foliation is defined by biotite grains. Alteration of biotite leading to the formation of hornblende in prograde metamorphism was suspected (Figs. 4.3 – 4.7).

3. Biotite Granite Gneiss

These rocks unit occurs as low lying outcrops and are concordant to the gneissic units at the western parts of the Ibadan metropolis. This unit was mostly found around Odo-Ona area of Ibadan metropolis. Petrological studies of the sampled rocks revealed abundance of quartz, plagioclase and some microcline alkali feldspars. Subhedral zircon grains were observed in abundant and scattered among the numerous feldspar and quartz grains. Feldspars include microcline (Mc) and plagioclase (Plag) of probable sodic composition based on the boundary association with a microcline (Mc) as observed under cross Nicol (Fig. 4.8). Opaque minerals were observed as small grains sharing grain boundary with some biotite grains. Large grains of plagioclase (Plag), quartz (Qtz) and biotite (Bt) describe granophyric texture (Fig. 4.8).

4. Schistose Quartz

This rock unit occurs at the central part of Ibadan metropolis. They are associated with an almost north-south trending unit of the migmatite gneiss complex which was later intruded by the Pan-African granitic rocks of adammelitic and pegmatitic varieties (Okunlola et al., 2009). Schistose quartz form prominent features around Apata, west of Ajibode and Sango areas of Ibadan metropolis. Petrological studies revealed that this rock unit consists largely of quartz and minor opaque minerals embedded within the quartz (Fig. 4.9). Quartz foliations were also observed.

5. Other minor rocks

Other minor rocks units encountered during this study include pegmatite, amphibole-schist and amphibolite. Pegmatite occurred as intrusions mostly around Felele area and are discordant virtually to all the rock types. Amphibolite and amphibole-schists were observed around Olode, Olodo and Iyana Church areas. They occurred as greenish fissile bodies. Petrological studies showed the presence of hornblende, quartz, plagioclase and minor biotite (Fig. 4.10).

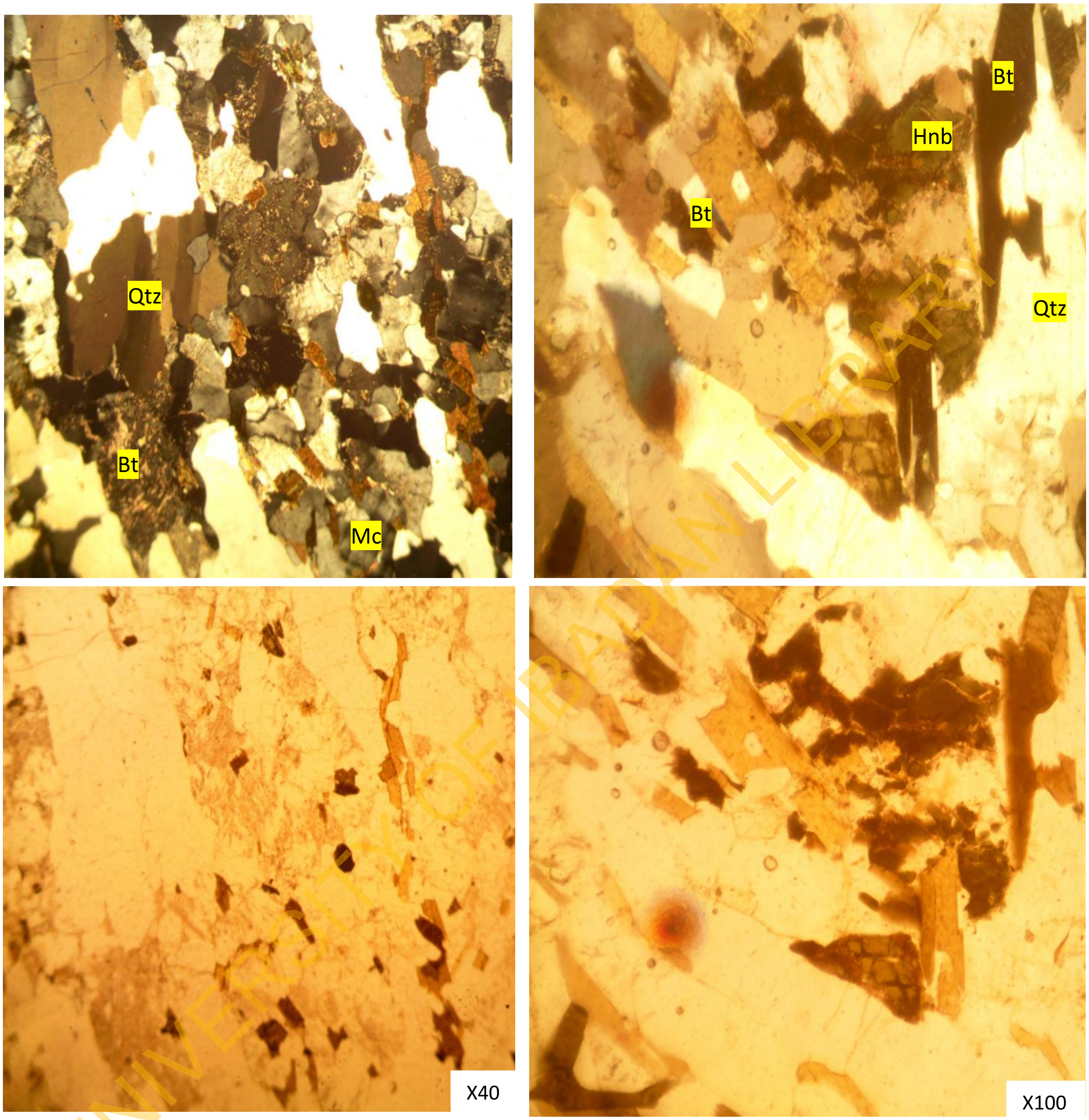


Figure 4.3. Photomicrographs of biotite gneiss from Ajibode area of Ibadan under plane and crossed polarized light.

Mineralogical composition composes of quartz grains that showed evidence of deformation by exhibiting undulose extinction (upper left of cross Nicol). Other minerals include microcline (Mc) and biotite (Bt). Foliation is defined by biotite grains (right side of the plane polarised light). Alteration of biotite leading to the formation of hornblende in prograde metamorphism

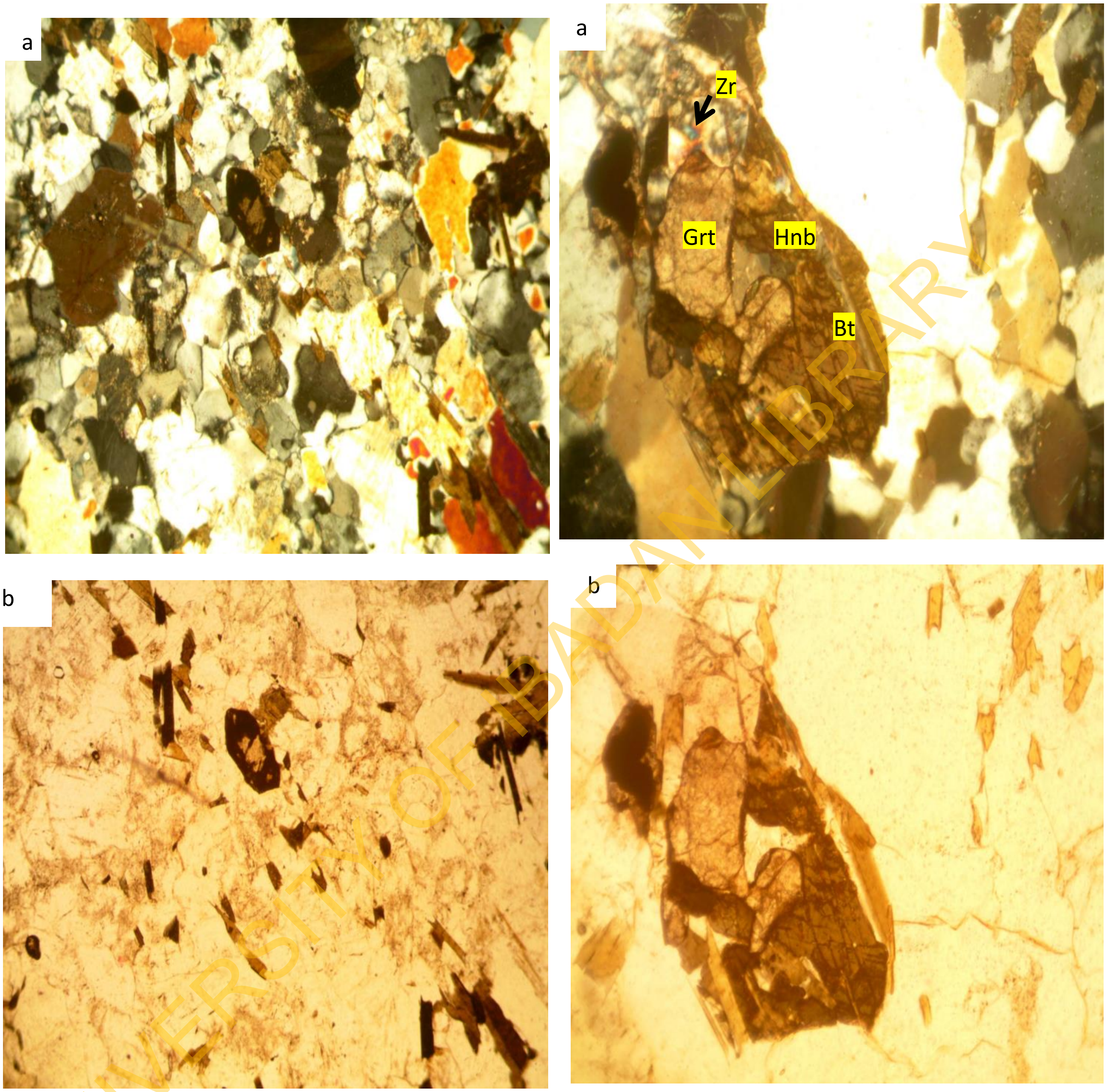


Figure 4.4. Photomicrographs of biotite-hornblende gneiss

High relief garnet (Grt) mineral with a trapezohedron habit is distinctly set along the foliation plane defined by biotite (Bt) flakes which is better observed in plane polar (b). Quartz (Qtz) grains form partial interstitial mosaic with some biotite flakes. Biotite formed as an alteration product from the reaction involving hornblende (Hnb) and garnet (Grt). Zircon halo forms as a small inclusion.

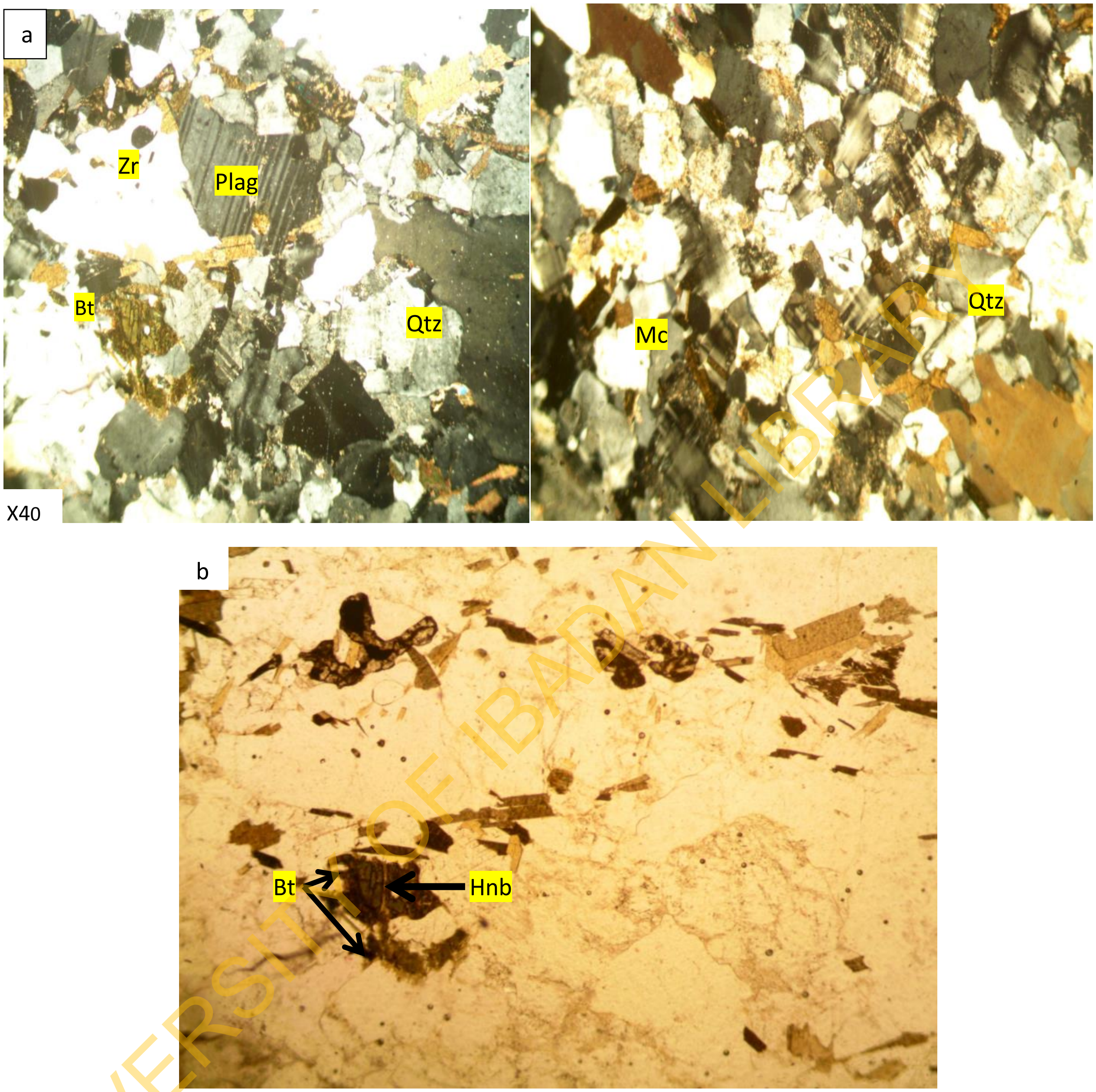


Figure 4.5. Photomicrographs of Biotite-Gneiss at UI under plane and cross polarized light. *Plagioclase (Pl) and quartz (Qtz) grains forming felsic band (Top of Photomicrograph) and straddled by platy biotite (Bt) grains to define foliation and lineation within the rock. Minute zircon (Zr) grain was observed as isolated halo within a biotite flake (Top left) while biotite flakes rim hornblende (Hnb) mineral (Bottom left). Abundance of Alkali feldspar grains (Microcline crystals, evident with tartan twinning) was concentrated at the center. Grain boundaries of the microcline (Mic) crystals with closely formed subhedral to euhedral flakes of biotite (Bt), describe subhedral grain shape for the alkali feldspars. Minute flakes of muscovite (Mc) is seen at the top right.*

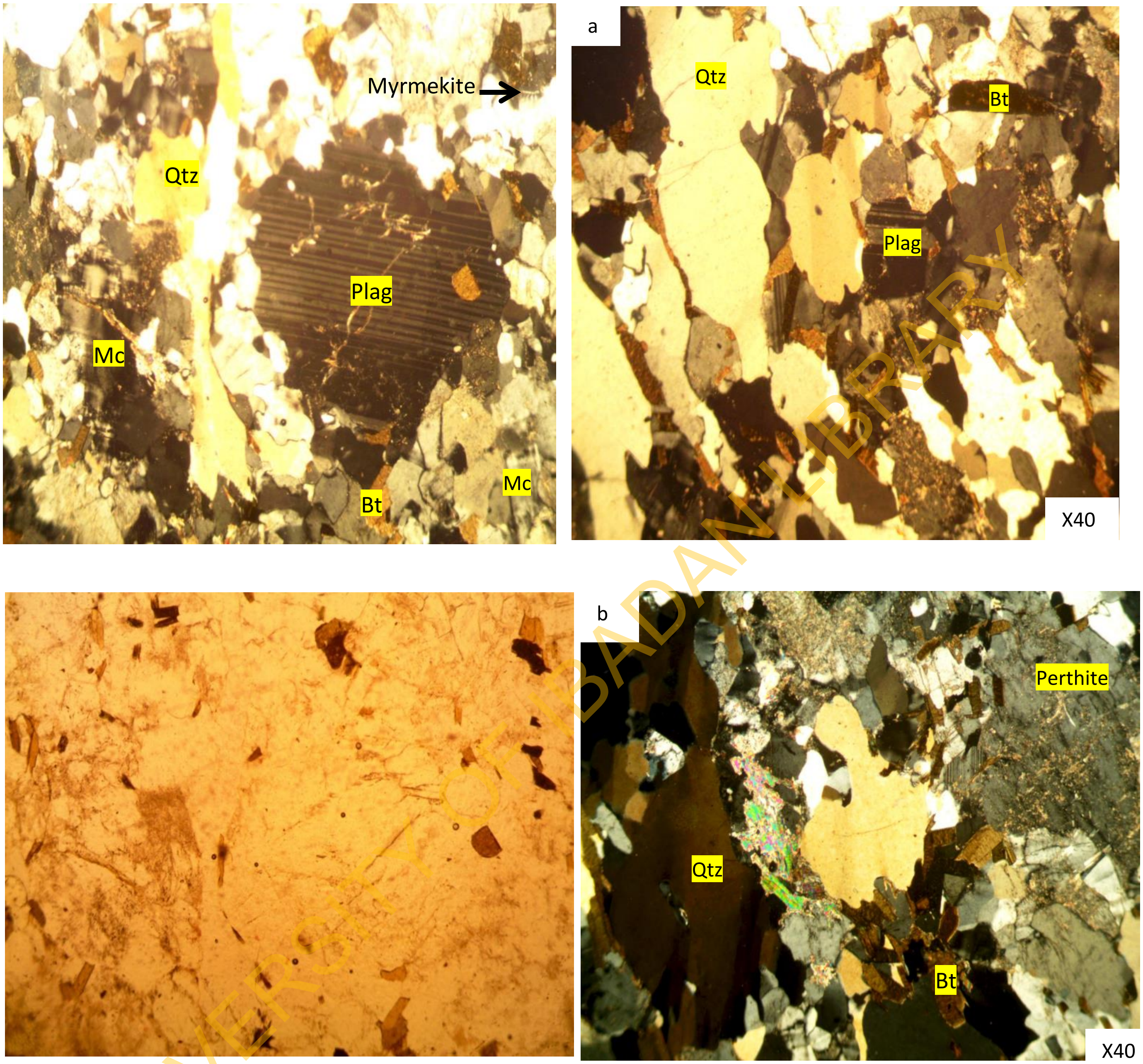


Figure 4.6. Photomicrographs of hornblende gneiss at Abadina

Plagioclase (Plag), biotite (B), microcline (Mc) and quartz (Qt) constitute the mineralogy. Myrmekite formation is observed at the top right corner of the photomicrograph under cross polar. a) Polysynthetic twinning after the albite law is observed in different direction for the plagioclase (Plag) crystals. Biotite (B) and quartz grains define foliation and lineation bands for the rock. b) Deformation lamellar is noticed in the quartz grain (left side) while biotite grains show pleochroism from brown to yellowish-green.

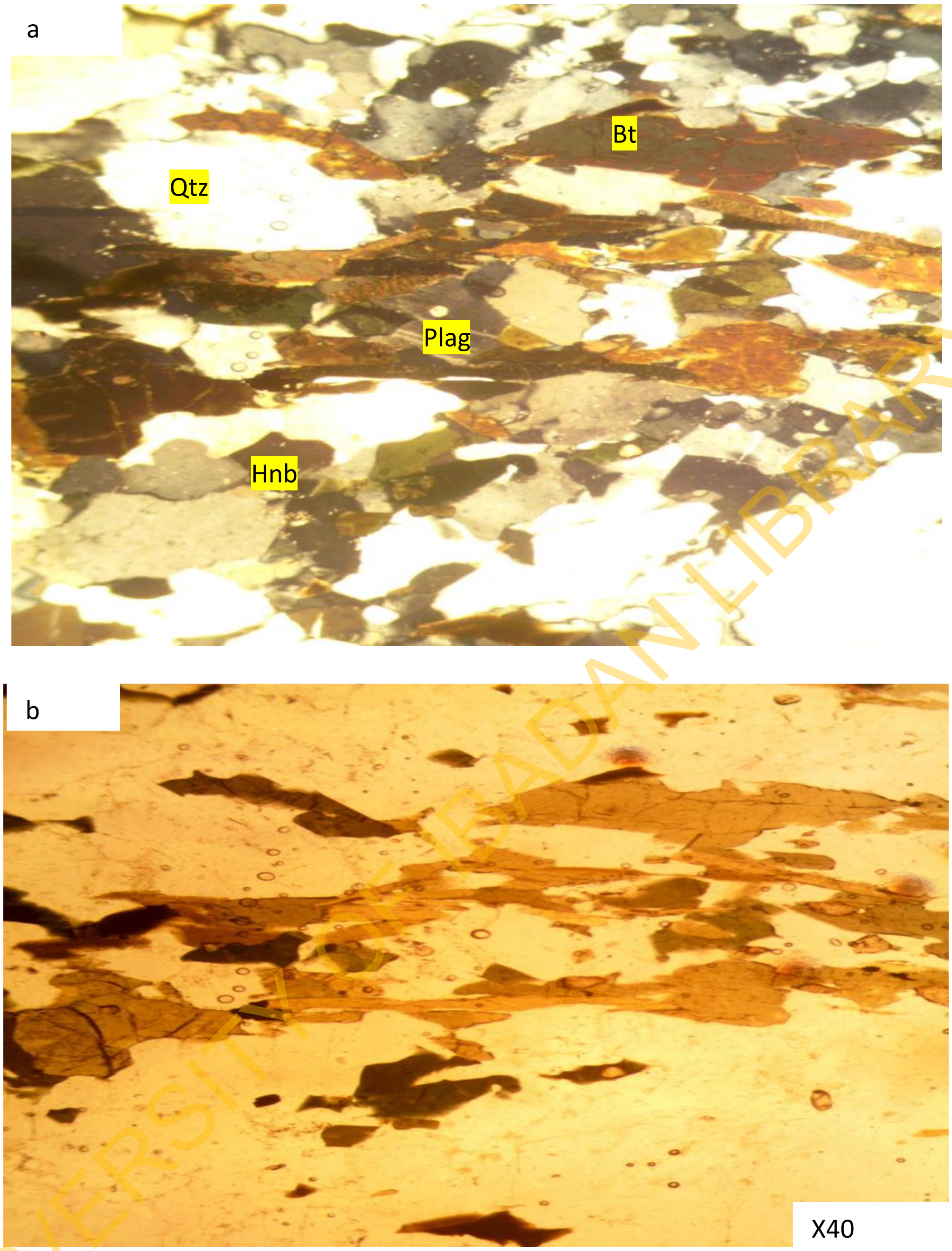


Figure 4.7. Photomicrographs of Biotite-Hornblende Gneiss from UI

a) Biotite (Bt) and hornblende (Hnb) are the dominant minerals forming the mafic bands.
b) Plagioclase (Plag) and quartz (Qtz) sub grains form crushed and rotated porphyroclasts. Mafic bands defining foliation is seen mantling porphyroclasts to describe Theta (θ) type sense of shearing (arrow)

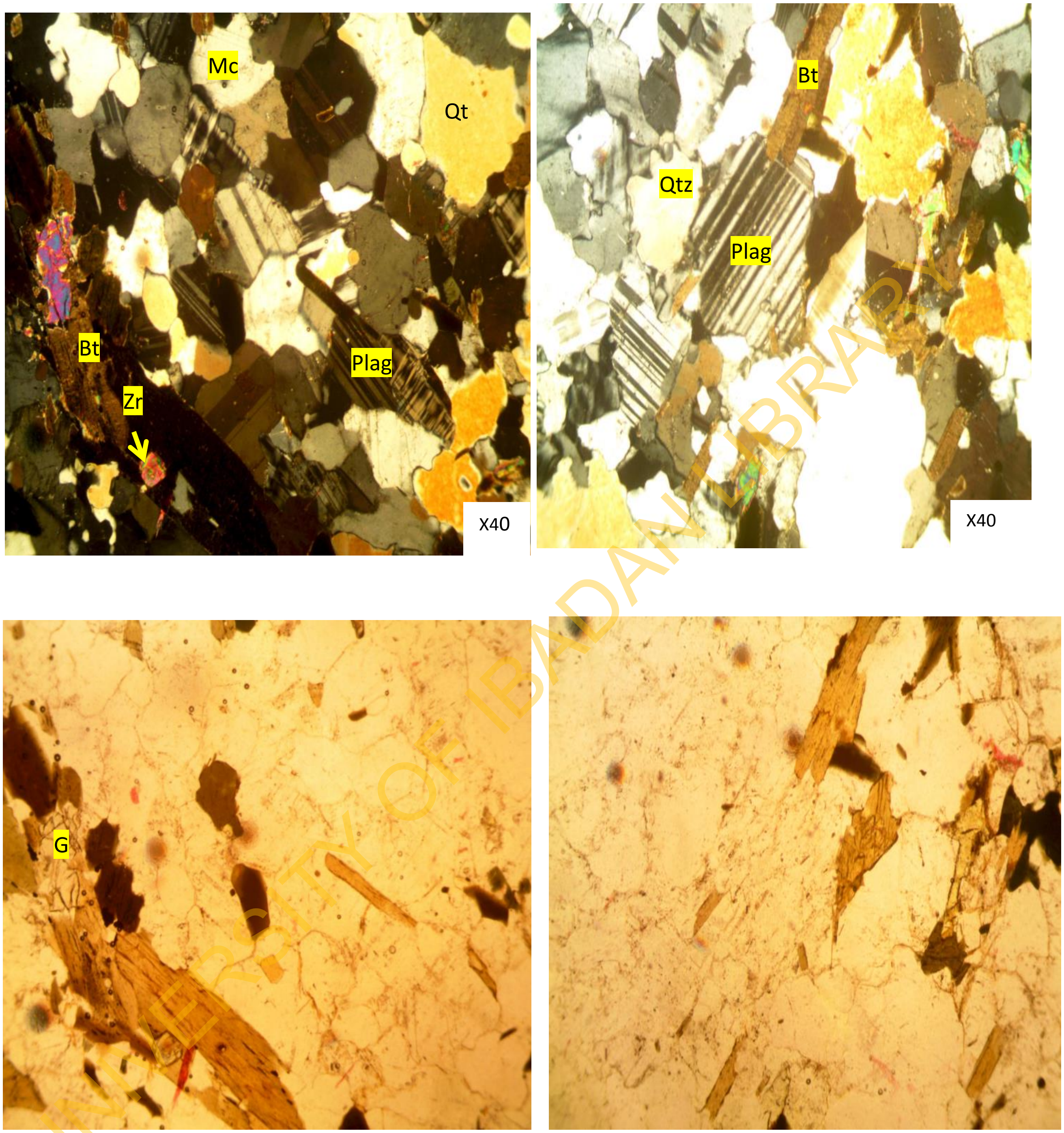


Figure 4.8. Photomicrographs of Biotite Granite Gneiss @ Crown Trust Quarry, Arapaja

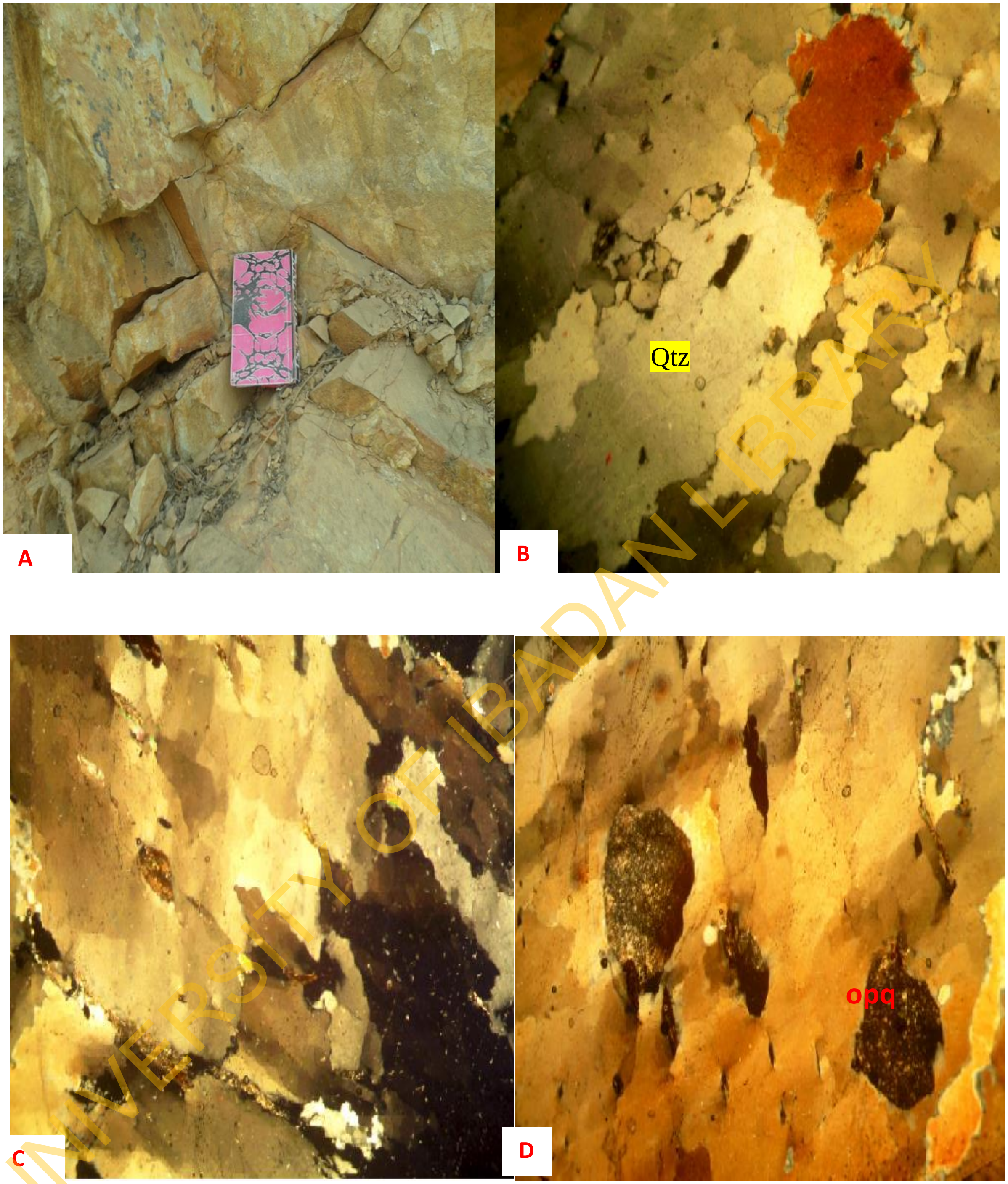


Figure 4.9. Photomicrographs and field picture of Quartzite @ Apata Ibadan

b) Field picture of quartzite; b) quartz in cross polarized light; c) quartz foliation; d) inclusion of opaque minerals in quartz (Mag. X40)

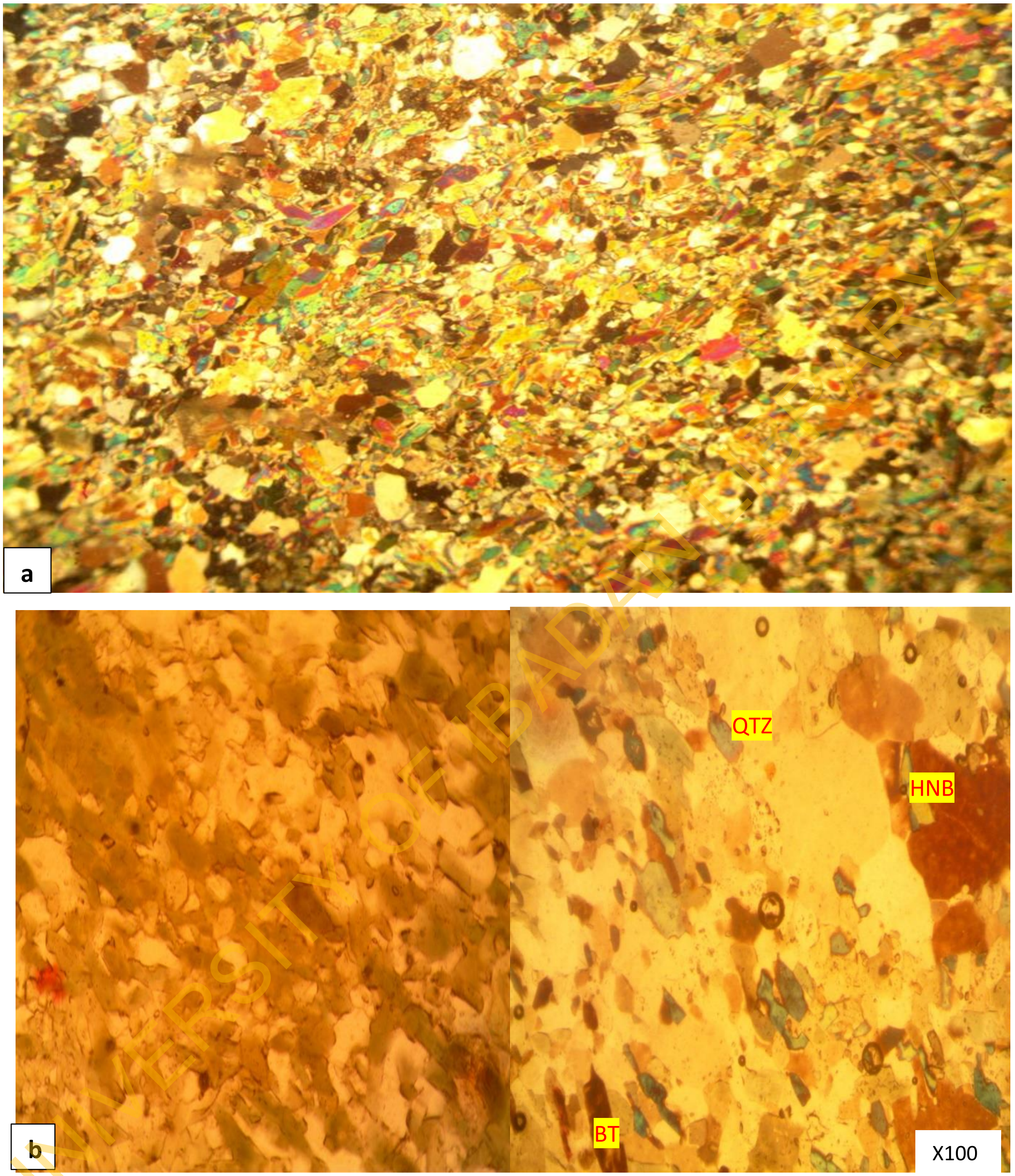


Figure 4.10. Photomicrographs of amphibolite @ Olode area in Ibadan *(Mag. X40)*
a=crossed polar; b= plane polar; Qtz = Quartz, HNB = Hornblende, BT = Biotite

4.2 Stratigraphic Succession of Lagos Metropolis

The geology of Lagos area is dominated by continuous and monotonous repetition of clayey and sandy horizons (Olatunji, 2006) (Fig.4.11). These horizons show lateral continuity in several parts of the area. The lithology is made up of successions of sandy – clay, sandy; clayey sands and gravely sands sequence. The sandy – clay layer ranges from reddish brown to pinkish, the clay units vary from whitish through pinkish, reddish to brown and dark brown in color (Olatunji, 2006). This Coastal Sands is well exposed around Ojota.

4.3 Mineralogy of Soils, Sediments, Dusts and Bedrocks

The mineralogical compositions of the selected rocks, soils, stream sediments and roadside dusts revealed the presence of clay-minerals such as kaolinite, illites-muscovite, etc. and non-clay minerals such as quartz, plagioclase, k-feldspars etc. (Table 4.1).

4.3.1 Mineralogy of Coastal Plain sands and soils from Lagos Areas

The mineralogical compositions of the powdered Coastal Plain sands underlying Lagos metropolis showed the presence of quartz, k-feldspar, plagioclase, kaolinite, calcite and biotite. Based on their relative abundance, quartz (79.8%) is the predominant mineral with some minor quantities of k-feldspar (7.3%), plagioclase (4.4%), kaolinite (4.4%) calcite (2.2%) and biotite (1.0%) (Table 4.1 & Fig. 4.12). Similarly, the soils from Lagos metropolis revealed the presence of quartz, plagioclase, k-feldspar, kaolinite, calcite, illite-muscovite, goethite, biotite, magnetite and Ilmenite. The relative abundance of these minerals showed quartz (75.3%) as the dominant mineral with some plagioclase (8.1%), k-feldspar (7.0%), kaolinite (2.6%) and calcite (2.2%) while illite-muscovite and goethite, biotite, magnetite and ilmenite were present as minor minerals (Table 4.1, Fig.4.13). The similarity in mineralogical compositions of Lagos Coastal Plain sands and soils showed that most of the soils were derived as a weathering product of the underlying materials.

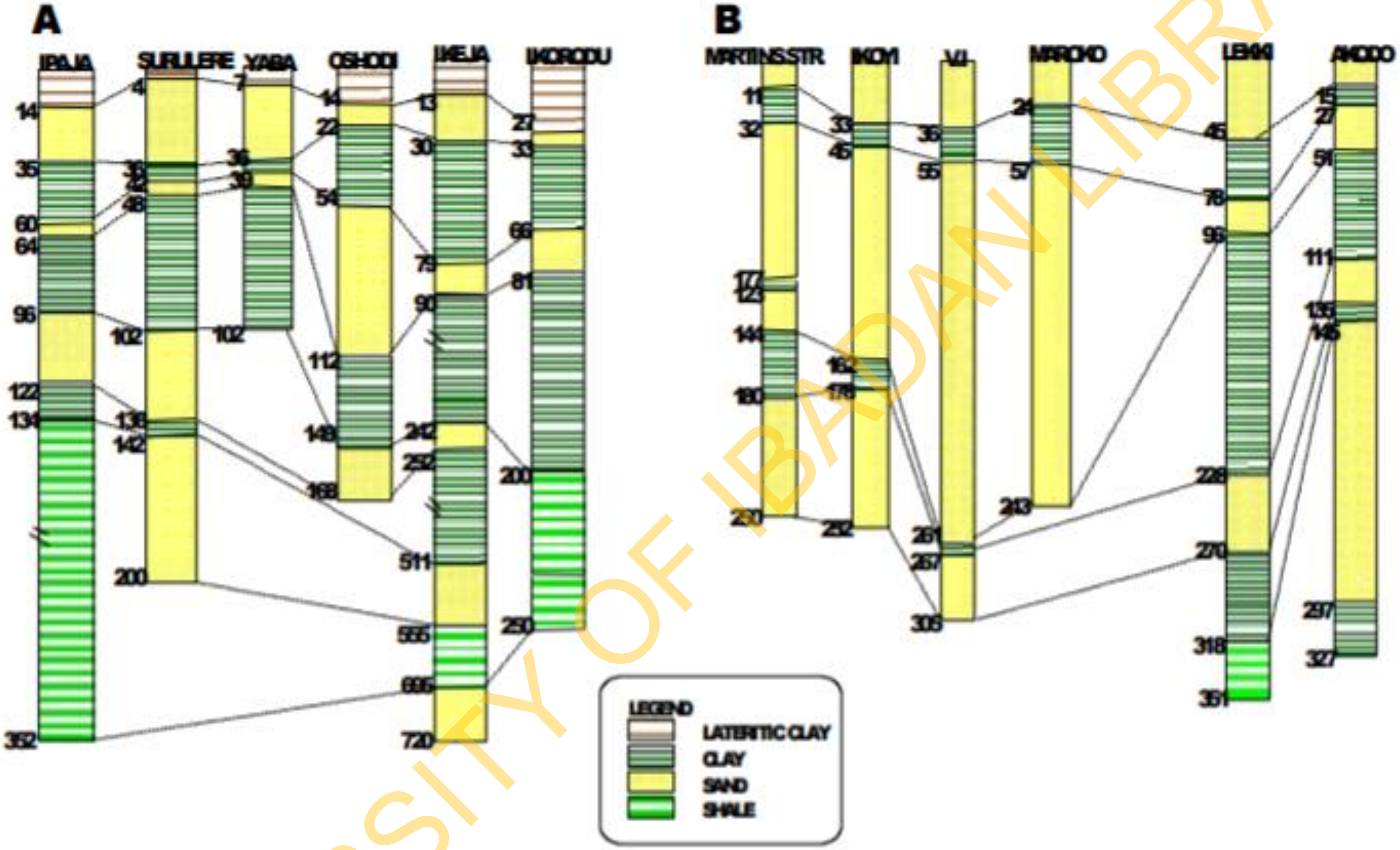


Figure 4.11 a. Stratigraphic Sequence of Coastal plain sands in Lagos (East-West)

b. Stratigraphic Sequence of Coastal plain sands in Lagos (West-East)

(Source: Olatunji and Abimbola, 2010)

Table 4.1. The Results of Quantitative Phase Analysis (Wt.%) XRD-Rietveld

MINERAL	IDEA FORMULA	Ibadan Soil	Ibadan Sediment	Ibadan MGC	Lagos CPS	Lagos Soil
Quartz	SiO_2	**47.1**	**56.7**	**33.6**	**79.8**	**75.3**
Kaolinite	$Al_2Si_2O_5(OH)_4$	**18.7**	**17.7**	0.7	4.8	2.6
Illite-Muscovite 2MI	$K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$-$KAl_2AlSi_3O_{10}(OH)$	6.7	5.1	NIL	NIL	1.3
Biotite	$K(Mg,Fe^{2+})_3AlSi_3O_{10}(OH)$	NIL	NIL	5	1	0.8
K-Feldspar	$KAlSi_3O_8$	**10.6**	8.6	**17.4**	**7.3**	**7**
Plagioclase	$NaAlSi_3O_8$-$CaAlSi_2O_8$	3.5	NIL	**33.6**	4.4	**8.1**
Calcite	$CaCO_3$	0.9	NIL	NIL	2	2.2
Ankerite-Dolomite?	$Ca(Fe^{2+},Mg,Mn)(CO_3)_2/Ca\ Mg(CO_3)_2$	NIL	0.2	0.5	NIL	NIL
Goethite	α-$Fe^{3+}O(OH)$	6.1	2.9	NIL	NIL	1
Hematite	α-Fe_2O_3	4.1	2.2	NIL	NIL	NIL
Magnetite	Fe_3O_4	NIL	NIL	NIL	NIL	0.6
Anatase	TiO_2	0.5	0.3	NIL	NIL	NIL
Rutile	TiO_2	0.8	NIL	NIL	NIL	NIL
Ilmenite	$Fe^{2+}TiO_3$	1.2	0.9	NIL	NIL	0.2
Actinolite	$Ca_2(Mg, Fe^{2+})_5Si_8O_{22}(OH)_2$	NIL	1	9.2	0.5	0.9
Zircon?	$ZrSiO_4$	NIL	0.3	NIL	NIL	NIL
Total		100	100	100	100	100

MGC – Migmatite gneiss complex; CPS- Coastal plain sands

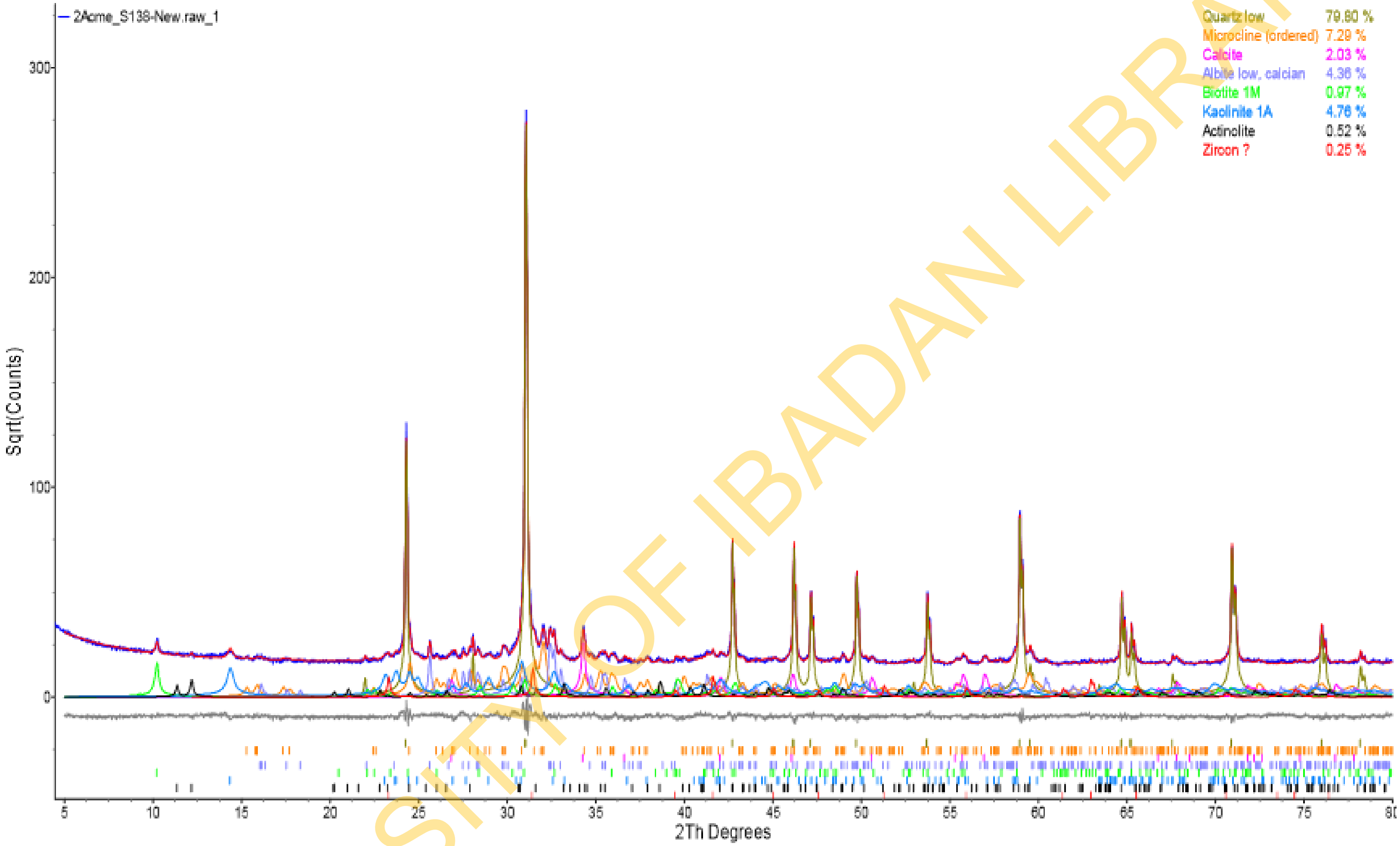


Figure 4.12. Diffractograms of selected Coastal Plain sands of Lagos area

In this figure, blue line represents the observed intensity at each step; red line represents the calculated pattern; solid grey line below represents the difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections while colored lines are the individual diffraction patterns of all phases.

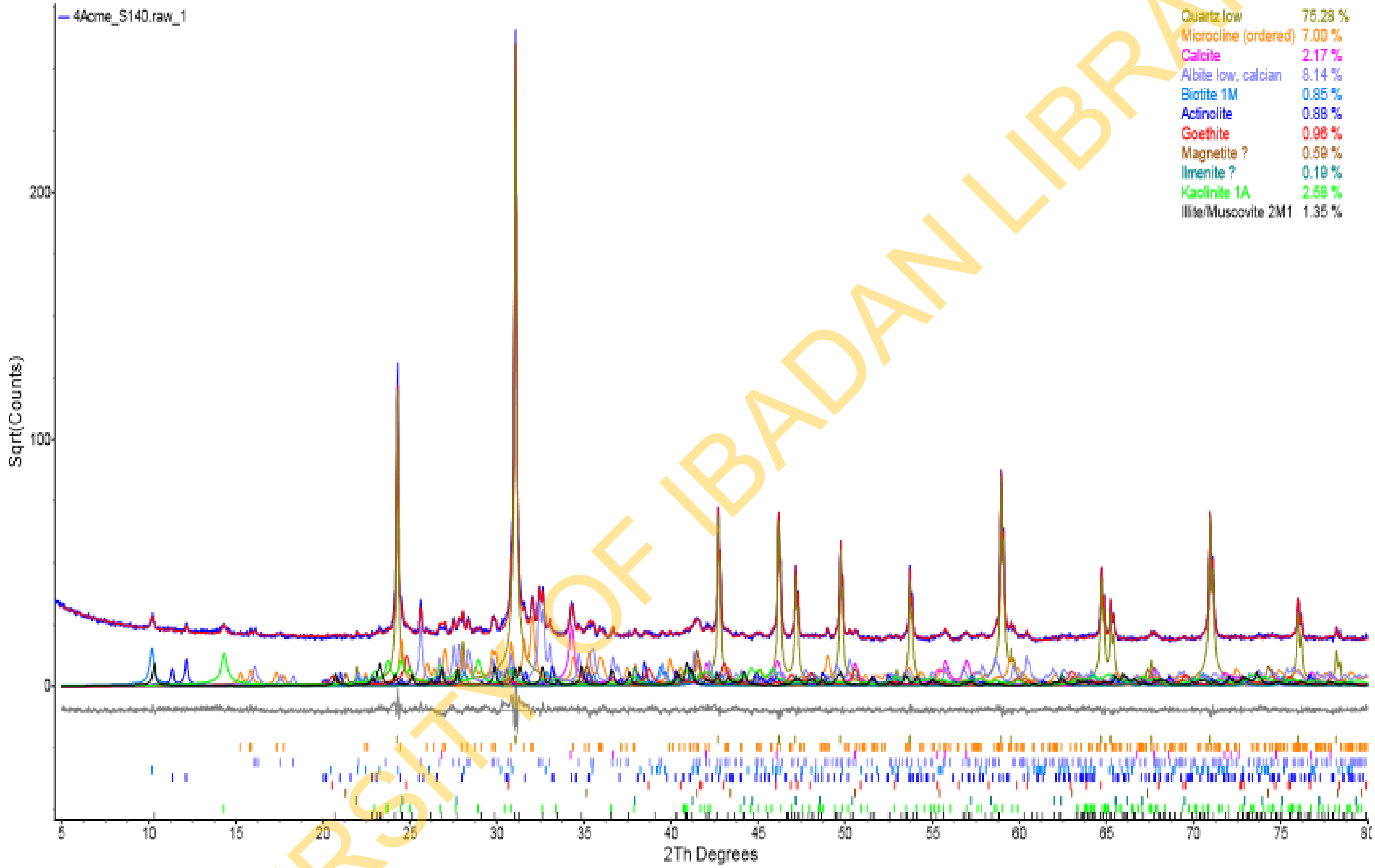


Figure 4.13. Diffractograms of selected soils in Lagos area

4.3.2 Mineralogy of rocks, soils and sediments of Ibadan Metropolis

The results of petrological studies of the representative rocks samples revealed the dominance of quartz, alkali-feldspar, biotite and hornblende with some little opaque minerals (Figs. 4.1 – 4.10). Using XRD, the following minerals were identified quartz (33.6%), k-feldspar (17.4%) and plagioclase (33.6%) (Table 4.1 and Fig. 4.14).

The results of XRD results for the Ibadan soils showed that quartz (47.1%), kaolinite (18.7%) and k-feldspar (10.6%) occurred as the dominant minerals while illite - muscovite (6.7%), goethite (6.1%), hematite (4.1%) and plagioclase occur in minor quantities with traces of ilmenite, rutile, anatase and calcite (Table 4.1 & Fig. 4.15). The relative low abundance of alkali feldspars and plagioclase as well the absence of biotite in soils can be attributed to their susceptibility of these minerals to weathering and leaching as compared to the more resistant quartz in soils.

The mineralogical composition of the Ibadan sediments revealed quartz and kaolinite as the dominant minerals as well as small amount of k-feldspar (8.6%), illite-muscovite (5.1%), goethite (2.9%) and hematite (2.2%) while actinolite (1%), ilmenite (0.9%), zircon, anatase and ankerite-dolomite occurring in minor quantities (Fig.4.16). The relative low quantity of alkali feldspars may be attributed to their susceptibility to weathering as compared to the more resistant quartz in soils. The mineralogical compositions of Ibadan rocks, soils and sediments as contained in table 4.1 and diffractograms in Figures 4.14 – 4.16 showed a close similarity an indication that soils and sediments were derived from the bedrocks.

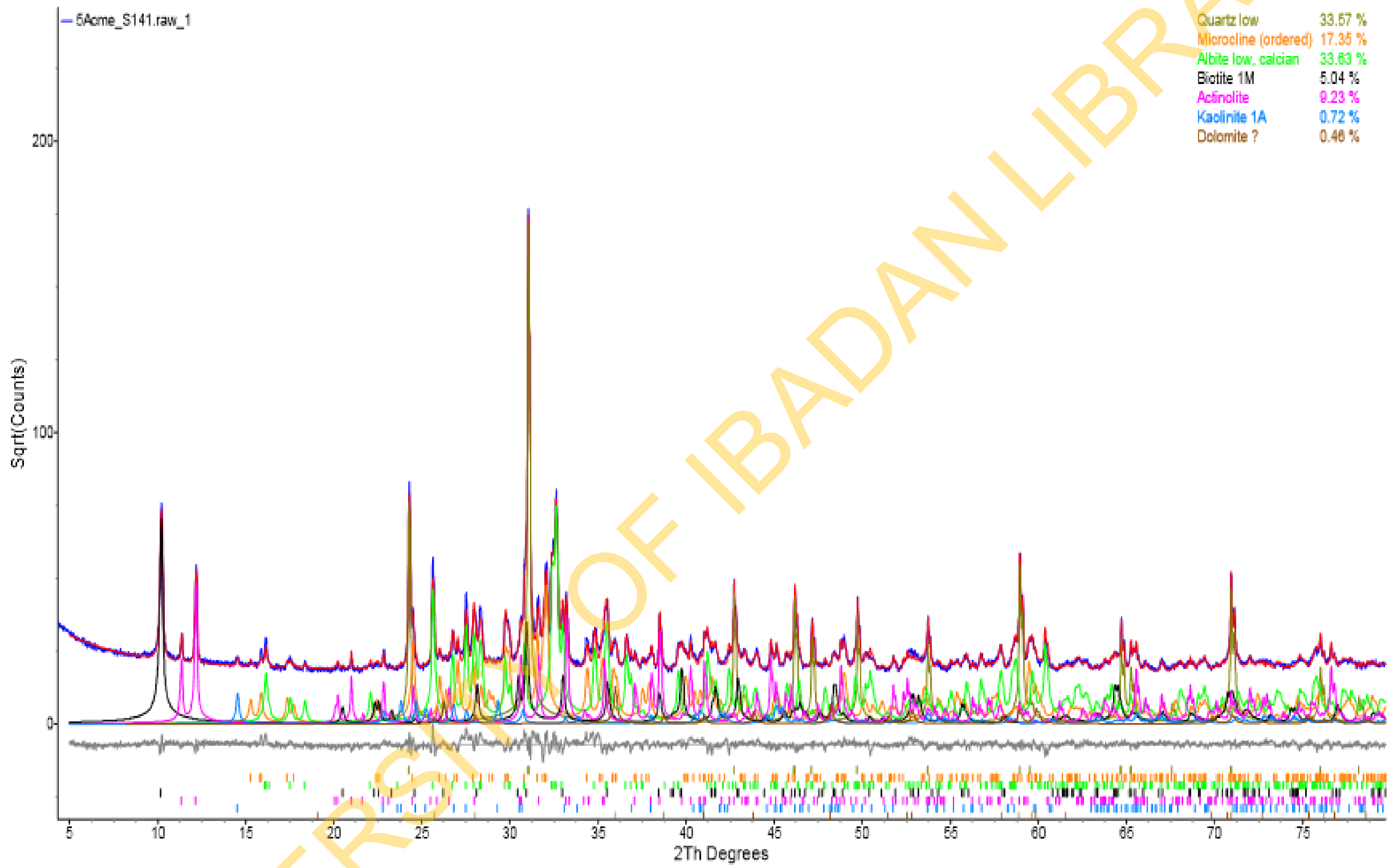


Figure 4.14. Diffractograms of selected MGC samples in Ibadan study area

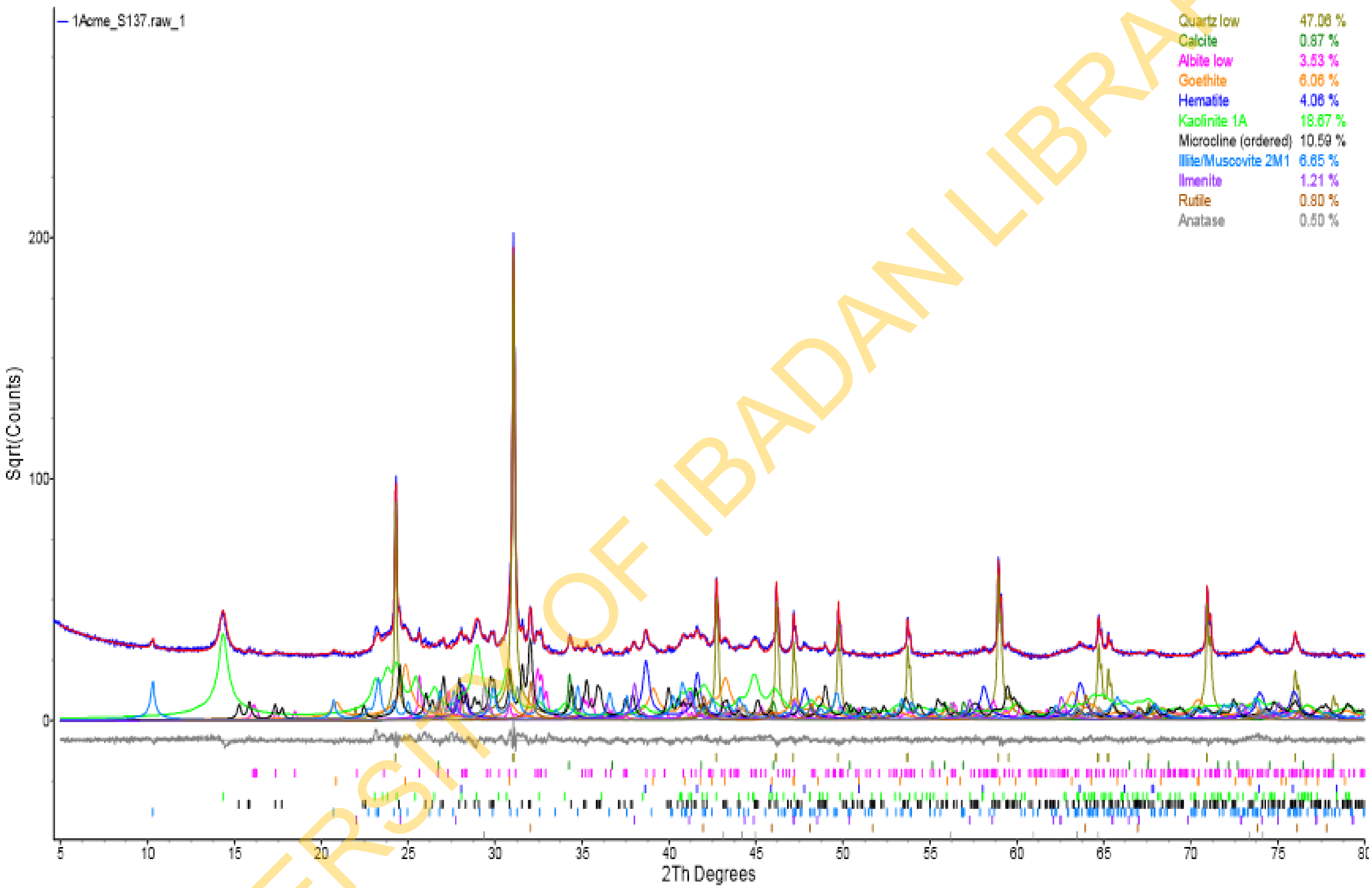


Figure 4.15. Diffractograms of selected soil samples in Ibadan study area

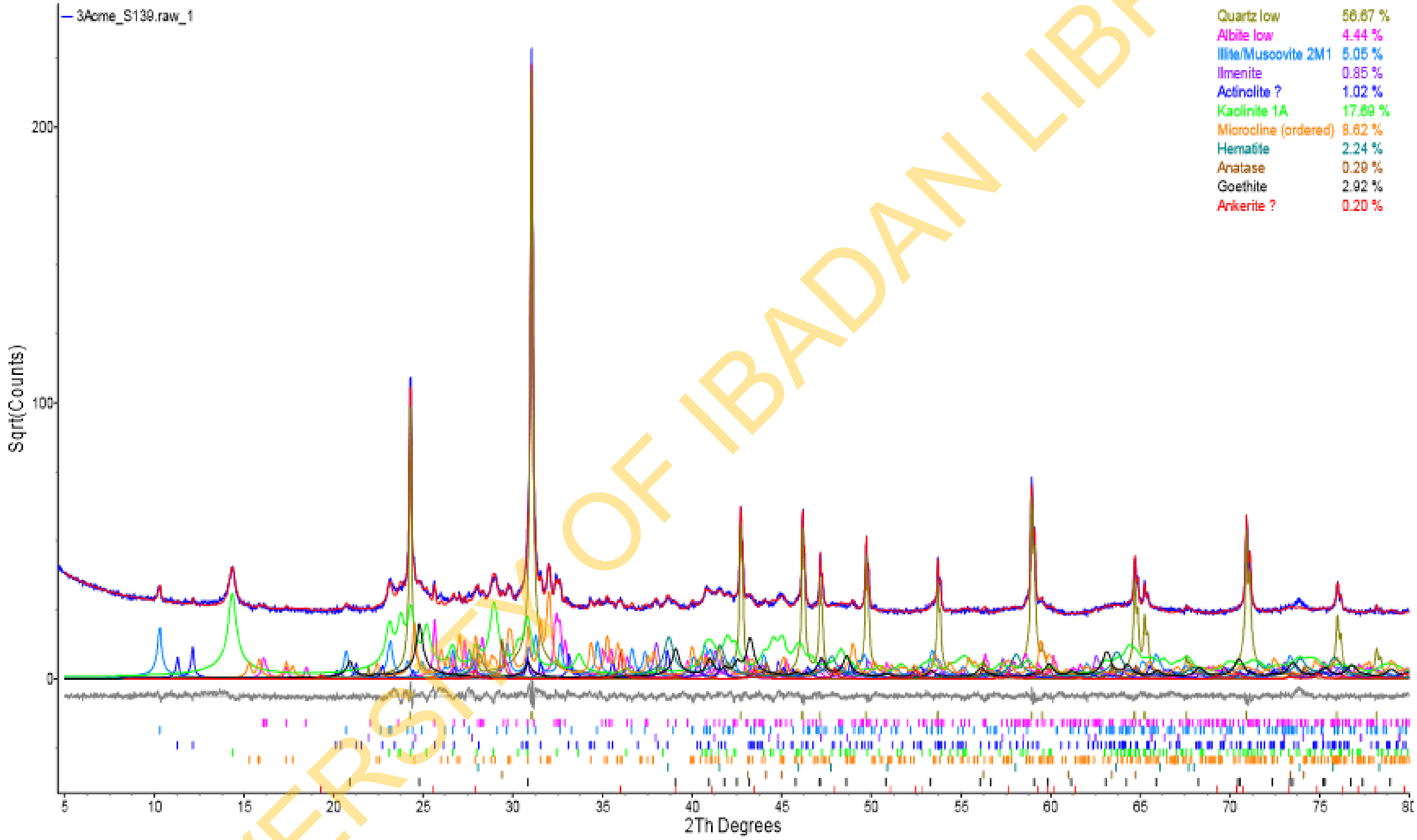


Figure 4.16. Diffractograms of selected stream sediment samples in Ibadan study area

4.4 Whole Rock Geochemistry

The rock types in Ibadan are quartzite and gneisses of various types with minor amphibolite while Lagos is mainly dominated by Coastal Plain sands and Alluvium underlying it. These gneisses and Coastal Plain sands were used for geochemical analyses in order to serve as baseline data to normalize whatever geochemical data observed in the soils, sediments and dusts from Ibadan and Lagos (Table 4.2 - 4.4).

4.4.1 Major Oxide Compositions of Basement Rocks in Ibadan

The concentrations of SiO_2 in amphibolite varied from 67% in amphibole-schist to 69% in amphibolite while the concentrations of silica in migmatite gneisses varied from 69.34% in banded gneiss to 72% in granite gneiss. The concentrations of K_2O exceeded that of Na_2O in all the representative rock samples. Similarly, Al_2O_3 and CaO ranged from 13.4 to 13.73% and 1.7 to 3.1%, respectively. The presence of plagioclase feldspars in the gneisses may explain the higher concentrations of these oxides (Al_2O_3 and CaO). K_2O and Fe_2O_3 ranged from 3.2% to 4.44%. In all the gneiss samples, the concentrations of K_2O exceeded that of Na_2O. The migmatite gneiss samples with higher concentrations of silica consistently displayed higher contents of K_2O, Al_2O_3 and TiO_2 but lower MgO, Fe_2O_3, CaO and P_2O_5. Sample of quartzite has the highest concentration of silica (97.10%) but significantly low in other oxides. The alkalis (K_2O and Na_2O) have low to moderate concentrations (0.12 to 4.72%). Increase in the concentrations of Al_2O_3 and Fe_2O_3 correspond to decrease in the concentrations of silica in all the studied rock samples from this complex (Table 4.2). This is an indication of weathering and chemical alteration.

Using the plot of Na_2O/Al_2O_3 versus K_2O/Al_2O_3 after Garrels and McKenzie, (1971), it showed that gneisses and the schistose amphibolite samples plotted within the field of igneous and metaigneous (Fig. 4.17). This indicated that these rocks are of igneous or metaigneous origin. The Na_2O+K_2O-Fe_2O_3t-MgO ternary diagram showed that the various gneisses and the schistose amphibolite of Ibadan MGC have calc alkaline affinity. This is further supported by the K_2O versus SiO_2 plot where all the samples plotted along the calc alkaline field and are more of metaluminous/peraluminous in nature (Figs 4.18 to 4.19). Okunlola *et al*, 2009 has concluded that the schistose amphibolite of Ibadan area has distinct petrogenetic characters from most of the amphibolitic rocks of the basement complex of Nigeria which are mostly tholeiitic with Archean metabasalt affinity.

Table 4.2. Results of Major Oxides in Ibadan MGQC Samples

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	LOI	TOT/C	Sum	Rock Types
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
R001	71.41	13.70	3.37	0.87	1.73	3.19	4.37	0.34	0.05	0.04	0.002	0.7	0.07	99.77	Augen Gneiss
R003	69.51	13.54	3.82	1.78	2.76	3.14	3.94	0.31	0.08	0.07	0.009	0.7	0.07	99.64	Banded Gneiss
R004	69.34	13.44	4.14	2.09	3.11	3.18	3.41	0.31	0.09	0.07	0.012	0.6	0.09	99.80	Banded Gneiss
R005	71.25	13.72	3.31	0.85	1.74	3.14	4.44	0.34	0.04	0.04	<0.002	0.9	0.07	99.78	Gneiss
R006	66.91	14.56	4.54	1.79	3.42	3.32	3.38	0.49	0.12	0.07	0.006	1.2	0.22	99.78	Amphibole Schist
R007	69.20	13.67	4.57	1.64	2.64	3.12	3.88	0.44	0.07	0.07	0.007	0.5	0.06	99.81	Amphibolite
R008	71.77	13.73	3.20	0.82	1.76	3.18	4.40	0.33	0.06	0.05	0.002	0.5	0.08	99.79	Grey Gneiss
R012	97.15	1.40	0.59	0.08	0.08	0.12	0.39	0.09	0.04	0.01	0.002	0.1	0.01	99.99	Quartzite

Table 4.3. Summary of the Major Oxides in Rock and Coastal Plain Sands Samples

	Basement Rock Samples		**Recent Alluvium /Coastal Plain Sands Samples**	
Oxides	**Range**	**Mean ± Std. Dev.**	**Range**	**Mean ± Std. Dev.**
SiO_2	65.66 - 97.15	72.5 ± 9.48	50.83 - 92.23	71.53 ± 29.27
Al_2O_3	1.40 - 14.56	12.3 ± 4.11	3.60 - 25.10	14.35 ±15.20
Fe_2O_3	0.59 - 5.05	3.6 ± 1.31	1.54 - 9.86	5.70 ± 5.88
MgO	0.08 - 2.09	1.2 ± 0.67	0.02 - 0.06	0.04 ± 0.03
CaO	0.08 - 3.97	2.4 ± 1.17	0.04 - 0.04	0.04 ± 0.00
Na_2O	0.12 - 3.32	2.8 ±1.02	ND	ND
K_2O	0.39 - 4.72	3.7 ± 1.31	0.06 - 0.13	0.10 ± 0.05
TiO_2	0.09 - 0.62	0.4 ± 0.15	0.28 - 1.58	0.93 ± 0.92
P_2O_5	0.04 - 0.27	0.1 ± 0.07	0.02 - 0.08	0.05 ± 0.04
MnO	0.01 - 0.07	0.05 ± 0.02	0.00 - 0.02	0.01 ± 0.01
Cr_2O_7	<0.002 - 0.01	0.01 ± 0.004	0.00 - 0.02	0.01 ± 0.01
LOI	0.10 - 2.90	0.9 ± 0.81	2.20 - 12.10	7.15 ± 7.0
TOT/C	-	-	0.05 - 0.09	0.07 ± 0.03
TOT/S	-	-	0.00 - 0.04	0.02 ± 0.03

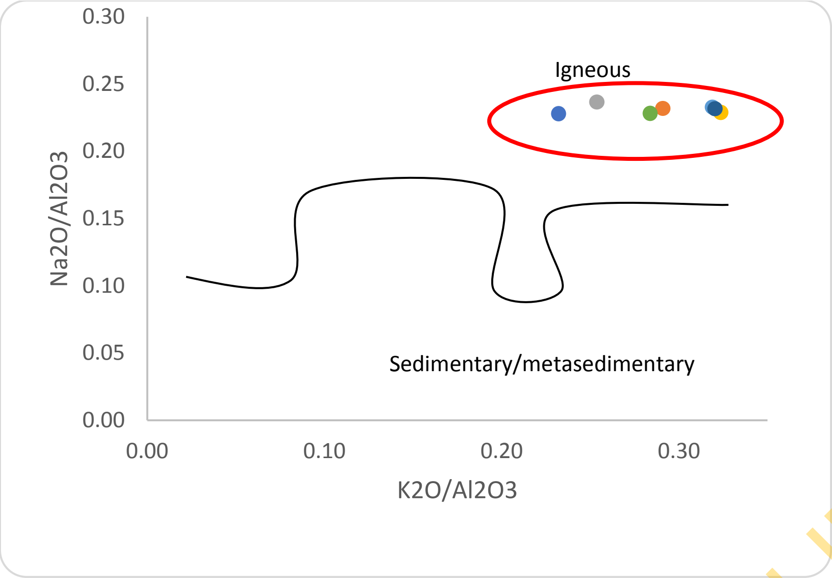


Figure 4.17 (a). Plot of Na_2O/Al_2O_3 against K_2O/Al_2O_3 of Gneisses and Schistose amphibolite of Ibadan MGC (after Garrets and Mckenzie, 1971)

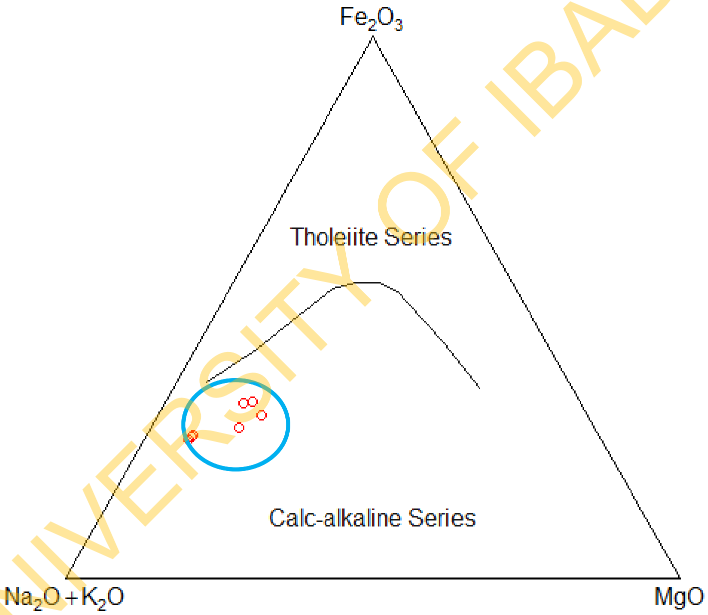


Figure 4.17(b). AFM Plot of Gneisses and Schistose amphibolite of Ibadan MGC (after Irvine and Baragar, 1971)

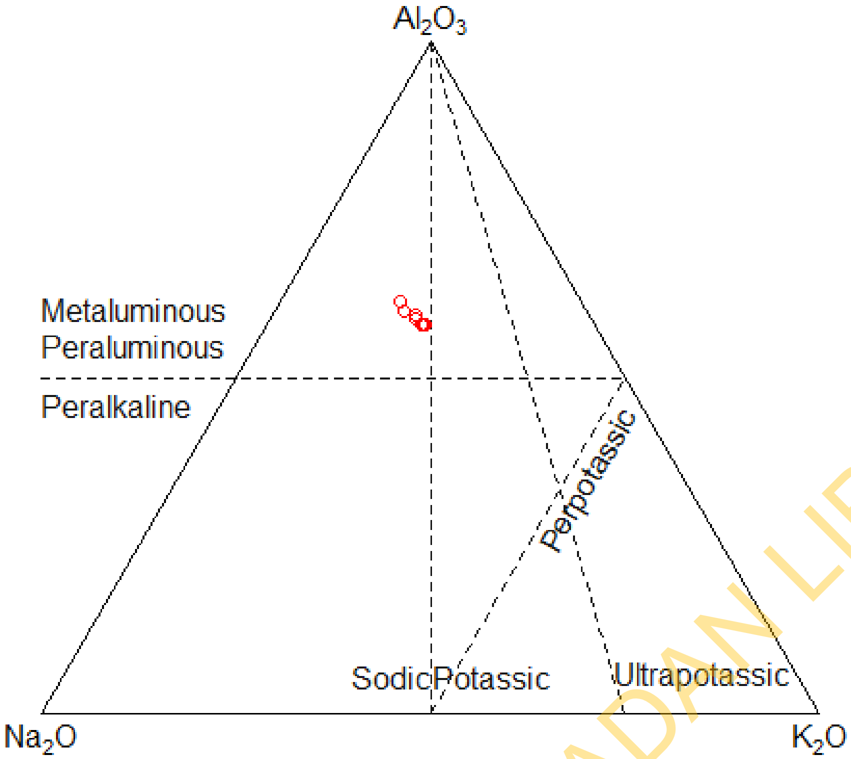


Figure 4.18. Molar Na_2O-Al_2O_3-K_2O Plot of Gneisses and Schistose amphibolite of Ibadan MGC

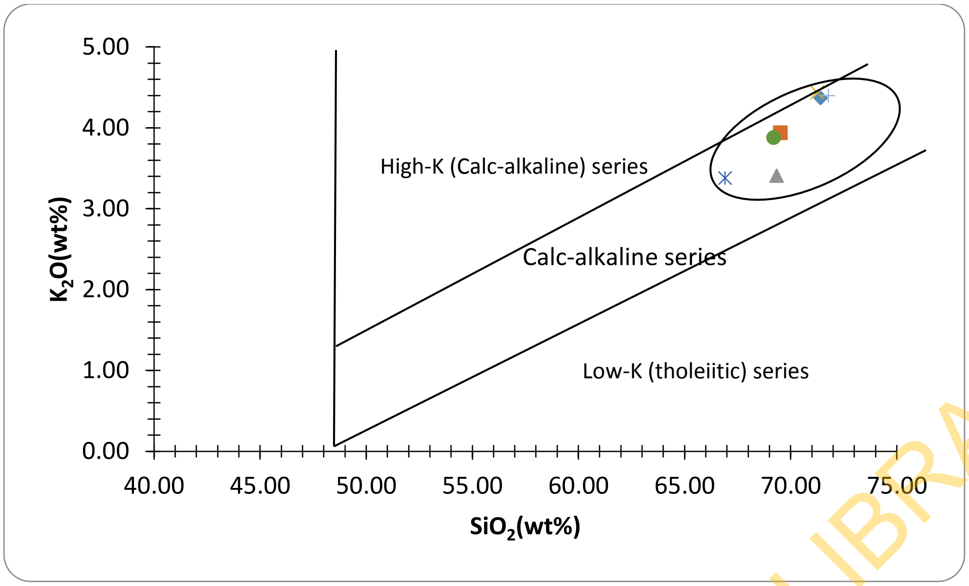


Figure 4.19. Plot of K_2O vs. SiO_2 of Gneisses and Schistose amphibolite of Ibadan MGC (After Le Maitre et al, 1989)

4.4.2 Major Oxide Compositions of the Recent Alluvium and Coastal Plain Sands

The summary of the results of geochemical analysis of major oxides of the selected Coastal Plain sands samples of Lagos and its environs as presented in Table 4.3 showed wider variability in the concentrations of SiO_2 and Al_2O_3. The results revealed abundance of SiO_2 ranging from 50.83 - 92.23 wt.%, while other oxides such as TiO_2, MgO, CaO, P_2O_5, MnO, Cr_2O_3, K_2O and Na_2O were generally low (i.e. < 30wt%) most especially in the near surface samples (sandy layer) compared to samples (clayey) from deeper depth with the exception of Al_2O_3. Al_2O_3 ranged from 3.60 to 25.10 wt.% with an average of 14.35 wt.% while Fe_2O_3 ranged from 1.54 - 9.86 wt.% with a mean of 5.70%.

The concentrations of TiO_2, MgO, CaO, P_2O_5, MnO, Cr_2O_3, K_2O and Na_2O were significantly reduced as compared to other oxides in the near surface samples (Figs. 4.20a-c). However, these oxides showed elevated concentrations in deeper depth samples which are more or less clayey in nature. The trend of increasing K_2O with decreasing SiO_2 is sensitive to grain size, probably due to the increase in clay content in the finer Coastal Plain Sands. Generally, most elements decrease with rise in Al_2O_3 from sandstone to sandy siltstone (Gurel and Kadir, 2008). These trends may be controlled by the silt fraction present in the deeper depth (Roser et al., 1996). These samples show high K_2O/Na_2O ratios which can be attributed to the presence of potassium-bearing minerals such as k-feldspar (McLennan et al., 1983; Nath et al., 2000; Zhang, 2004). A positive correlation between K_2O and Al_2O_3 was also observed in these samples, this implied that the concentrations of k-bearing minerals have no significant influence on aluminum distribution. This suggested that the abundance of these elements is primarily uncontrolled by the content of clay minerals (McLennan et al., 1983; Jin et al., 2006).

4.4.3 Trace and Rare Earth Elements Geochemistry of Ibadan MGC

Trace and REEs (Pb, Zn, Cu, Ni, Th, Ba, Y, Zr, Sm, Dy, Eu and Er) concentrations of the analyzed Ibadan MGC representative samples showed appreciable variations (Table 4.4 and 4.5). The result of the trace elements revealed that Mo, Cu, Pb, Th, Ba, Sr and Sc are relatively higher in the various gneisses' samples while amphibolite samples were higher in Co, Sr, V and Cr. Migmatite gneisses were richer in plagioclase and contained higher content of Sr than amphibolite and quartzite. The average content of Rb in the migmatite samples (134ppm) is tending towards the average Rb value of Okene/Lokoja migmatite gneisses which were described as orthogneisses (Odigi, 2002) but significantly lower than the paragneisses (22ppm) of Auchi (Okeke and Meju, 1985). The ratios of La/Ce in analyzed samples varied from 1:7 to 1:2, the ratios for amphibolite are slightly lower than that of migmatite gneisses. All the gneiss samples are characteristically enriched in light REEs and depleted in HREEs with the exception of Y than amphibolite (Table 4.4). The consistent negative Eu signatures of the chondrite normalized rare earth elements plots suggested the possibility that the Ibadan MGC are derived from anatexis of undepleted upper to middle crustal photolith or supracrustal with possible later metasomatic alterations (Okunlola et al., 2006) (Fig.4.20).

Table 4.4: The Results of Trace Elements in Ibadan MGC in ppm

Sample Types	La	Sc	Ba	Be	Co	Sn	Sr	Th	U	V	Mo	Cu	Pb	Zn	Ni	Au	Tl
R001	65.2	5	693	6	4.5	4	131.3	24.7	3.7	27	0.4	11.5	5.3	101	2.6	2.5	0.3
R003	58.3	9	755	2	10.4	3	142.1	20.5	2.8	43	0.7	9.6	20.3	88	35.0	0.6	0.3
R004	47.2	9	624	2	10.9	3	171.7	14.1	2.1	74	0.3	7.6	8.0	75	52.0	<0.5	0.3
R005	74.1	5	758	2	5.2	4	136.8	27.2	4.4	27	2.7	7.1	6.1	94	2.5	<0.5	0.3
R006	34.1	8	743	<1	12.4	2	305.9	12.3	4.0	76	2.1	103.7	2.9	72	8.3	1.0	0.2
R007	59.4	9	563	1	11.5	4	124.2	21.7	4.5	56	1.3	21.0	4.6	114	6.7	1.5	0.3
R008	91.3	5	694	3	5.1	3	138.8	34.4	4.5	30	1.0	17.9	11.3	91	2.2	<0.5	0.4

R001 = Augen Gneiss; R003 & R004 = Banded Gneiss; R008=Granite; R005= Grey Gneiss; R006= Schistose Amphibolite; R007=Amphibolite

Table 4.5: The Result of the Rare Earth Elements of Ibadan MGC Samples

	Zr	Y	La	Ce	Ga	Pr	Nd	Sm	Nb	Eu	Gd	Cs	Tb	Dy	Ho	Er	Tm	Yb	Hf	Rb	Lu
R001	276.1	50.2	74.1	150.1	22.0	15.50	50.7	10.28	28.5	0.89	9.64	1.1	1.57	8.76	1.68	4.77	0.75	4.77	6.3	143.1	0.63
R003	185.1	47.4	65.2	128.5	20.6	13.10	43.3	7.80	22.5	0.86	7.38	0.8	1.28	8.22	1.67	4.89	0.71	4.81	7.6	122.2	0.72
R004	220.8	40.2	58.3	104.3	20.4	12.05	41.7	8.12	28.1	0.95	7.43	1.3	1.22	7.56	1.51	4.41	0.63	4.11	9.4	141.4	0.59
R005	159.1	38.2	47.2	86.2	19.1	9.44	33.2	6.25	20.9	0.86	6.00	0.8	1.01	5.85	1.19	3.65	0.53	3.45	5.3	112.3	0.50
R006	261.2	57.5	91.3	179.6	21.8	18.42	64.3	11.46	26.8	0.93	10.83	1.2	1.66	9.25	1.96	5.45	0.81	5.67	9.5	148.5	0.84
R007	163.1	30.8	34.1	62.8	19.1	6.73	24.3	4.70	14.6	0.75	4.94	1.3	0.86	5.42	1.13	3.35	0.50	3.40	4.7	97.8	0.51
R008	200.6	52.1	59.4	116.8	19.8	11.87	40.7	7.44	22.9	0.92	8.16	1.3	1.33	8.27	1.62	4.43	0.77	4.94	7.5	124.5	0.76

R001 = Augen Gneiss; R003 & R004 = Banded Gneiss; R008=Granite; R005= Grey Gneiss; R006= Schistose Amphibolite; R007=amphibolite

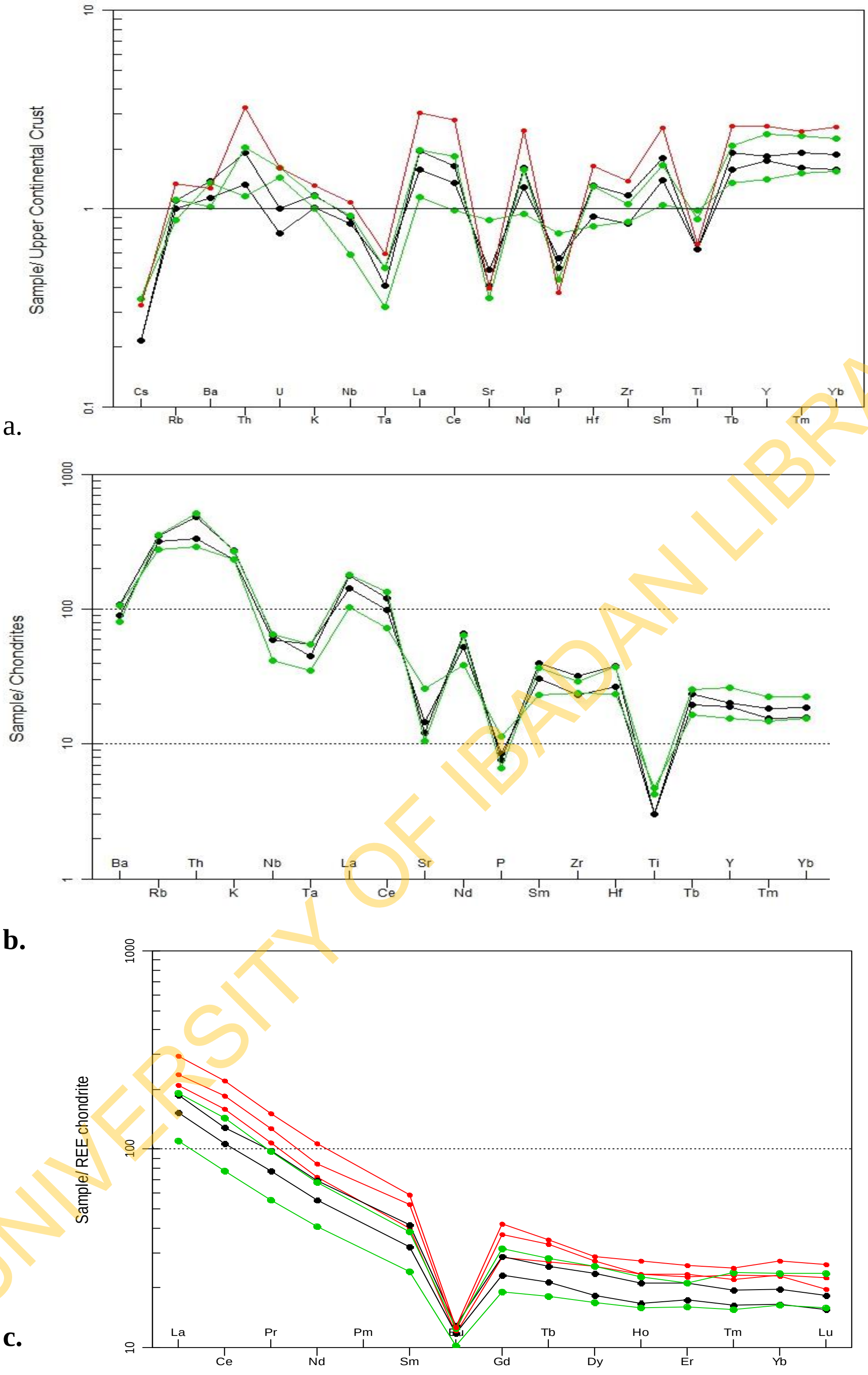


Figure 4.20. a) Spider Plot-Upper Continental Crust after Taylor and McLennan, 1995 b) Spider-Plot-Chondrites after Thompson, 1982 c) Spider plot-REE Chondrite after Boynton,1984

4.5. Heavy Metals Distribution in Sediments, Soils and Dusts

4.5.1 Heavy Metals Distributions in Sediments

The results obtained from geochemical heavy metals analysis of sediments samples from the study areas (Ibadan and Lagos) were subjected to statistical analyses and the summary for Pb and other metals concentrations are presented in Table 4.6. Pb ranged from 22 – 830 ppm and 89 – 3288 ppm with a mean of 289 ± 65.7 ppm and 979 ± 657.56 ppm in Lagos and Ibadan sediments, respectively. Zn ranged from 0.06 - 1454.40 ppm and 90 - 2090.20 ppm with mean of 889.80 ± 405.3 ppm and (840.68 ± 545.94) ppm; Cu ranged from 0.04 - 194.6 ppm and 49.7-688.5ppm with mean (112.86 ± 43.72) ppm and 213.12 ± 193.26 ppm. Mn ranged from 0.06 - 781.0 ppm with a mean content of (140.6 ± 282.42) ppm in Lagos sediments while its concentrations in Ibadan sediments ranged from 467 - 4945.00 ppm with a mean of (1188.35 ± 881.90) ppm. Arsenic (As) ranged from 0.2 - 10.2 ppm with a mean of (4.4 ± 2.2) ppm in Lagos sediments while its concentrations in Ibadan sediments ranged from 0.6 - 19.00 ppm with a mean of (4.44 ± 4.6) ppm.

Similarly, Cd in Ibadan ranged from 0.13 - 2.56 ppm with a mean of (0.73 ± 0.71) ppm while its concentrations in Lagos sediments ranged from 0.25 – 2.48 ppm with an average of (0.89 ± 0.58) ppm. Based on their mean concentrations, the observed magnitude of increasing metals concentrations in the Lagos sediments is in the order Zn >> Pb > Ba > Mn > Cu > Sr > Cr >V while for Ibadan sediments, it is Mn > Pb > Zn >> Cu > Ba > Cr >V.

The concentrations of Ag, Ni, Co, Th, V, La, Ba, U and Cr were significantly enriched in Ibadan sediments relatively to sediments from Lagos metropolis while Hg and Sr showed elevated concentrations in Lagos sediments when compared with its counterpart from Ibadan. In general, the comparison of the mean contents of the analysed metals with their respective background values (in both Lagos and Ibadan) showed that almost all the metals displayed enrichment values far above their respective background values (10 - 300-folds).

In addition, the concentrations of selected potentially harmful metals (PHMs) such as Zn, Pb, Cu e.tc were compared with the results reported from other urban settings and some regulatory standards. It was observed that the present Pb concentrations in Lagos sediment is about ten folds of what was reported in Lagos lagoon sediments in 2006 (Olatunji, 2006); greater than the average Pb reported in Korea, Indian, Uganda, China, Turkey and Germany. While Pb in Ibadan sediments surpassed the reported values from Ibadan stream sediments in 2004 (Tijani et al., 2004), Korea, Tunisia, Uganda, China, Turkey and Germany (Fig.4.21).

Furthermore, Pb, Cu and Zn concentrations in Lagos and Ibadan sediments were found to be higher than the standards set by Department of Petroleum Resources value (DPR), Canadian Environmental Quality Criteria value (CEQC), Dutch Target Value (DTV), Dutch Intervention Value (DIV), European Community Regulation value (ECR) and Australia Ecological Investigation level (AEIL) with the exception of Pb which were lower than ECR and AEIL (Table 4.7 and Figs. 4.22 – 4.24).

When compared with Probable Effect Levels (PELs) of the Canadian Environmental Quality Guidelines for stream sediments (CCME, 1997), mean Cd, Cu, Pb and Zn concentrations of the Ibadan sediments can be considered contaminated with a potential to cause hazard ecological effects. In comparison, Cu, Pb and Zn concentrations of the Lagos sediments were generally above the corresponding PELs. The intervention values recommended by the Netherlands Sediment Quality Guidelines (Department of Soil Protection, Netherlands, 1994) represent the maximum threshold values of trace metals in sediments, above which remedial actions should be considered. A comparison with the intervention values showed that thirty-one of the thirty-five Ibadan sediments and twenty of the twenty-five Lagos sediments exceeded the intervention limits of Cu, Zn and Pb concentrations (Table 4.7). Hence, the present concentrations of Zn, Pb, Cu and other PHMs strongly revealed that further investigation is needed (remedial action), especially in Ibadan rivers channels as these may pose environmental health risks and hazards if left unattended.

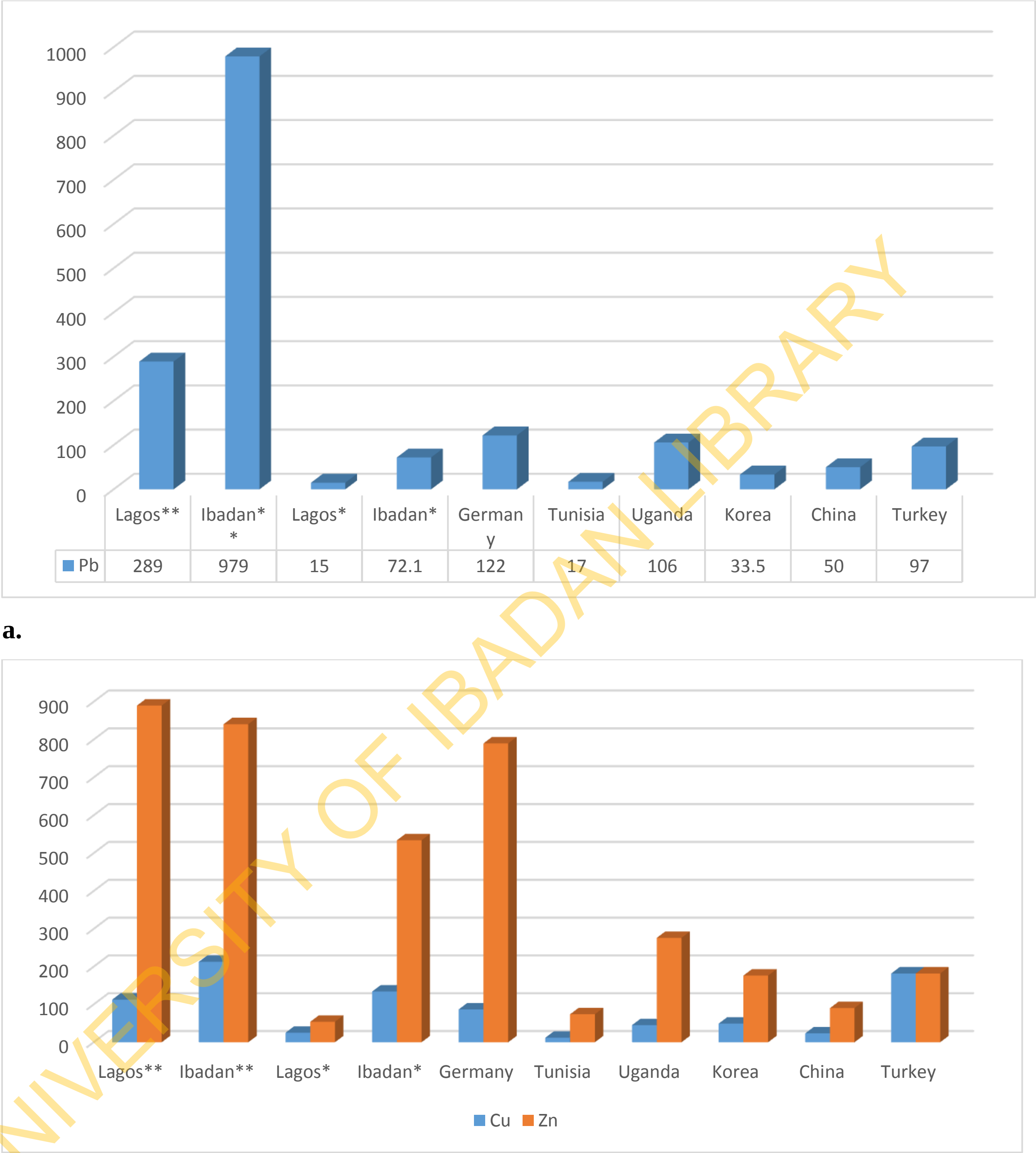
Table 4.6. Summary of Heavy metals in Sediments from Lagos and Ibadan metropolis

Element	**Lagos-Sediments**			**Ibadan-Sediments**		
	N	**Range (ppm)**	**Mean ± S.D.**	**N**	**Range (ppm)**	**Mean ± S.D.**
Pb	25	22 - 830	289 ± 65.74	35	89 - 3288	979 ± 657.56
Mo	25	0.1- 2.05	2.0 ± 0.59	35	0.55 - 18.26	3.78 ± 4.33
Cu	25	0.04 - 194.61	112.86 ± 43.72	35	49.73 - 688.47	213.12 ± 193.26
Zn	25	0.06 - 1454.40	889.80 ± 405.3	35	90 - 2090.20	840.68 ± 545.94
Ag	25	0.0 - 1.5	0.1 ± 0.36	35	0.03 – 2.597	0.478 ± 0.612
Ni	25	0.4 - 10.0	2.6 ± 3.68	35	9.5 - 100.0	31.65 ± 20.68
Co	25	0.02 - 15.0	2.4 ± 4.99	35	11.2 - 45.50	22.01 ± 8.58
Th	25	1.20 - 8.50	3.97 ± 2.48	35	3.6 - 20.30	9.88 ± 5.03
Mn	25	0.06 - 781.0	140.6 ± 282.42	35	467 - 4945.00	1188.35 ± 881.90
Hg	25	0.034 – 3.804	0.985 ± 1.303	35	0.028 – 2.083	0.224 ± 0.364
As	25	0.20 - 10.20	3.70 ± 2.24	35	0.6 - 19.00	4.44 ± 4.55
V	25	11.0 - 156.0	40.4 ± 34.28	35	33 - 216.0	116.52 ± 51.05
Sr	25	11.0- 175.0	90.8 ± 54.99	35	12.4 - 51.40	32.08 ± 10.90
Cr	25	19 - 110	43.9 ± 22.26	35	36.1 - 444.80	175.91 ± 125.98
Ba	25	24 - 430	154.8 ± 91.48	35	111.50 - 573.40	217.93 ± 91.95
U	25	0.78 - 1.64	1.07 ± 0.28	35	0.89 - 3.70	2.26 - 0.80
Cd	25	0.25 - 2.48	0.89 ± 0.58	35	0.13 - 2.68	0.73 ± 0.41

Table 4.7. Comparison of geochemical data with previous studies and regulatory standards

	BGV		Regulatory Standards						Previous studies		This study			
Elements	Lagos	Ibadan	DTV	ECR	CEQC	AEIL	NSQG	DPR	Benin soils	Akure soils	Lagos Soil	Ib-Soil	Lag Sed.	Ib-Sed.
Pb	5	8.4	85	300	25	600	530	85	232.3	38.9	686.3	183	289	979
Cu	9.6	23.5	36	140	30	100	190	36	119.7	22.2	101.4	37.4	112.9	213
Zn	10.3	81.3	140	300	60	20	720	146	533.1	131.7	844.1	155.9	889.8	840.7
Ni	-	15.6	35	75	20	60	-	35	-	10.4	19.32	14.6	2.6	31.7
Co	-	8.6	20	-	-	-	-	20	7.3	-	6.37	16.5	2.4	22
Cr	-		100	-	20	-	-	100	45.3	32.9	42.2	56.5	43.9	175.9

Background values (BGV), Department of Petroleum Resources (DPR), European Community Regulation (ECR) value, Canadian Environmental Quality Criteria (CEQC), Dutch Target Value (DTV), Australia Ecological Investigation level (AEIL), Netherland Sediment Quality Guideline (NSQG)

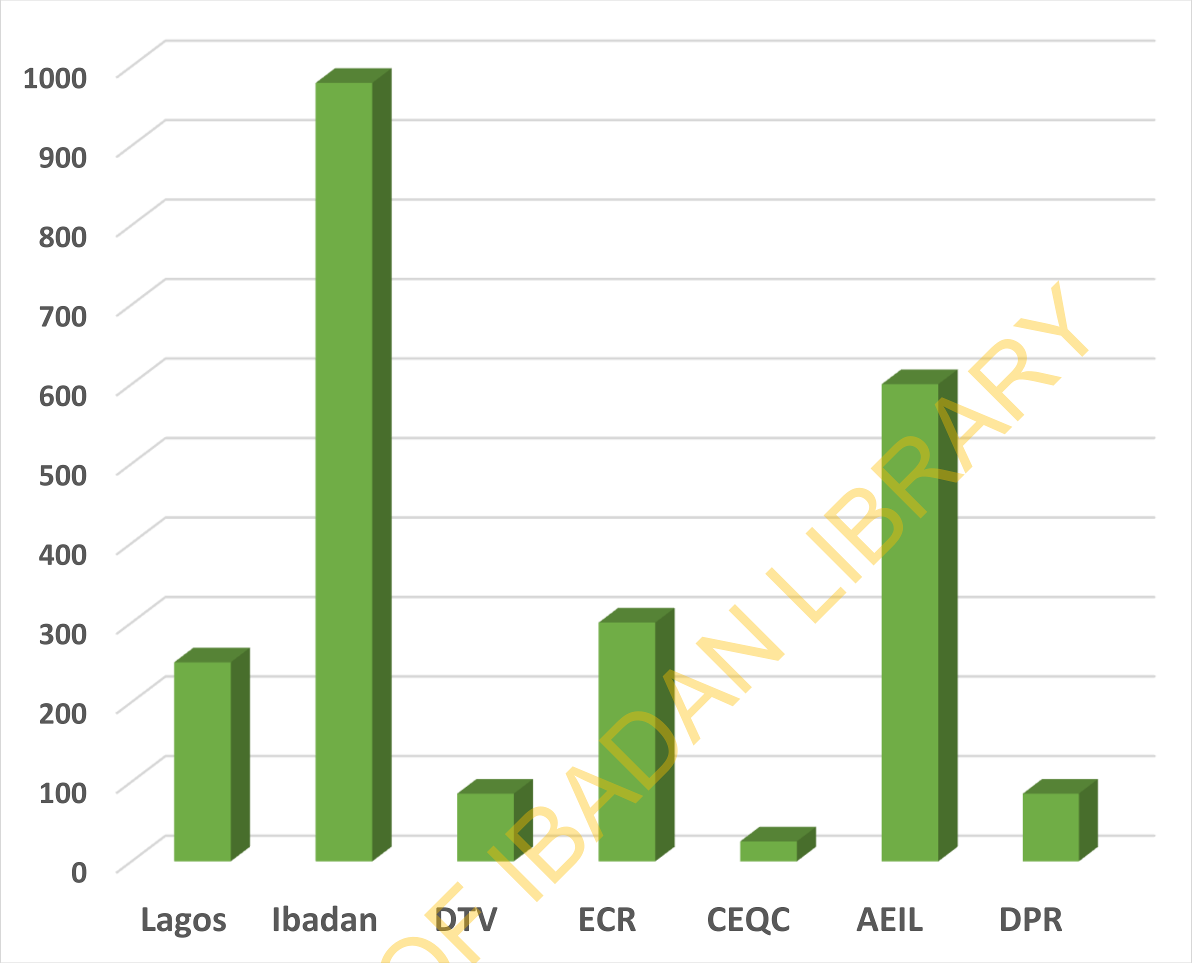


a.

b.

*** present study, * previous studies*

Figure 4.21. a) Average Pb contents b) Cu and Zn contents in sediments from the study areas with other studies



Department of Petroleum Resources (DPR), European Community Regulation (ECR) values, Canadian Environmental Quality Criteria(CEQC), Dutch Target Value (DTV), Australia Ecological Investigation level (AEIL)

Figure 4.22. Average Pb contents in sediments from the study areas with some world standards

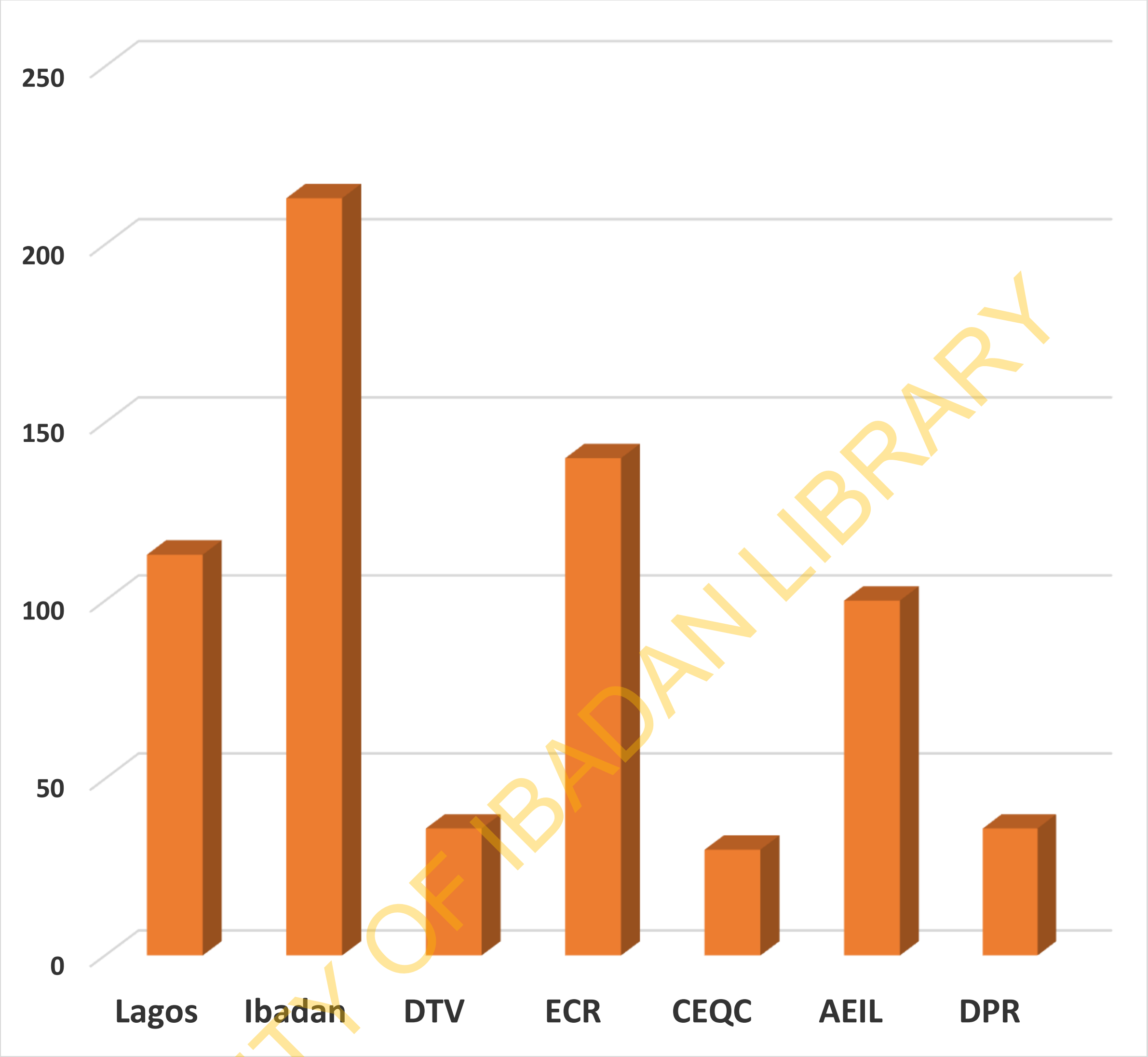


Figure 4.23. Average Cu contents in sediments from the study areas with some regulatory standards

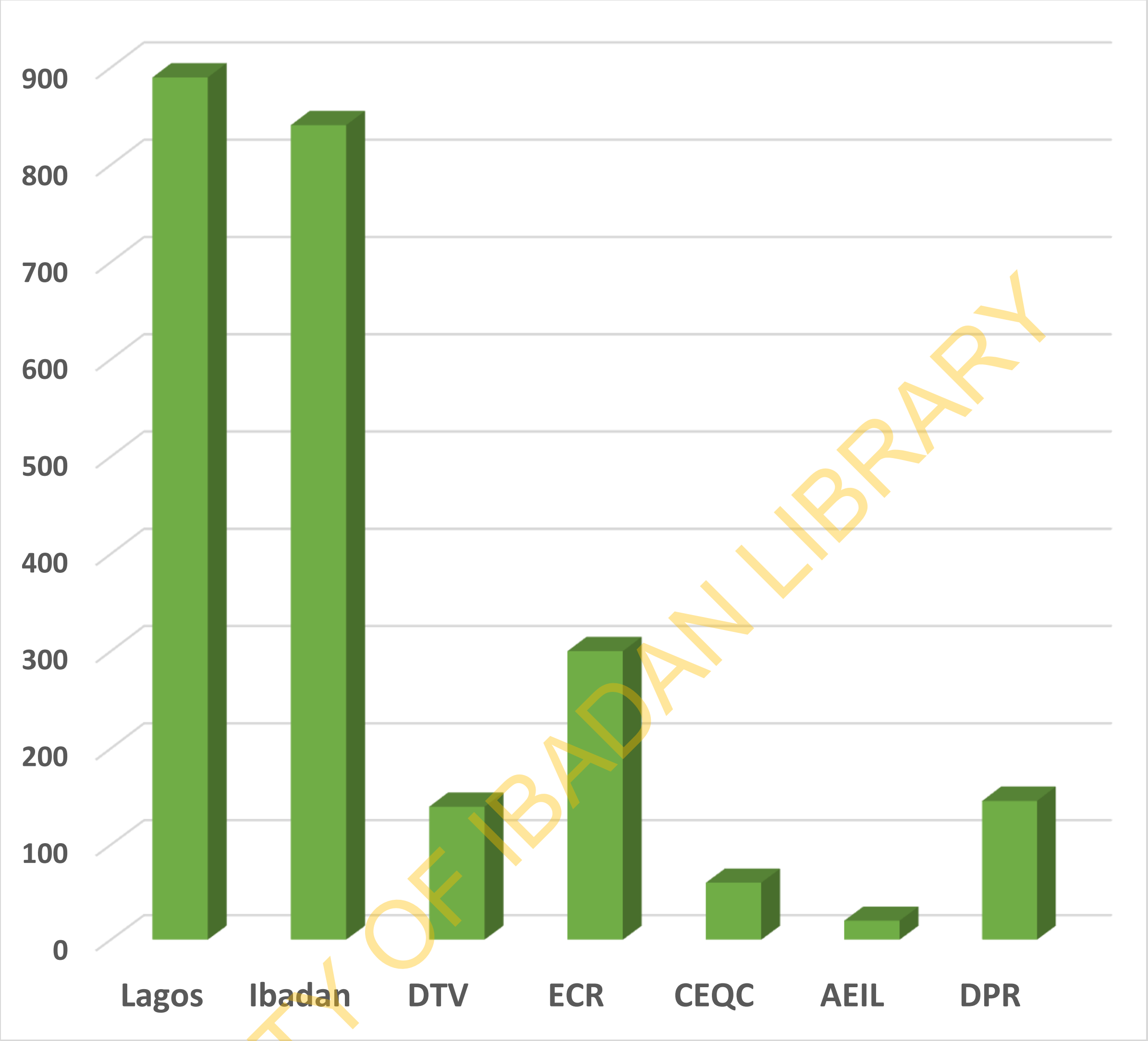


Figure 4.24. Average Zn contents in sediments from the study areas with some regulatory standards

4.5.2 Heavy Metals Distribution in Soils

The results of geochemical data of Lead (Pb) and other metals in Lagos and Ibadan soils are presented in Table 4.8. Over 90% of the analysed metals displayed heterogeneities in their distributions as shown by their high standard deviations, an indication of contributions from different sources. Pb has the highest variability in soils of Lagos metropolis when compared to Ibadan soils, with concentration ranging from 21.0 to 1963.3 ppm and a mean 686.3 ± 432.7 ppm while in Ibadan soils, it ranged from 13.0 to 470.0 ppm with mean of 183.0 ± 135.42 ppm. Zinc (Zn) ranged from 17 to 1712 ppm with a mean of 884.0 ± 411.6 ppm and 17.0 - 621.0 ppm with a mean value of 255.7 ± 186.6 ppm in soils from Lagos and Ibadan metropolises respectively. Mn ranged from 88.0 to 1253 ppm with a mean of (428.3 ± 252.2) ppm and 440.0 - 1553.0 ppm (981.2 ± 324.6) ppm in both soils respectively. Similarly, Copper (Cu) in Lagos and Ibadan ranged from 7.0 - 368.37 ppm, mean (101.44 ± 66.92) ppm and 15.0 – 178.7 ppm (87.90 ± 34.53) ppm, respectively, while other PHMs such as Ba, Co, Ni, Sr, La, Th and V varied significantly and were more enriched in Ibadan soils compared to Lagos soils. The elevated concentrations of these metals can be attributed to additional contribution from the geologic units in Ibadan.

The ranges of concentrations and the mean contents of the selected PHMs were compared with their respective concentrations in the local bedrocks. The evaluation revealed that almost all the analysed PHMs in Lagos soils exceeded their respective concentrations in the bedrocks (higher than their local background values). Similarly, in Ibadan soils, Pb, Zn, Cu, Mn, Co, Cr, Mo, Cd, Hg, As and V were observed to display significant enrichment over their respective concentrations in the bedrocks while La, Ag, Ba and Th showed concentrations below their respective background values. Furthermore, average values of some the metals were compared with previous studies and global standard values. This revealed that the present average concentrations of Pb and Zn in Lagos soils are greater than the reported average concentrations from Benin City, Warri, Torino, Hong Kong, Aberdeen, Texas, Norway, Palermo, Jordan and UK but slightly lower than the reported concentrations in London soils (Fig.4.25). The average concentrations in Ibadan soils is lower than the reported values from UK, London, Torino and Palermo, equal to the values reported from Hong Kong and Aberdeen but greater than average concentrations from Texas, Norway, Jordan, Abeokuta and Akure.

In addition, the average concentrations of Cu, Pb, Zn, Ni, Cr and Co in the studied soils were compared with the regulatory global environmental standards. The comparison revealed that Ni and Co in Lagos soils were below the regulatory standards, Pb in Lagos soils was found greater than DPR, CEQC, ECR and DTV but less than AEIL recommended values while its concentrations in Ibadan soils was less than the guideline values recommended by the Department of Petroleum Resources (DPR), European Community Regulation (ECR) , Dutch Target Value (DTV), Australia Ecological Investigation level (AEIL) but higher than the Canadian Environmental Quality Criteria (CEQC) value (Table 4.7 and Fig. 4.26). The average Zn concentrations recorded in Lagos soils is greater than all the recommended values while its average value in Ibadan is less than but exceed all the recommended values with the exception of ECR. Similarly, average Cu concentrations in Lagos exceed all the recommended standards except ECR while in Ibadan its concentrations slightly exceed all but ECR and AEIL standards (Fig. 4.27).

Table 4.8. Summary of PHMs in soils from Lagos and Ibadan metropolis

Element	**Lagos-Soil**			**Ibadan-Soils**		
	N	**Range (ppm)**	**Mean ± S.D.**	**N**	**Range (ppm)**	**Mean ± S.D.**
Pb	48	21.0 - 1963.0	686.3 ± 432.67	22	13.0 - 470.0	183.00 ± 135.42
Mo	48	0.00 - 5.0	1.2 ± 1.12	22	0.0- 22.00	1.380 ± 4.79
Cu	48	7.0 - 368.37	101.44 ± 66.92	22	15.0 - 178.7	87.90 ± 34.53
Zn	48	17.0- 1712.0	844.1.10 ± 411.55	22	17.0 - 621.0	255.85 ± 186.57
Ag	48	0.0 - 2.3	0.4 ± 0.53	22	0 - 0.4	0.1 ± 0.36
Ni	48	4.0 - 42.0	13.8 ± 8.10	22	5.0 - 57.0	14.60 ± 12.41
Co	48	2.0 - 11.0	4.7 ± 1.91	22	4.0 - 44.0	16.50 ± 8.64
Th	48	1.30 - 11.50	3.51 ± 2.42	22	0.0 -10.0	3.90 ± 2.79
Mn	48	88.0 - 1253.0	428.3 ± 252.2	22	440.0 - 1553.0	981.15 ± 324.58
Hg	48	0.066 – 1.099	0.452 ± 0.327	22	Bdl	Bdl
As	48	0.01 - 14.10	3.92 ± 2.54	22	Bdl - 4.46	2.4 ± 1.34
Sr	48	5.0 - 109.0	41.7 ± 23.40	22	8.0 - 137.0	31.45 ± 28.57
V	48	10.0 - 92.0	31.7 ± 17.77	22	30.0 - 134.0	64.65 ± 26.05
La	48	4.0 - 19.0	8.8 ± 3.34	22	9.0 - 36.0	17.45 ± 6.54
Cr	48	12.0 - 85.0	36.4 ± 13.44	22	19.0 - 202.0	56.45 ± 40.05
Ba	48	34.0 - 337.0	95.7 ± 65.67	22	38.0 - 219.0	109.90 ± 45.85
Cd	48	0.25 - 3.12	1.04 ± 0.56	22	0.24 - 1.60	0.76 ± 0.45

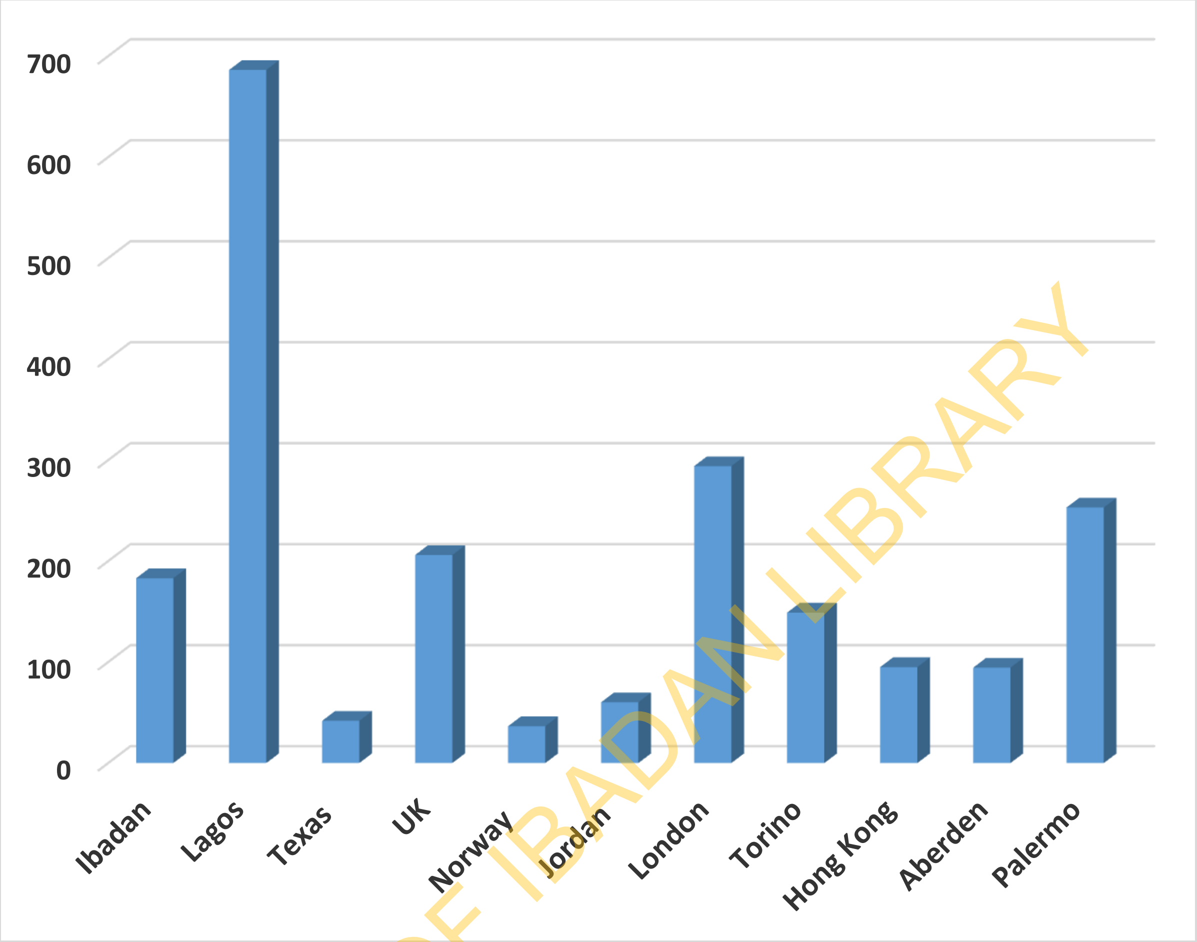
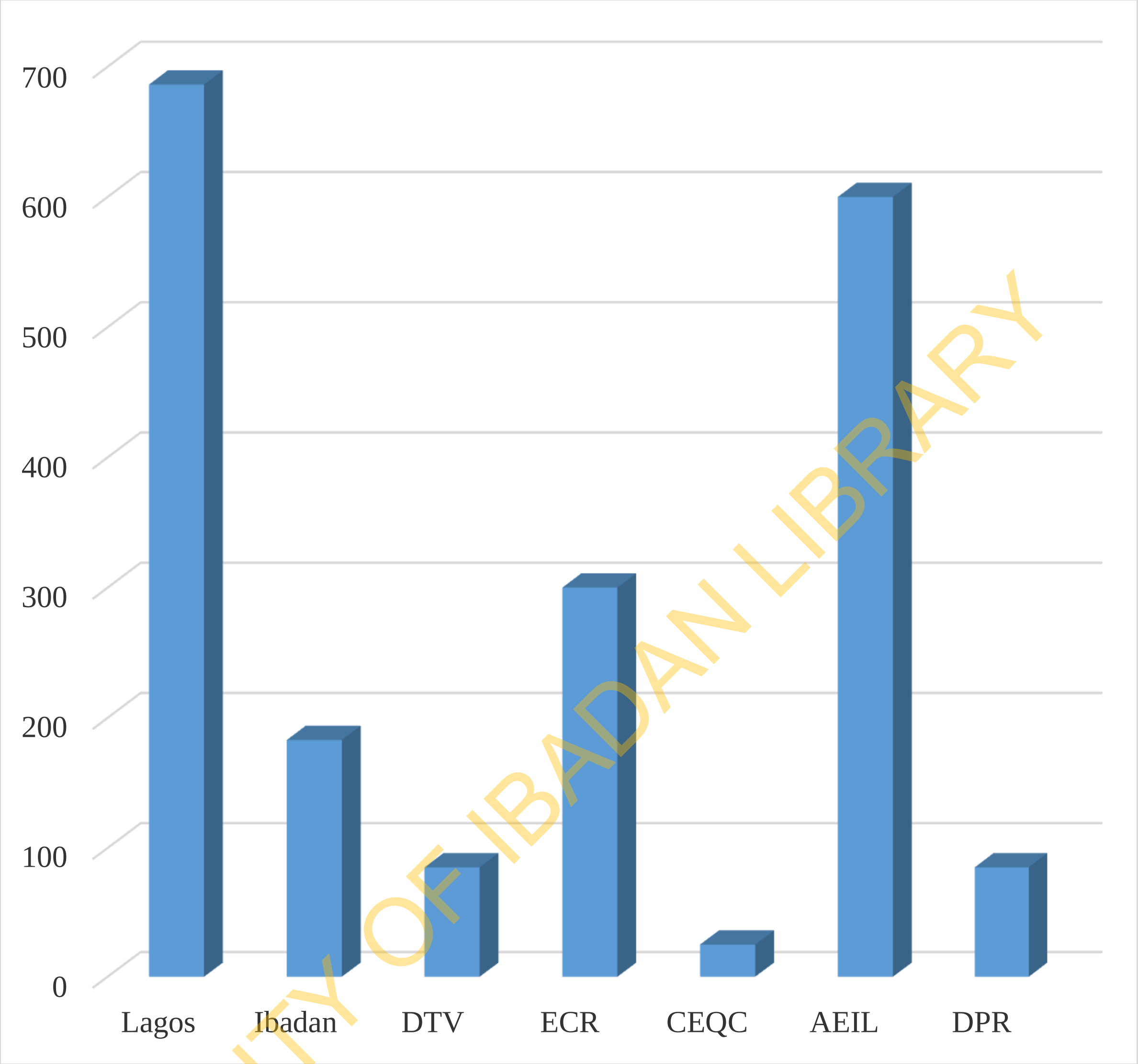


Figure 4.25. Average Pb contents in soils with other studies in some parts of the world



Department of Petroleum Resources (DPR), European Community Regulation (ECR) values, Canadian Environmental Quality Criteria (CEQC), Dutch Target Value (DTV), Australia Ecological Investigation level (AEIL)

Figure 4.26. Average Pb contents in soils from the study areas with some regulatory standards

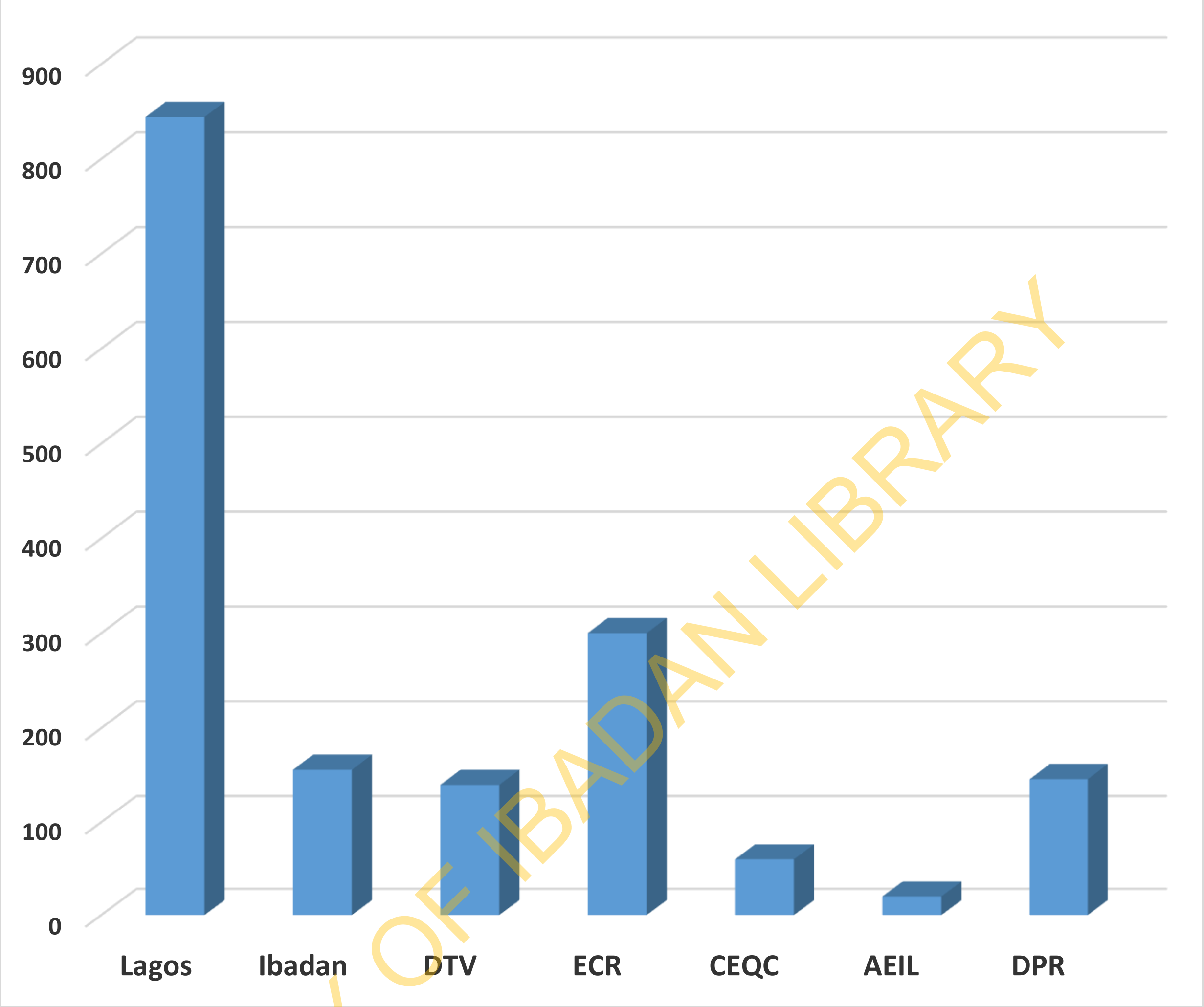


Figure 4.27. Average Zn contents in soils from the study areas with some regulatory standards

4.5.3 Heavy Metals in Roadside Dusts

The summary concentrations result of Pb, Zn, Cu, As, Cd, Ni, Cr, Mn, Ni e.tc. (ppm) in Lagos road dusts are presented in Table 4.9. The concentrations of Pb ranged from 23 - 829 ppm and a mean value of (355.6 ± 182.5) ppm, Zn ranged from 140 - 1586.4 ppm with a mean of (614.8 ± 409.2) ppm, Copper varied in concentrations from 20 - 655.49 ppm with a mean of (142.5 ± 182.9) ppm and Mn ranged from 130 - 693 ppm with an average of 333 ± 136 ppm. Similarly, Ni and Co concentrations ranged from 9.3 - 28.1 ppm and 3.0 - 7.9 ppm respectively while As and Cd varied from 0.2 - 7.6 ppm and 0.23 – 11.62ppm although the mean values of these potentially toxic metals were below 15 ppm (Table 4.9).

The mean concentrations of heavy metals in the dusts samples revealed comparative enrichments of the metals which tends to decrease in the following order of magnitude Zn>Mn>Pb>Cu>>Cr. The average concentrations of Zn, Pb, Mn, Cu, As and Cd were compared with their respective concentrations in the Lagos Coastal Plains sands: Zn (10.3); Pb (5.0); Cu (9.6); Mn (47.6); As (5.5) and Cd (0.01) in ppm. In general, the concentrations of these heavy metals were found to be significantly enriched in road dusts ranging from 10 - 20 folds of the background values. Higher concentrations of these metals especially Zn, Pb, Cu, Mn and Cr were recorded in samples collected within the Agege - Iyanapaja/Dopemu areas of the metropolis around Nigerian Railway Mega-station.

The average concentrations of some selected PHMs in the analysed road dusts from Lagos metropolis were compared with some reported values from industrialized cities where similar studies have been carried out. The results showed that the present average concentrations of Cu in Lagos dusts is higher than the reported values in road dusts from Benin city, Kayseri, Manchester, Luanda, Tokat, Xian and Aquba city but less than values from Hong Kong, Aviles, Birmingham and Amman. The average Pb in Lagos dusts was found to be less than values reported from Aviles and London but exceeded values in Benin, Amman, Coventry, Honk Kong, and many other cities (Table 4.10 and Fig.4.28). Zn concentrations in Lagos dusts was found to be less than values from Aviles, Hong Kong, London and Manchester but exceeded that of Benin, Amman, Coventry, Luanda e.tc. (Table 4.10).

Table 4.9. Summary of Pb and other PHMs in Road dusts of Lagos metropolis

	N	**Range (ppm)**	**Mean ± S.D. (ppm)**
Pb	17	23.0 - 829.0	355.6 ± 254.47
Mo	17	1.0 - 3.70	2.40 ± 0.64
Cu	17	20 - 655.49	142.54 ± 182.85
Zn	17	140.0 - 1586.40	614.83 ± 409.21
Ag	17	0.0 - 1.3	0.2 ± 0.38
Ni	17	5.0 - 27.0	13.7 ± 5.85
U	17	0.56 - 3.48	1.30 ± 0.94
Co	17	3.0 - 6.0	4.1 ± 0.95
Th	17	2.10 - 8.00	6.02 ± 1.81
Mn	17	130.0 - 693.0	333.0 ± 136.03
Hg	17	0.011 – 0.438	0.136 ± 0.146
As	17	0.2 - 7.60	4.1 ± 2.78
Sr	17	18.0 - 63.0	34.4 ± 15.69
V	17	19.0 - 112.0	37.2 ± 23.61
La	17	5.0 - 26.0	10.6 ± 5.17
Cr	17	27.0 - 105.0	47.0 ± 19.34
Ba	17	46.0 - 171.0	87.2 ± 40.15
Cd	17	0.23 - 11.62	3.42 ± 2.76

Table 4.10. Comparing the mean of selected PHMs in Lagos dusts with other cities in the world

City	**Pb**	**Cu**	**Cd**	**Zn**
Lagos (This study)	**355.6**	**142.5**	**3.42**	**614.8**
Benin City[a]	100.9	80.9	0.7	279.9
Amman[b]	236.0	**177**	1.7	358.0
Aviles[c]	**514.0**	**183**	22.3	**4829.0**
Birmingham[c]	48.0	**466.9**	1.6	534.0
Coventry[c]	47.1	**226.4**	9.0	385.0
Hong Kong[d]	181.0	**173.0**	3.8	**1450.0**
Kayseri[c]	165.5	66.7	10.1	-
London[c]	**1030.0**	**155.0**	3.5	**680.0**
Manchester[c]	265.0	**113.0**	-	**653.0**
Luanda[c]	315.0	42.0	1.1	317.0
Aqaba City[c]	206.0	53.000	2.5	153.0

[a]Asowata, 2010; [b]Al-Khashman, 2006; [c]Al-Khashman, 2007; [d]Li *et al.*, 2004

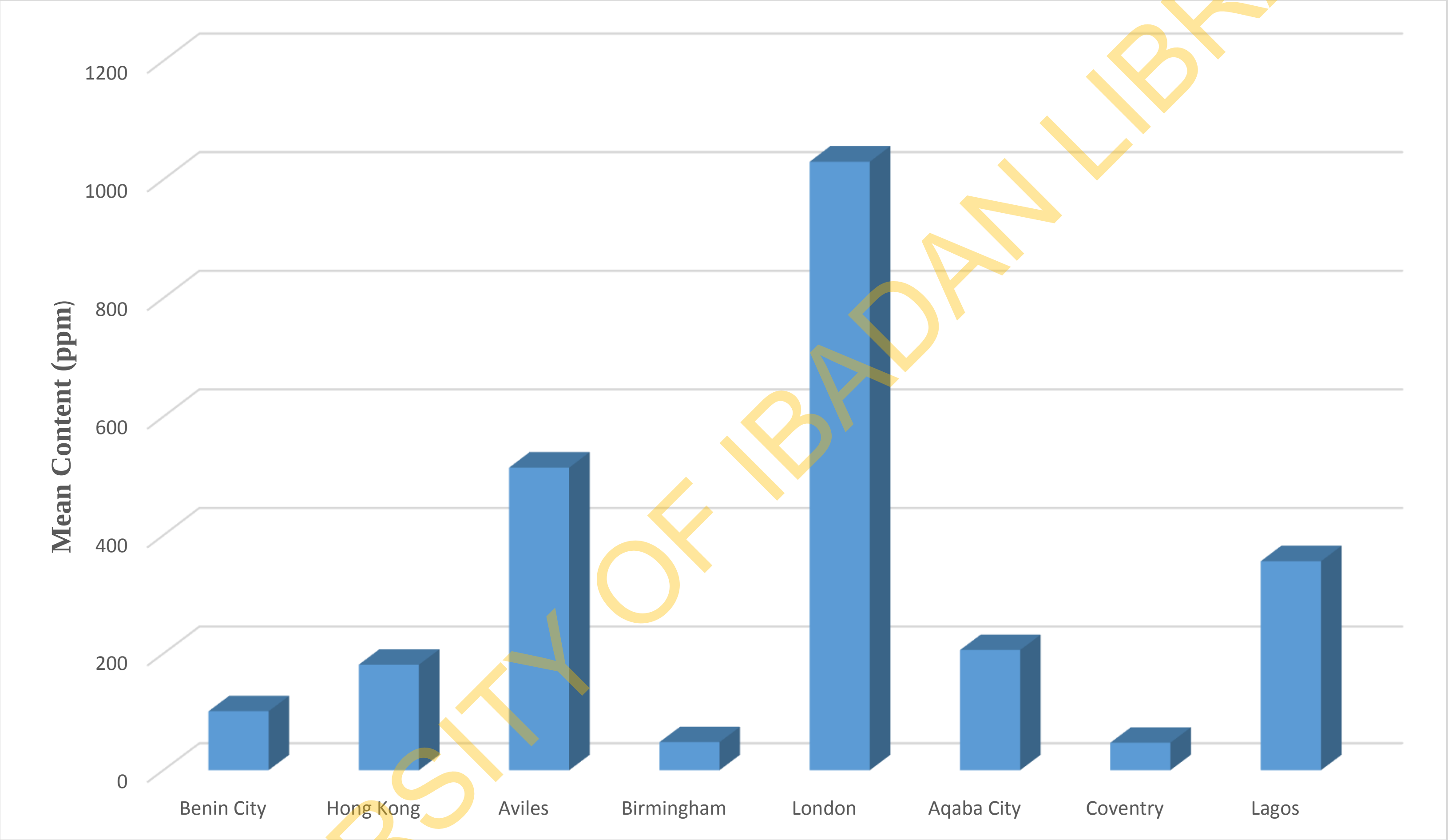


Figure 4.28. Comparing Pb contents in road dusts from the study areas with some previous studies

4.5.4 Heavy Metals distributions in Sediments, Soils and Dusts of the Study areas

4.5.4.1 Zinc Distributions in the Study Areas

Zinc (Zn) in Lagos sediments ranged from 0.06 to 1454.4 ppm with a mean concentration of (889.80 ± 405.3) ppm (Table 4.6 and Fig. 4.29). In Lagos soils, it ranged from 17 to 1712 ppm with a mean of (884.1 ± 411.6) ppm (Table 4.8) while its concentrations in dusts ranged from 140 to 1586 ppm with a mean of (614.83 ± 409.21) ppm (Table 4.9). Elevated concentrations of Zn in soils and sediments were recorded in samples from Abule-Nla, Atan, Ojota, Shomolu, Mushin, Oyingbo Palmgroove, Bariga, Itire and Agege areas and Yaba areas. These areas of Lagos metropolis are characterised by several industrial and commercial activities, high traffic congestion, high population density, lots of motor parks, mechanic workshops and dumpsites. Anomalous concentrations of Zn were recorded in samples collected along Oshodi-Apapa Expressway, Palmgroove, Ilupeju and Mushin. High concentrations of Zn recorded on these roads may be attributed to accumulation from galvanizing of iron and steel from corrosion protections, wearing and tearing of vulcanized tyres and tubes as well as paints.

The concentrations of Zn in soils, sediments and dusts in Lagos metropolis were compared with their background values (8.59 - 10.63ppm**)** in the Coastal Plain /Alluvia sands underlying Lagos metropolis. It was observed that Zn showed significant enrichment in sediments, soils and road dusts over the background values. All the values were far above the average background value (10 ppm). The Enrichment ratios of Zn in the samples to background values ranged from 16 to 145 folds for soils, 14 to 151 folds for road dusts and 13 to 132 folds for sediments. This is a reflection of high level of anthropogenic input of Zn into these urban media as a result of complex urban activities such as wearing and tearing of tires and brake linings, vulcanizing activities, corrosion of zinc coated roofs and incinerations.

Zn concentrations in Ibadan sediments ranged from 38 to 2090.2 ppm with a mean of (840.68 ± 545.94) ppm (Table 4.8). Elevated concentrations of Zn were recorded in most samples collected from downstream of Rivers Ogunpa, Ogbere, Ona and Omin. Zn in Ibadan soils ranged from 17 to 621 ppm with a mean value of (255.9 ± 186.57) ppm

(Fig.4.30 and Table 4.8). Relatively higher concentrations of Zn were recorded in samples collected at Ojoo, Moniya, Bodija, Ojurin, Bashorun, Alakia/Gbagi, Odo-Ona, Felele, Olunloyo and Olomi areas of the metropolis. These areas are notable for high commercial activities, that often result in indiscriminate discharge of waste water, worn-out tires, breaking linings, rusting roofs, incinerations of waste materials, combustion of woods e.tc. All these activities aid the release of Zn into the water bodies within the metropolis. All samples displayed high and significant enrichment over the background values similar to what was observed in Lagos sediments. The depletion/enrichment ratios for all the samples with respect to their background values, ranged from 1 to 23 folds (Fig.4.30).

The presence of this metal in high concentrations around areas with high population density and industrial activities is a reflection of its introduction by anthropogenic activities. Generally, it was observed that the spatial distributions of Zn followed similar pattern, relatively higher concentration were found in similar locations, suggesting point source enrichment as well as activities relating to high vehicular traffic affecting the relatively high concentration in the soils and sediments of the study areas.

4.5.4.2 Lead (Pb) Variations in sediments, solis and dusts from the study areas

1. **Lead (Pb) Distributions in Sediments**

The concentrations of Pb in drainage sediments of Lagos ranged from 22 to 830 ppm with an average of (280 ± 65.74) ppm (Fig.4.31). Samples collected from Abule-Nla, Ojota and Mushin areas of Lagos metropolis showed elevated concentrations of Pb. These areas are characterized by very high population density, several industrial and commercial activities, high traffic density with several workshops and factories. The enrichment/depletion ratios ranged from 5 to 52 folds of background concentrations (Fig.4.32), a clear indication that the present Pb content in Lagos sediments has no relationship with the bedrocks but rather contributions from anthropogenic activities.

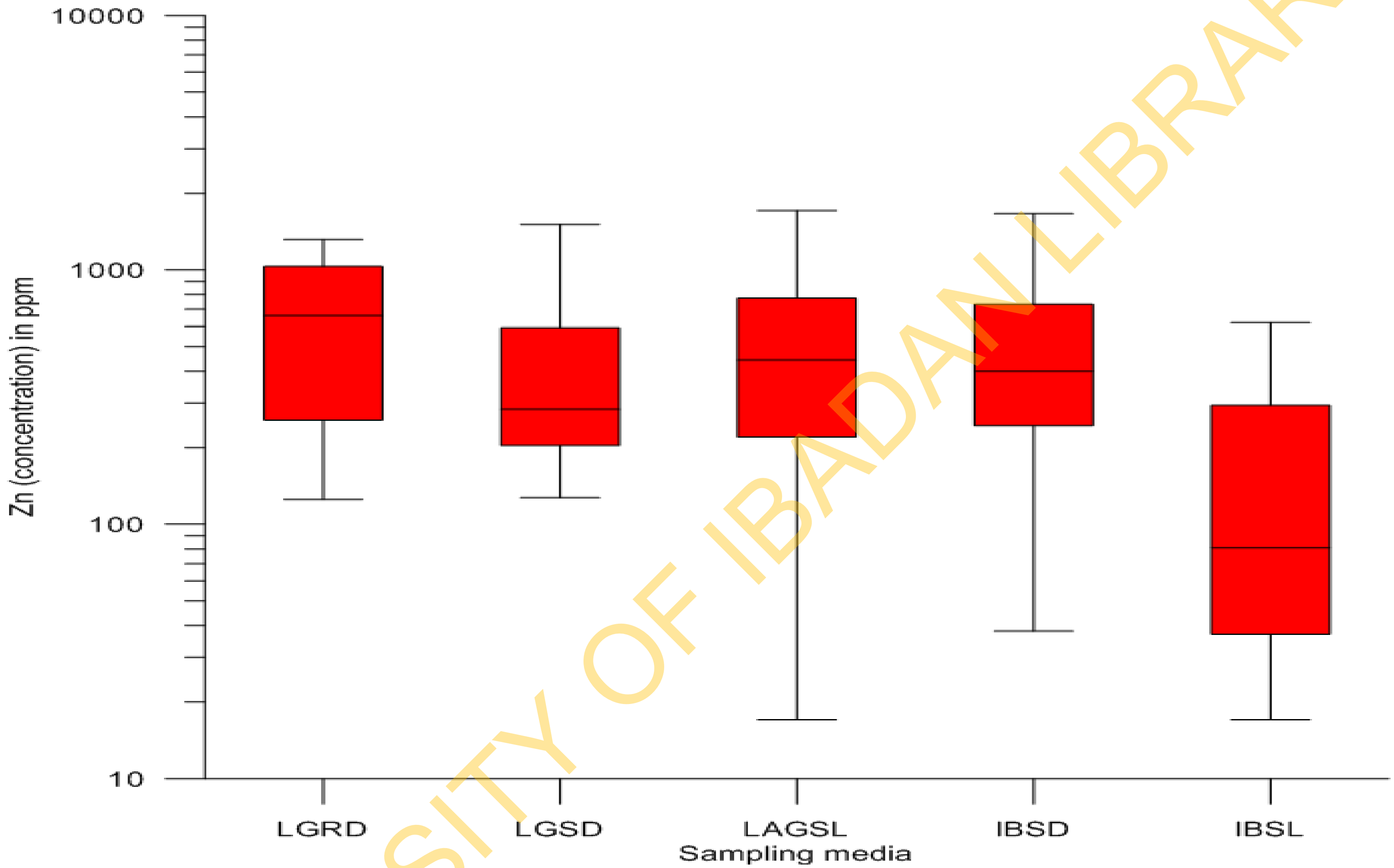


Figure 4.29. Variations of Zinc in the Study areas

IBSL = Ibadan Soil, IBSD = Ibadan Sediments, LAGSL = Lagos Soils, LGRD = Lagos Road dusts, LGSD = Lagos Sediments

The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

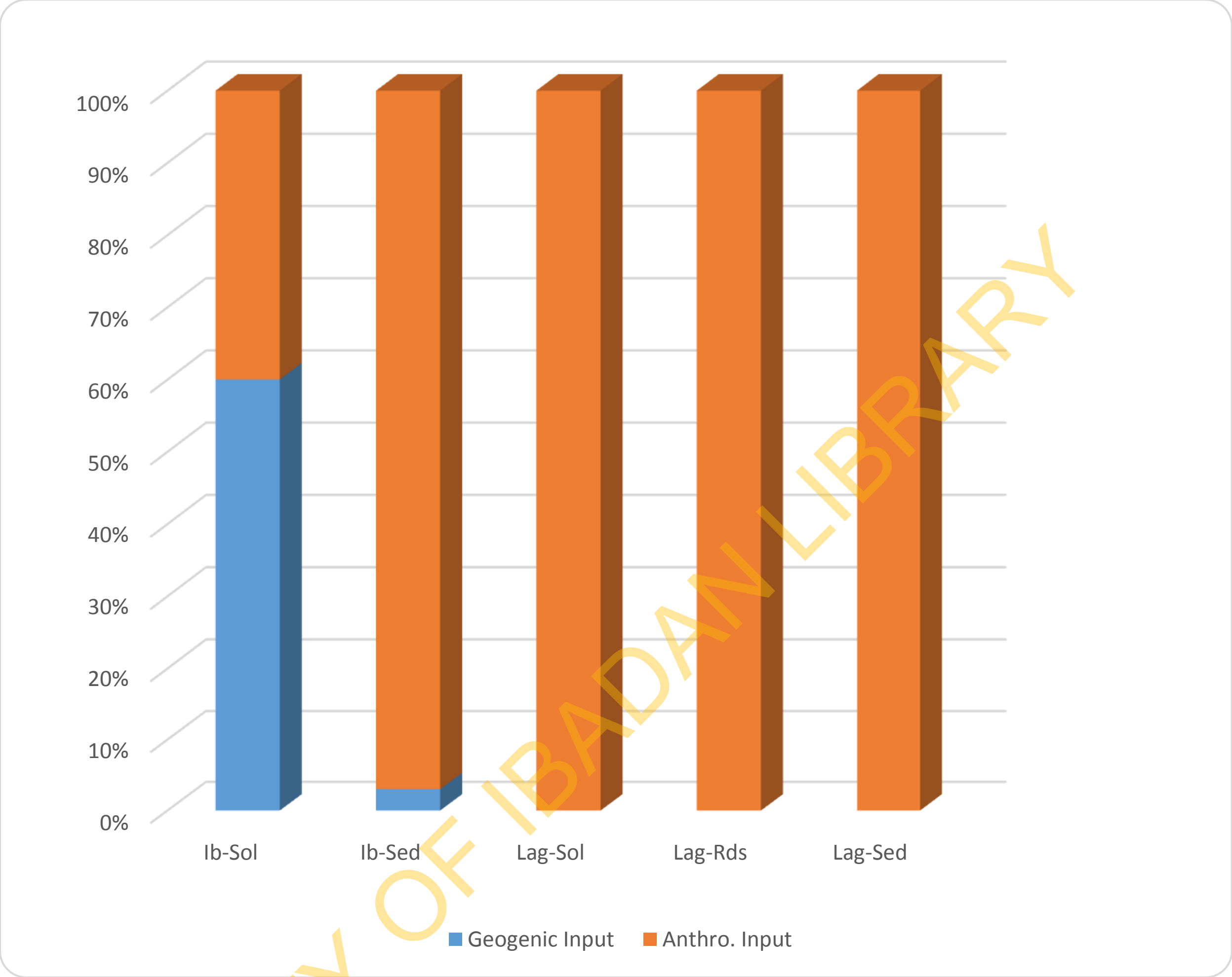


Figure 4.30. Contributtions of Zn by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Rds = Lagos Road dusts, Lag-Sed = Lagos Sediments

Similarly, Pb concentrations in the various river sediments in Ibadan metropolis ranged from 95 to 3288 ppm with a mean of (979 ± 657.56) ppm. Elevated concentrations of Pb were mostly recorded in River Ogunpa sediments and some locations along River Ogbere; River Omin and River Ona. Comparing the recorded mean in Ibadan sediments with the background values showed an up shoot of Pb with the enrichment ratios ranged from 11 to 354 folds of background concentrations for Pb in the sediments (Fig.4.31).

2. Lead (Pb) Distributions in Soils

Pb concentrations in Lagos soils ranged from 38 to 1963ppm with a mean of (686.3 ± 432.3) ppm (Fig.4.31). Most samples collected from Yaba, Jibowu, Oyingbo, Bariga, Agege, Itire and Ebute-Metta was significantly high in Pb. Pb in the soils from these areas have been greatly impacted, an indication of high anthropogenic input; Pb concentrations in all these samples being significantly higher than the average background value of Pb in the Coastal Plain sands (Fig. 4.32).

Similarly, a low to medium scale variations was observed in Pb contents in soil samples collected from Ibadan metropolis. Pb concentrations ranged from 13 to 470 ppm and a mean of (183 ± 135.42) ppm. Most of the soils samples collected from Bodija, Ojurin around mechanic village, Odo-Ona, Felele and Olunloyo areas of Ibadan showed elevated concentrations of Pb. Comparing the range of Pb concentrations in Ibadan soils with the background values showed that all sampled locations have concentrations far above the background values with enrichment ratios ranging from 1 to 50 folds.

3. Lead (Pb) Distributions in Dusts

Pb concentrations in dusts samples collected from both residential and commercial areas of Lagos Metropolis ranged from 23 to 729 ppm with a mean of (355.6 ± 254.5) ppm Most samples from motor parks and highways in Mushin, Itire, Ebute-Metta, Alimosho and Agege areas of Lagos showed high and elevated concentrations of Pb. All the sampled T-Junctions and highways were characterised by high traffic density with an average of over 1000 vehicles per hour. The enrichment metal ratios showed that Pb contents in the roadside dusts to the background values ranged from 5 - 146-folds (Fig.4.32). This showed that Lagos dust is highly enriched in Pb and could be probably linked to the atmospheric deposits and fallout from combustion of fossil fuel, break lining, vehicle exhaust, storage batteries and in-door and out-door paints.

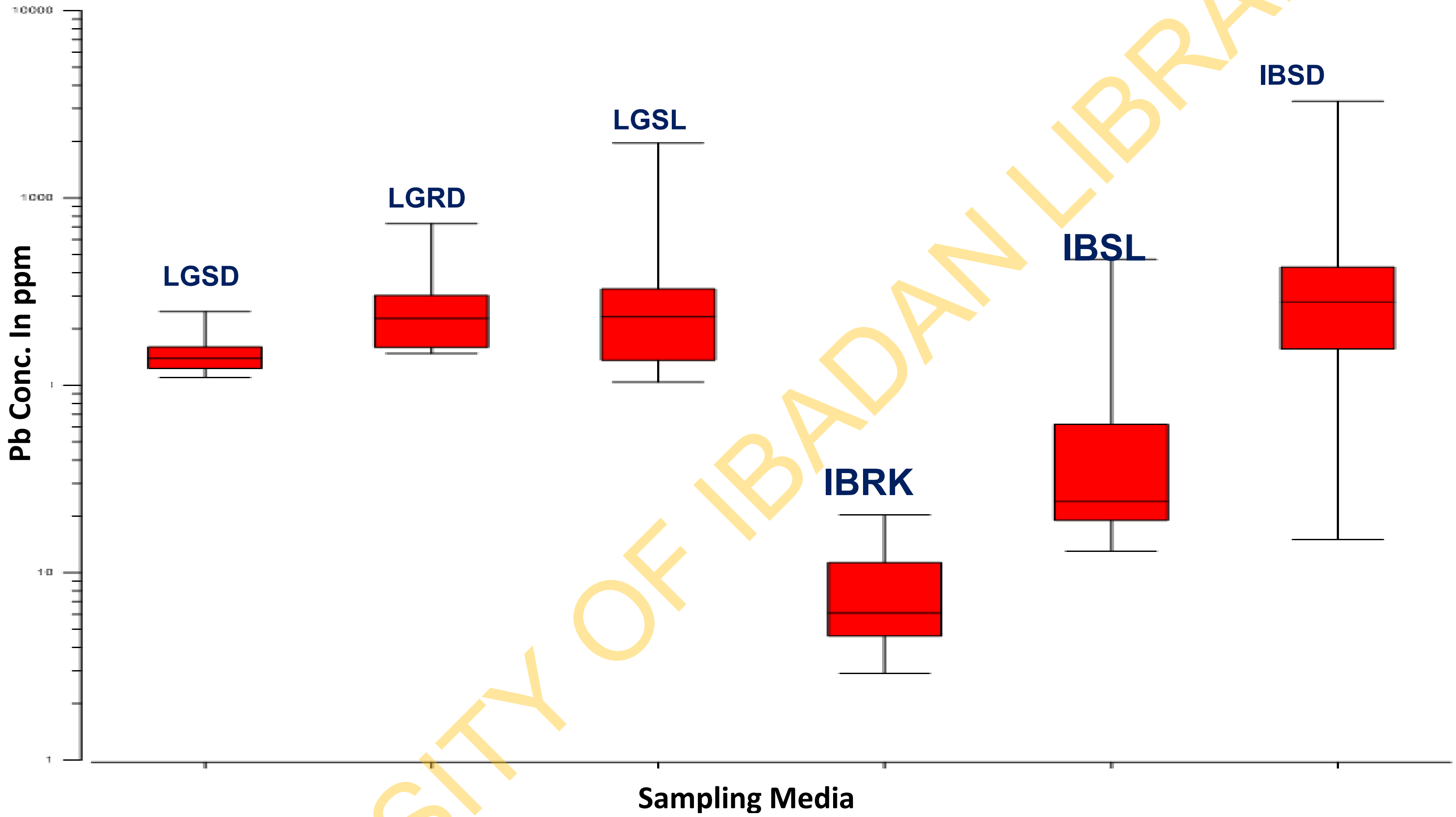


Figure 4.31. Variations of Pb concentrations in the Study areas

IBSL = Ibadan Soil, IBSD = Ibadan Sediments, LGSL = Lagos Soils, LGRD = Lagos Road dusts, LGSD = Lagos Sediments, IBRK=Ibadan rock. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

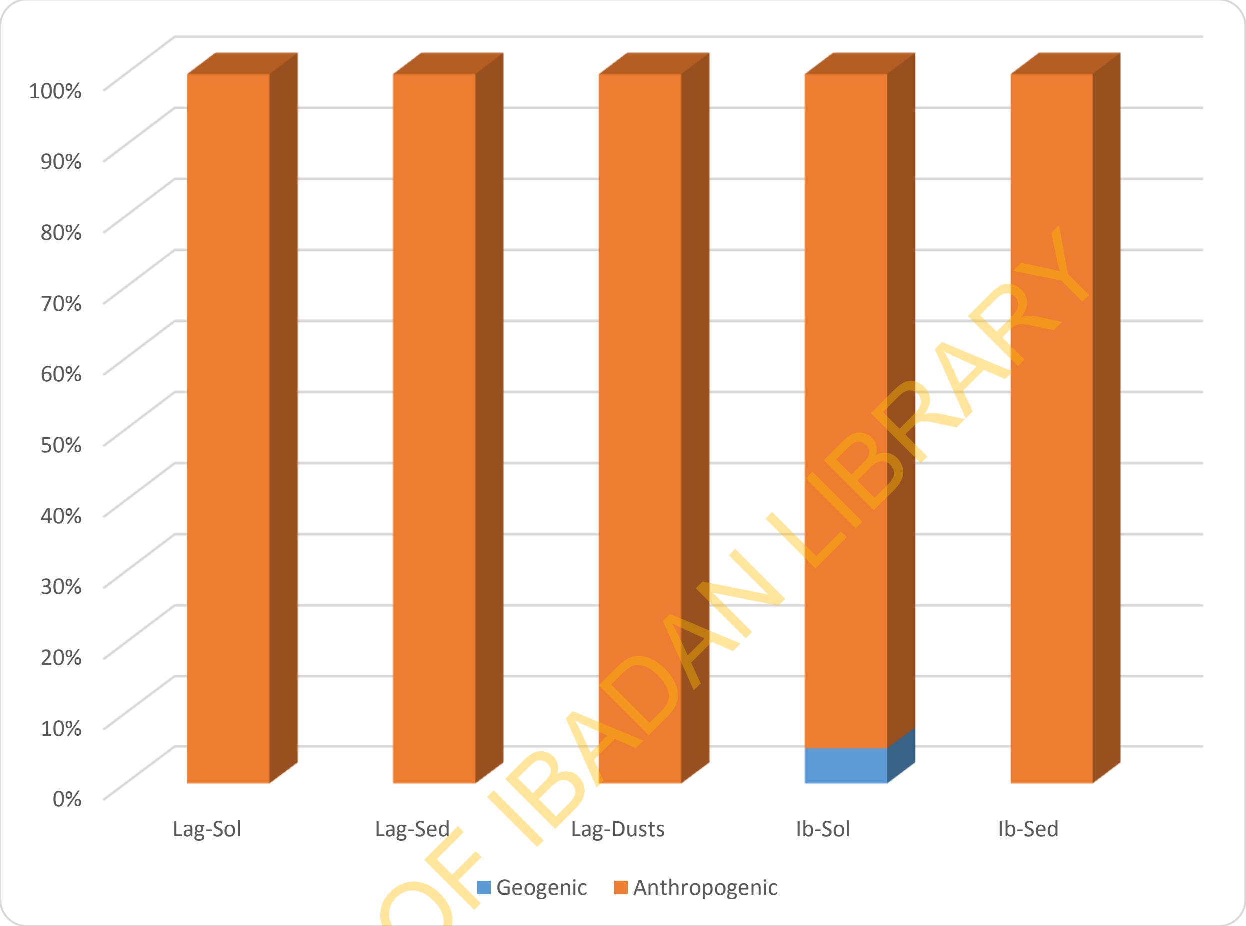


Figure 4.32. Contributtions of Pb by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Dusts = Lagos Road dusts, Lag-Sed = Lagos Sediments

4.5.4.3 Cu Distributions in Lagos and Ibadan Areas

Cu concentrations in Lagos soils ranged from 7 to 368.37ppm with a mean of 101.44 ± 66.9ppm while its concentrations in Lagos sediments ranged from 0.04ppm to 194.6ppm with a mean of 112.9 ± 43.7ppm (Fig.4.33). Elevated concentrations of Cu in soils and sediments were recorded in samples from Abule Oja, Shomolu, Oto, Atan, Abule-Nla, Alimosho, Agege and Mushin areas. Copper (Cu) concentrations in Lagos dusts ranged from 20.0 - 655.5ppm and a mean of 142.54 ± 182.9ppm. Higher concentrations of Cu were recorded in samples collected along the high traffic density highways in Alimosho, Idi Oro and Mushin areas. Comparing the range of values in soils, sediments and dusts with the background values showed that they were significantly higher than the range of values observed in the background values. The enrichment ratios relative to the background values ranged from 1 - 39 folds (soils), 0 - 18 folds (sediments) and 4 - 70 folds (dusts) (Fig. 4.34).

Furthermore, Cu concentrations in Ibadan soils ranged from 15.0 - 172.0 ppm with a mean of (37.4 ± 34.53) ppm while in Ibadan sediments, its concentrations ranged from 49.7 to 688.5 ppm with a mean of (213.1 ± 193.3) ppm (Fig.4.33). Elevated concentrations of Cu were recorded in samples collected downstream of Rivers Ogunpa and Ogbere. These Rivers are known to drain the central and ancient district of Ibadan metropolis. These areas are characterised by high population density and metal scrap workshops, lot of black smith workshops and steel markets. Comparing the ranges and the average concentrations of Cu in both soils and sediments of Ibadan metropolis with the background values revealed they were of higher concentrations. The enrichment ratios of Cu in soils and sediments ranged from 1 - 7 and 1 - 27 folds respectively relative to the background value. The relative percentage contribution of Cu showed that about 65% and 95% of Cu in Ibadan soils and sediments respectively were derived from anthropogenic inputs (Figure 4.34).

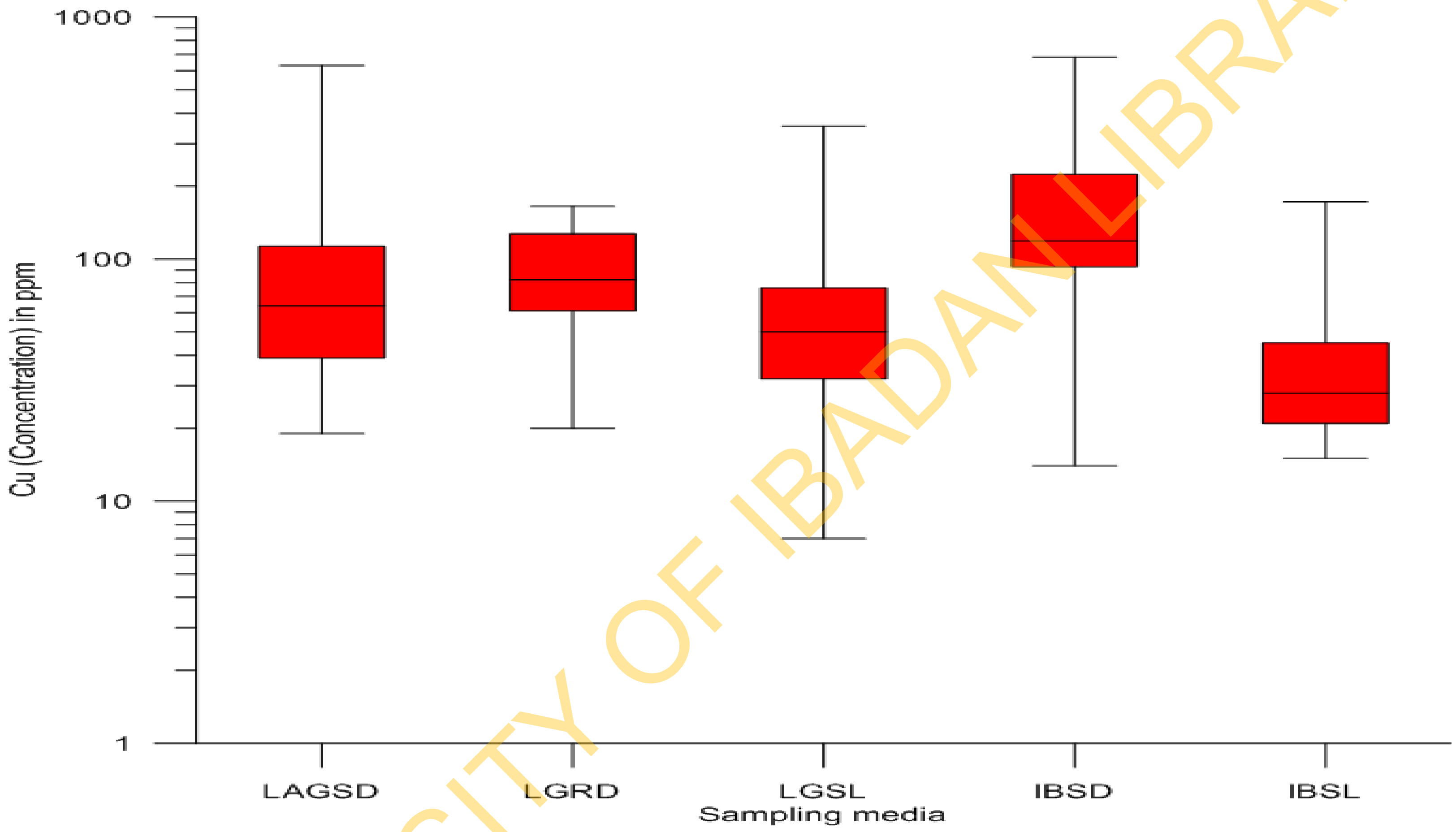


Figure 4.33. Cu Distributions in the Study areas

IBSL = Ibadan Soil, IBSD = Ibadan Sediments, LGSL = Lagos Soils, LGRD = Lagos Road dusts, LAGSD = Lagos Sediments

The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

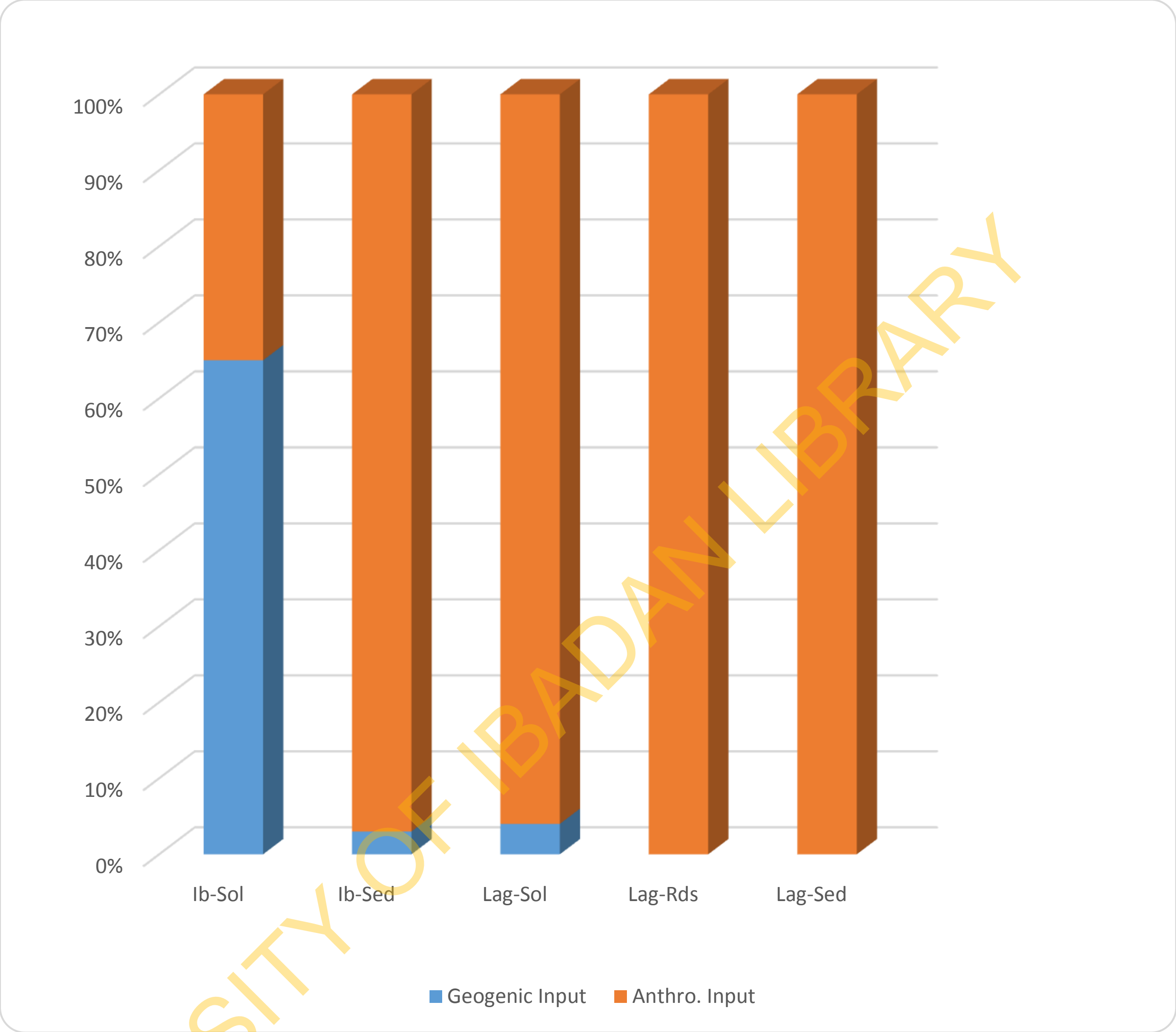


Figure. 4.34. Contributtions of Cu by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Rds = Lagos Road dusts, Lag-Sed = Lagos Sediments

4.5.4.4 Cadmium Abundance in Lagos and Ibadan metropolises

Cd concentrations in both the Lagos and Ibadan environments were in different range of values which are characteristic of urban soils and sediments. The concentrations in Lagos environments varied significantly depending on the medium. In Lagos soils, it ranged from 0.25 to 3.12 ppm with an average of (1.04 ± 0.56) ppm. Cd concentrations in Lagos sediments ranged from 0.20 to 2.48 ppm with an average of 0.89 ± 0.58 ppm while in dusts, it ranged from 0.23 - 11.62 ppm with an average of (3.4 ± 2.67) ppm (Fig. 4.35). Samples collected from Oko-Oba, Oyingbo, Alimosho and Agege areas showed elevated concentrations of Cd in soils while virtually all the dusts samples displayed higher concentrations compared to soil and sediment samples. The concentrations of Cd showed the following order of magnitude dusts > soils > sediments. Comparing Cd concentrations in these media in Lagos with the background values revealed enrichment ratios ranging from 22 to 312 folds and that almost 100 percent of Cd in these media were derived from anthropogenic inputs (Fig. 4.36).

Furthermore, the concentrations Cd in Ibadan soils ranged from 0.24 - 1.60 ppm with an average of (0.76 ± 0.45) ppm while in Ibadan sediments, the concentrations ranged from 0.13 to 2.68 ppm with an average of (0.73 ± 0.41) ppm (Fig.4.35). Elevated concentrations of Cd in river sediments of Ibadan were recorded in samples from Isale Afa, Adeoyo, Iso parts and Oje along Ogunpa and Ogbere Rivers. These areas are dominated by activities such as farming, metals scrappings, high trafficking e.tc which could have led to the release of Cd into the rivers sediments. The enrichment ratios of Cd in both soils and sediments to background values ranged from 8 to 53 and 4 to 89, respectively.

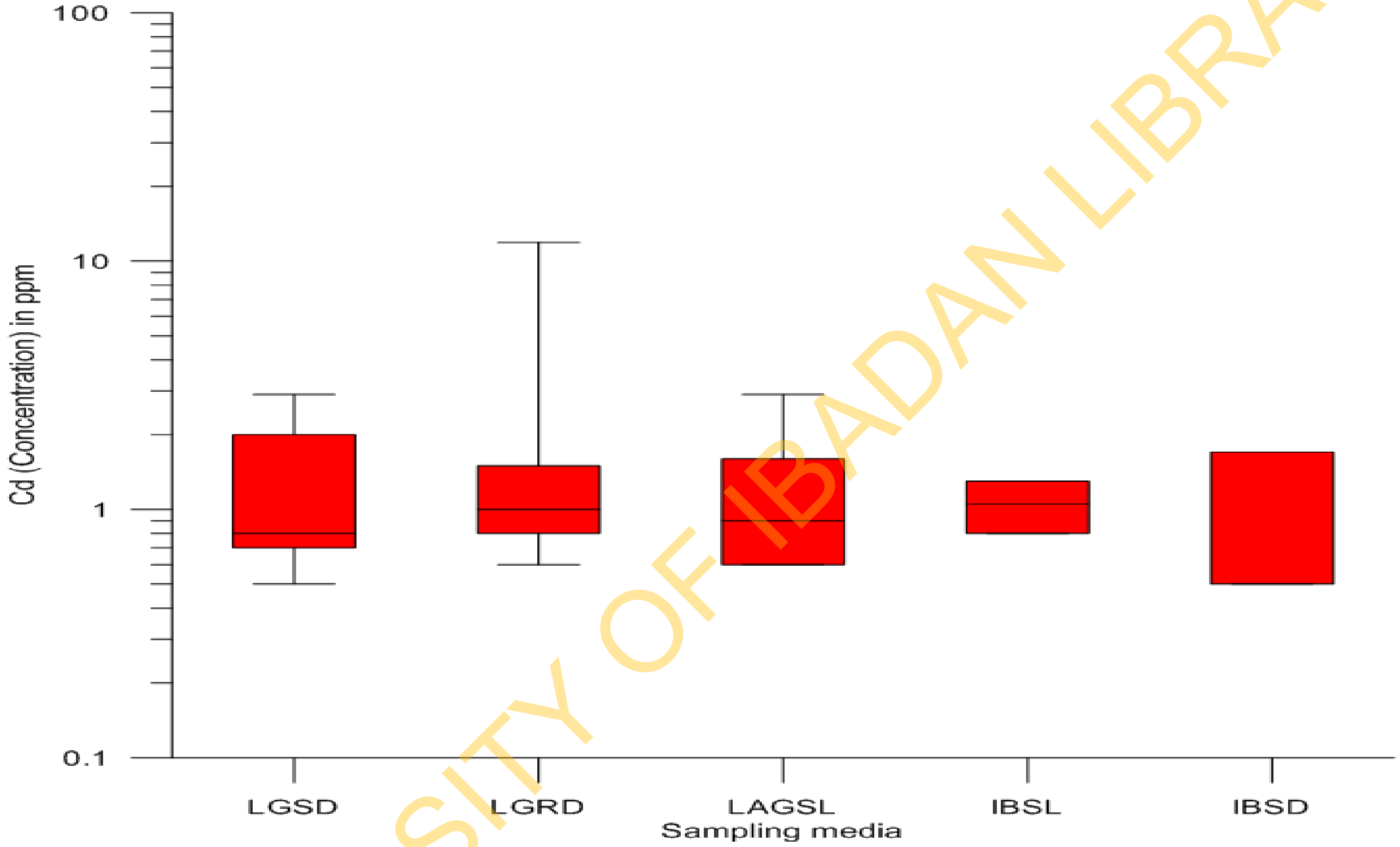


Figure 4.35. Variations of Cadmium concentrations in the Study areas

IBSL = Ibadan Soil, IBSD = Ibadan Sediments, LAGSL = Lagos Soils, LGRD = Lagos Road dusts, LGSD = Lagos Sediments

The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median; the whiskers extend to the Max and Min of the distribution.

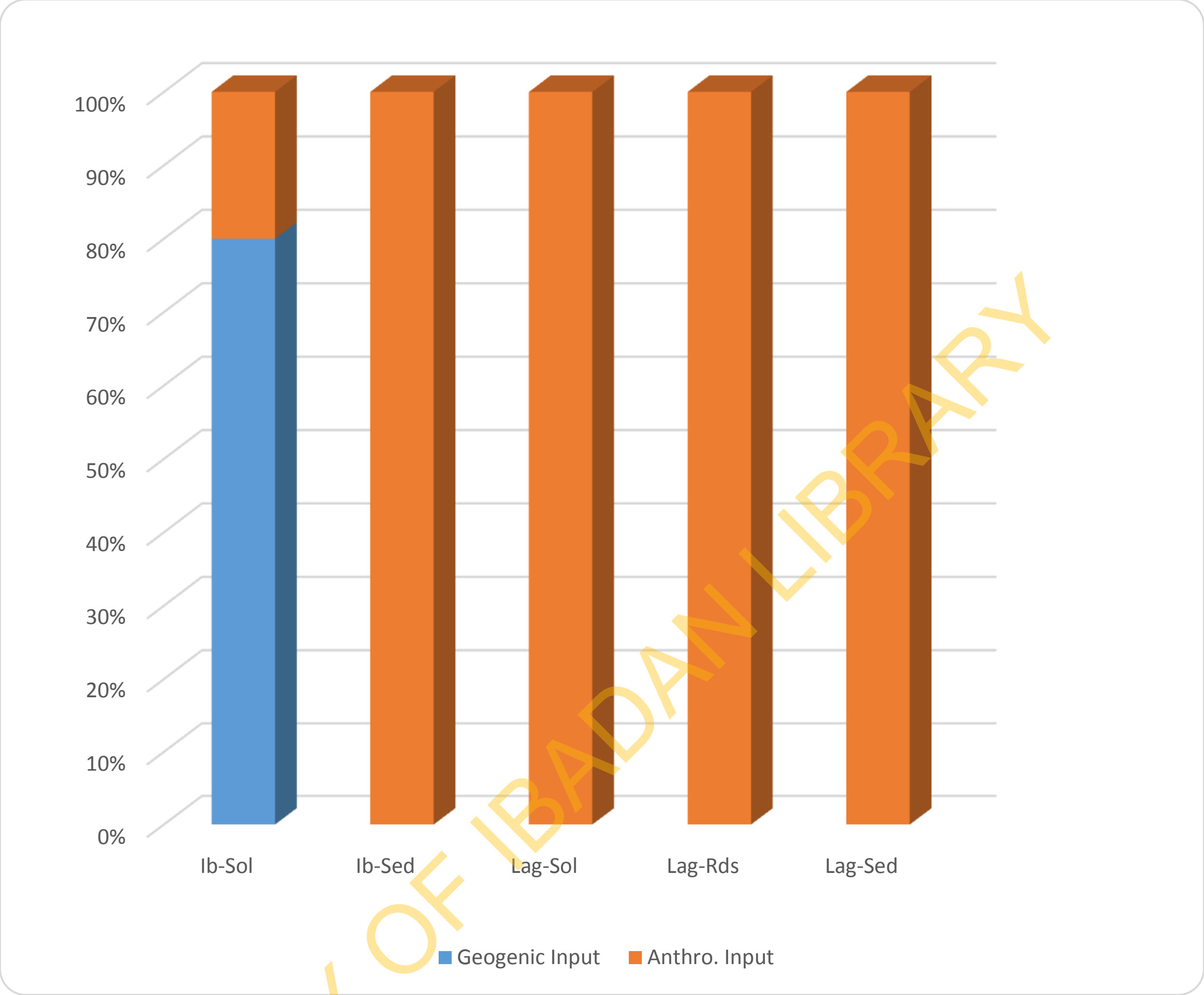


Figure 4.36. Contributtions of Cd by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Rds = Lagos Road dusts, Lag-Sed = Lagos Sediments

4.5.4.5 Arsenic Distributions in Lagos and Ibadan metropolises

As is a widely distributed metalloid in rocks, soils, sediments and particulate matters which is well known since the ancient times. Arsenic (As) concentrations in Lagos soils ranged from 0.01 to 14.1 ppm with an average concentration of (3.92 ± 2.54) ppm. In Lagos sediments, its concentrations ranged from 0.2 to 10.2 ppm with an average concentration of 3.7 ± 2.24 ppm while in dust samples, Arsenic concentrations ranged from 0.2 – 7.6 ppm with an average concentration of (4.1 ± 2.78) ppm (Fig. 4.37). Most samples collected around Abule-Nla, Apapa, Onipanu and from northern parts of Ebute-Metta, Yaba and some parts of Alimosho areas of Lagos metropolis recorded elevated concentrations of Arsenic when compared to other parts of the metropolis. Comparing these ranges of concentrations with the range of background values of 2.0 - 8.5 ppm (5.45 ppm) indicated that most of the datasets were within the local background values. The enrichment/depletion ratios of Arsenic in Lagos environments ranged from 0 to 2 folds of the background values.

However, Arsenic is a potentially toxic metal and may be of health implications if accumulated in large quantities in the tissues and cells of any animal and/or man. Arsenic (As) concentrations in Ibadan sediments ranged from 0.6 - 19.0ppm while in soils, its concentrations ranged from 1.4 - 4.16ppm with mean concentrations of (4.5 ± 4.55) ppm and (2.4 ± 1.34) ppm respectively (Fig. 4.37). These values were higher than the background value of 0.3 ppm. Elevated concentrations of Arsenic in Ibadan sediments were recorded in most of the samples collected along Rivers Ogunpa and Ogbere while soils collected from Bodija, Ojurin and Felele areas showed elevated concentrations of Arsenic when compared to other areas of Ibadan metropolis. The enrichment ratios of Arsenic in both Ibadan sediments and soils ranged from 1 to 27 and 2 to 11 folds of the background values while the contributing factors showed that 90% of As in sediments and 20% of As in soils were derived from anthropogenic activities (Fig.4.38).

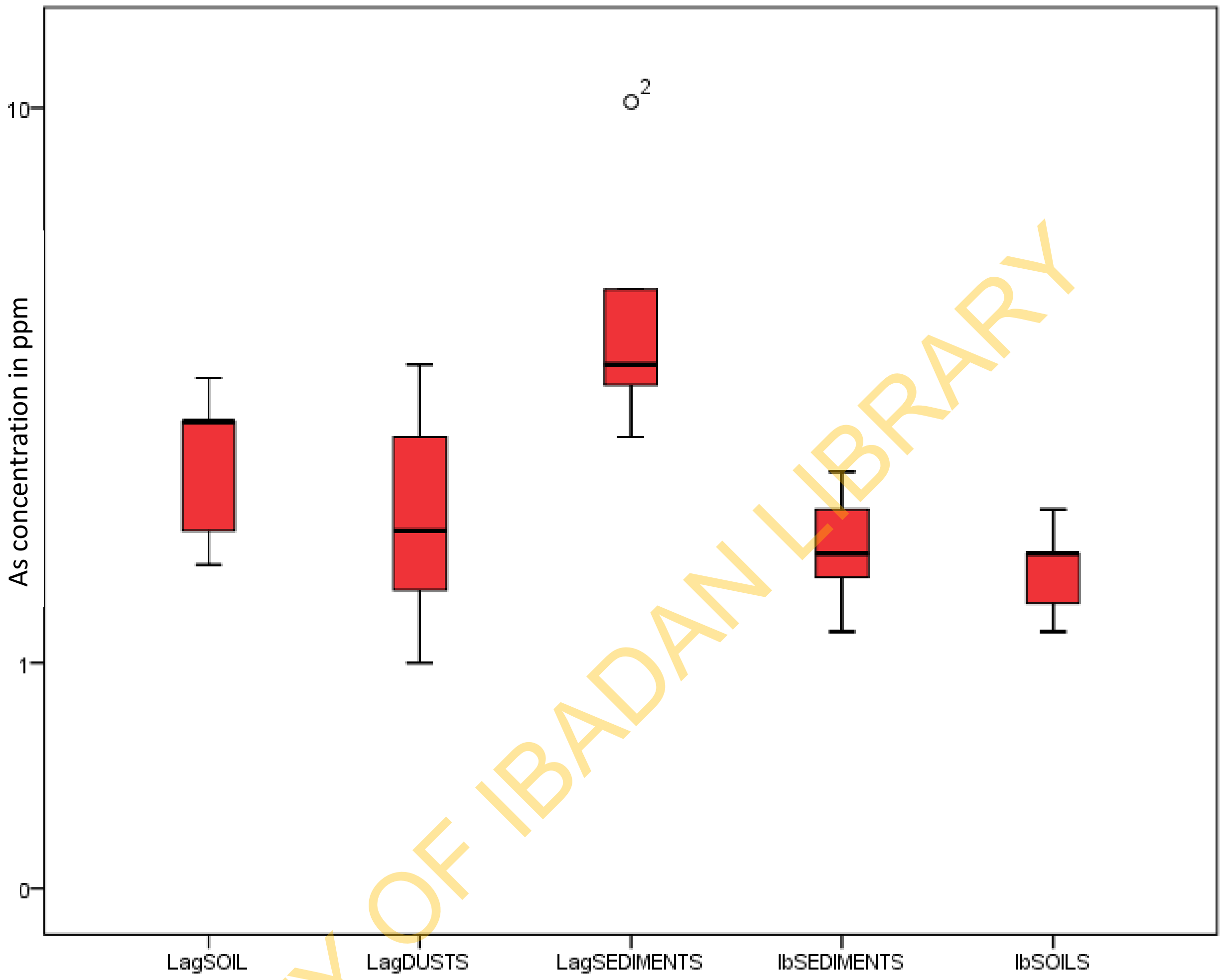


Figure 4.37. Variations of As in the Study areas

IbSOILS = Ibadan Soil, IbSEDMENTS = Ibadan Sediments, LagSOIL = Lagos Soils, LagDUSTS = Lagos Road dusts, LagSEDIMENTS = Lagos Sediments

The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median; the whiskers extend to the Max and Min of the distribution.

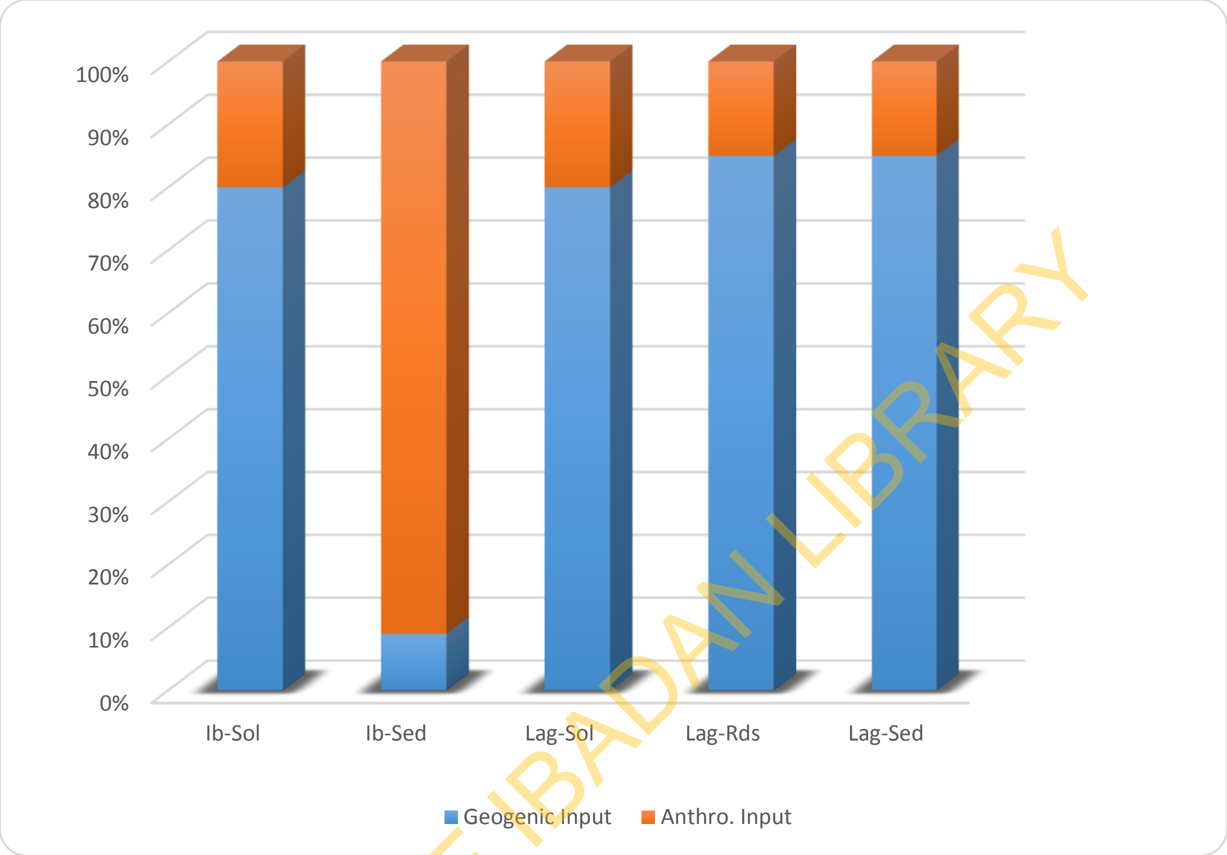


Figure 4.38. Contributtions of As by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Rds = Lagos Road dusts, Lag-Sed = Lagos Sediments

4.5.4.6 Manganese Distributions in Lagos and Ibadan metropolises

The concentrations of Mn in Lagos media varied significantly from what was recorded in Ibadan. The concentrations of Mn in Lagos soils ranged from 88.0 to 1253 ppm with a mean of (428.3 ± 252.2) ppm. In drainage sediments of Lagos, it ranged from 256.0 to 985.0 ppm with a mean of (489.33 ± 230.7) ppm while Lagos dusts, Mn concentrations ranged from 130 – 693 ppm with an average of (333.0 ± 136.03) ppm. These ranges of concentrations when compared with the background values were found to be higherand enriched relative to the background values with the enrichment ratios ranging from 2 to 26 folds.

Similarly, the concentrations of Mn in Ibadan soils ranged from 440 – 1553 ppm with a mean of (981.2 ± 324.58) ppm while its concentrations in sediments ranged from 467 – 4945 ppm with a mean value of (1188.35 ± 881.9) ppm in Lagos and Ibadan respectively (Fig. 4. 39). The enrichment-depletion ratios of Mn in Ibadan environs over the background value ranged from 2 - 8-folds and 3 - 26-folds in soils and sediments respectively (Fig.4.40). High and elevated concentrations of Mn were recorded in Ibadan soils and sediments when compared to the concentrations recorded in Lagos media. Hence the relative order of magnitudes of Mn concentrations in Lagos environs is as followed, soil > sediments > dusts while sediments > soil in Ibadan environs.

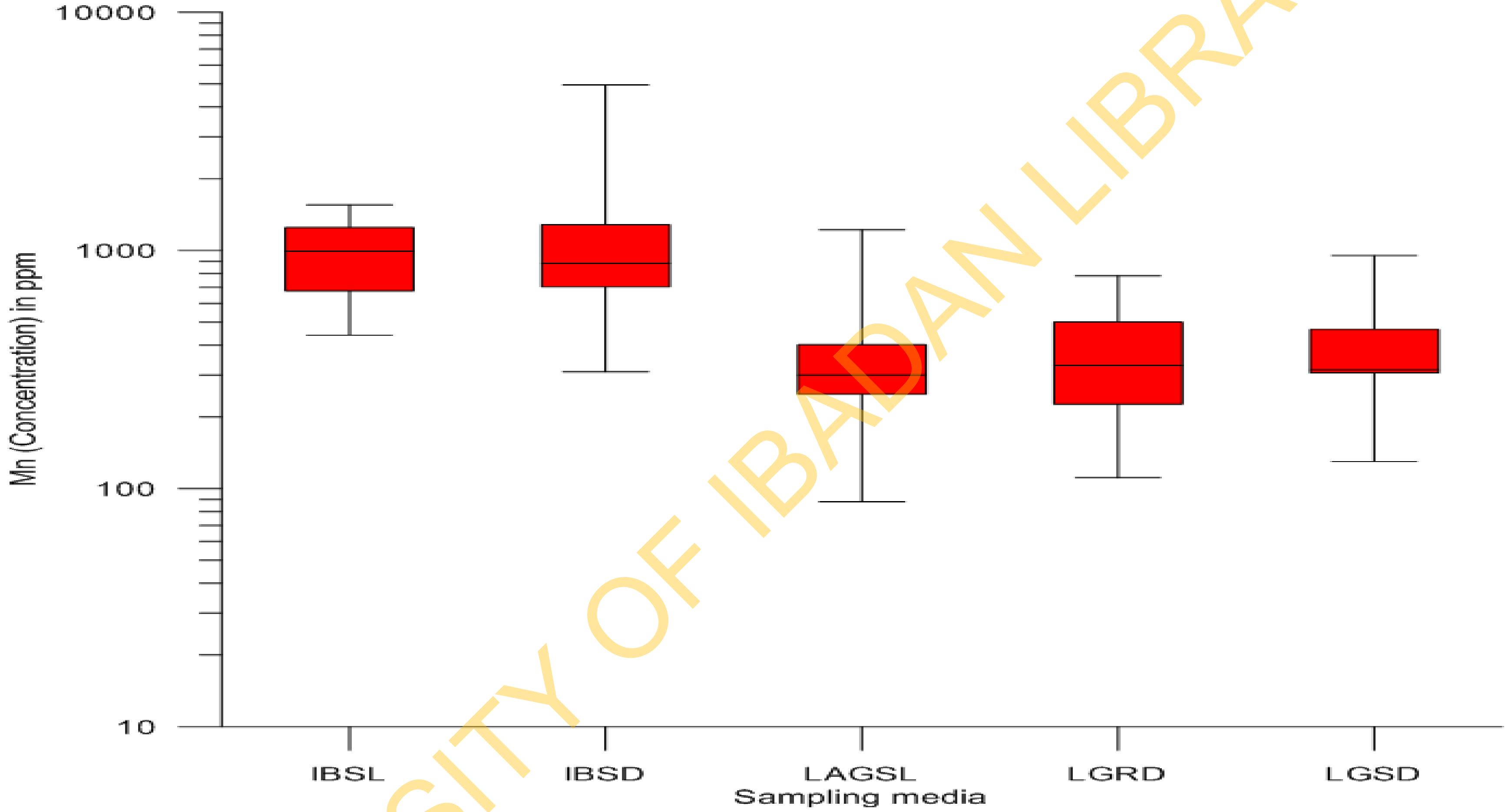


Figure 4.39. Variations of Mn in the Study areas

IBSL = Ibadan Soil, IBSD = Ibadan Sediments, LAGSL = Lagos Soils, LGRD = Lagos Road dusts, LGSD = Lagos Sediments

The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median; the whiskers extend to the Max and Min of the distribution.

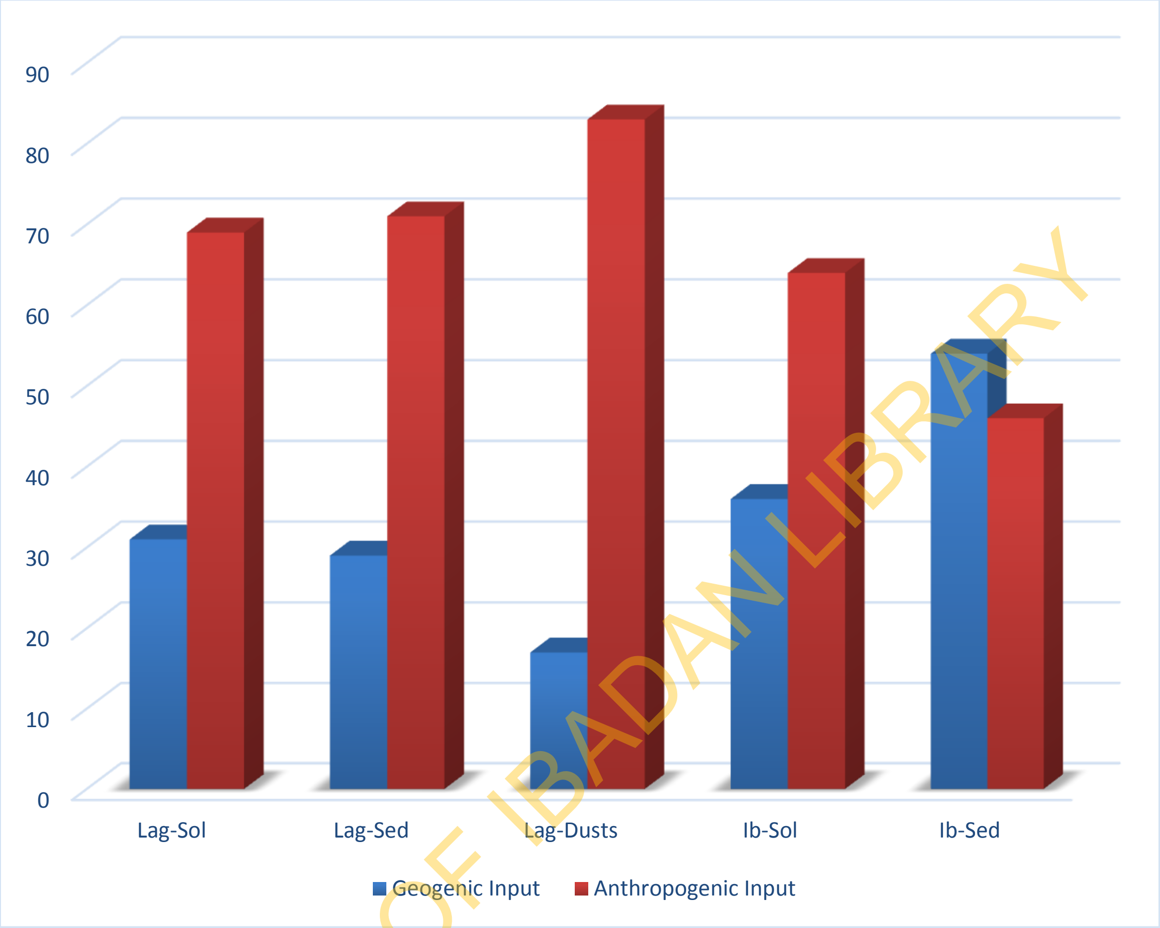


Figure 4.40. Contributions of Mn by Anthropogenic and Geogenic activities

Ib-Sol = Ibadan Soil, Ib-Sed = Ibadan Sediments, Lag-Sol = Lagos Soils, Lag-Dusts = Lagos Road dusts, Lag-Sed = Lagos Sediments

4.6 Spatial Distribution Maps of selected PHMs in soils, sediments and dusts

The results of geochemical analysis of some selected PHMs were used in production of geochemical maps using Arc view GIS (Figs. 4.41 - 4.53). The spatial distribution maps revealed that elevated concentrations of these metals were found in areas with intense human activities such as industries, metals and mechanic workshops, markets, waste dump sites, high traffic density, wetlands for agricultural farming and metal scrap-courts. Similarly, sediments collected from down-streams showed elevated concentrations of heavy metals in both study areas.

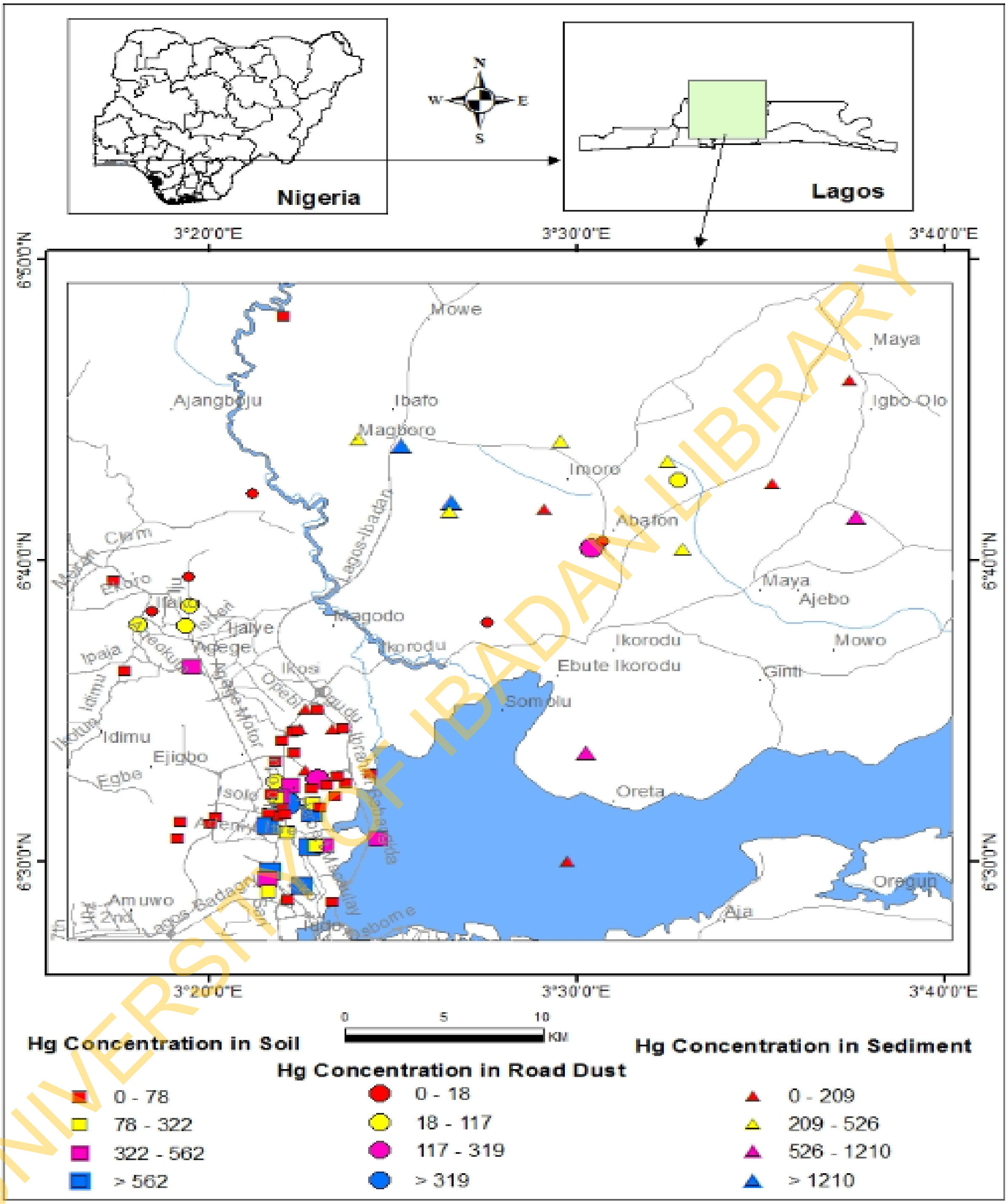


Figure 4.41. Spatial distributions of Hg in the Lagos environmental media

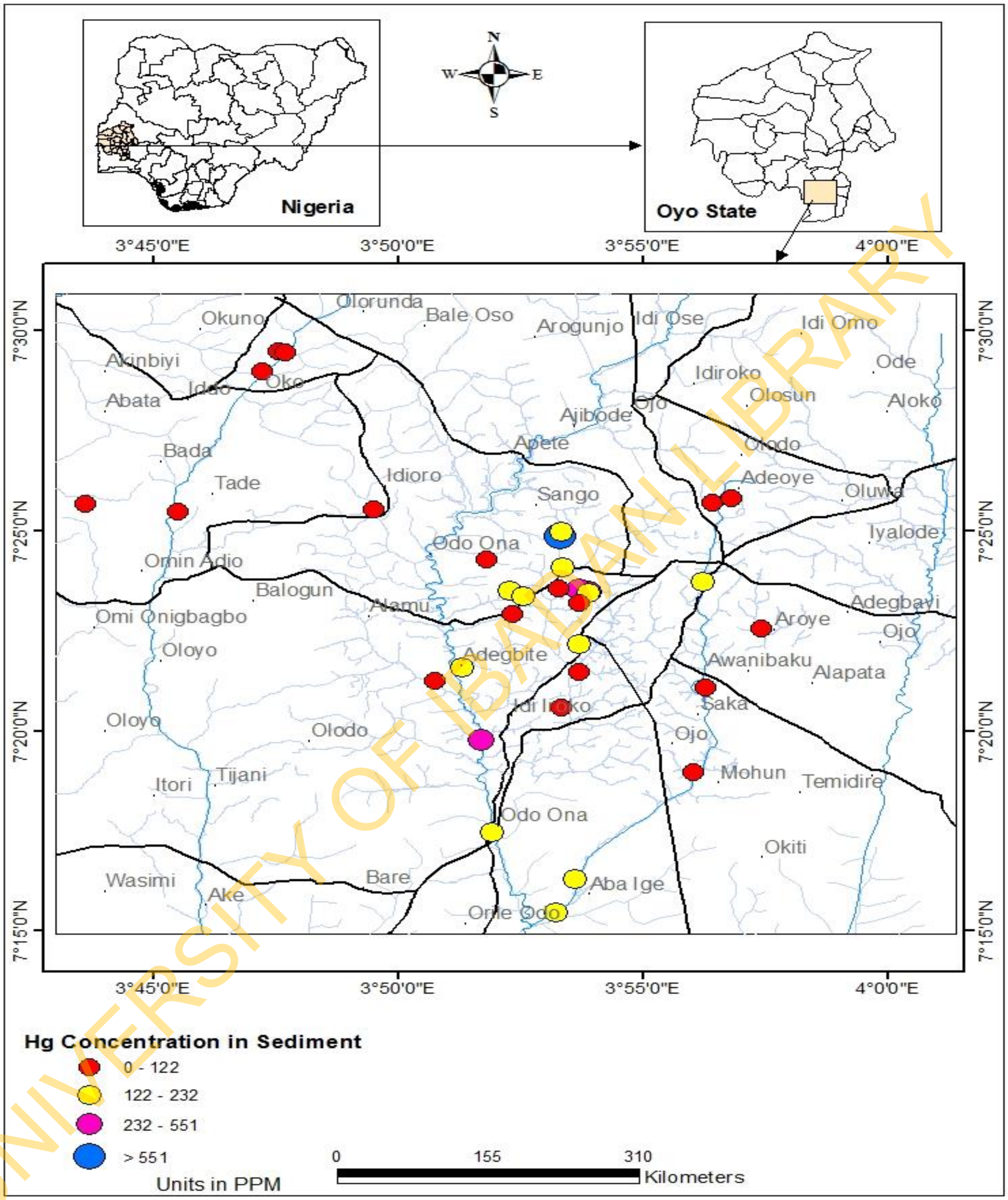


Figure 4.42. Spatial distributions of Hg in the Ibadan media

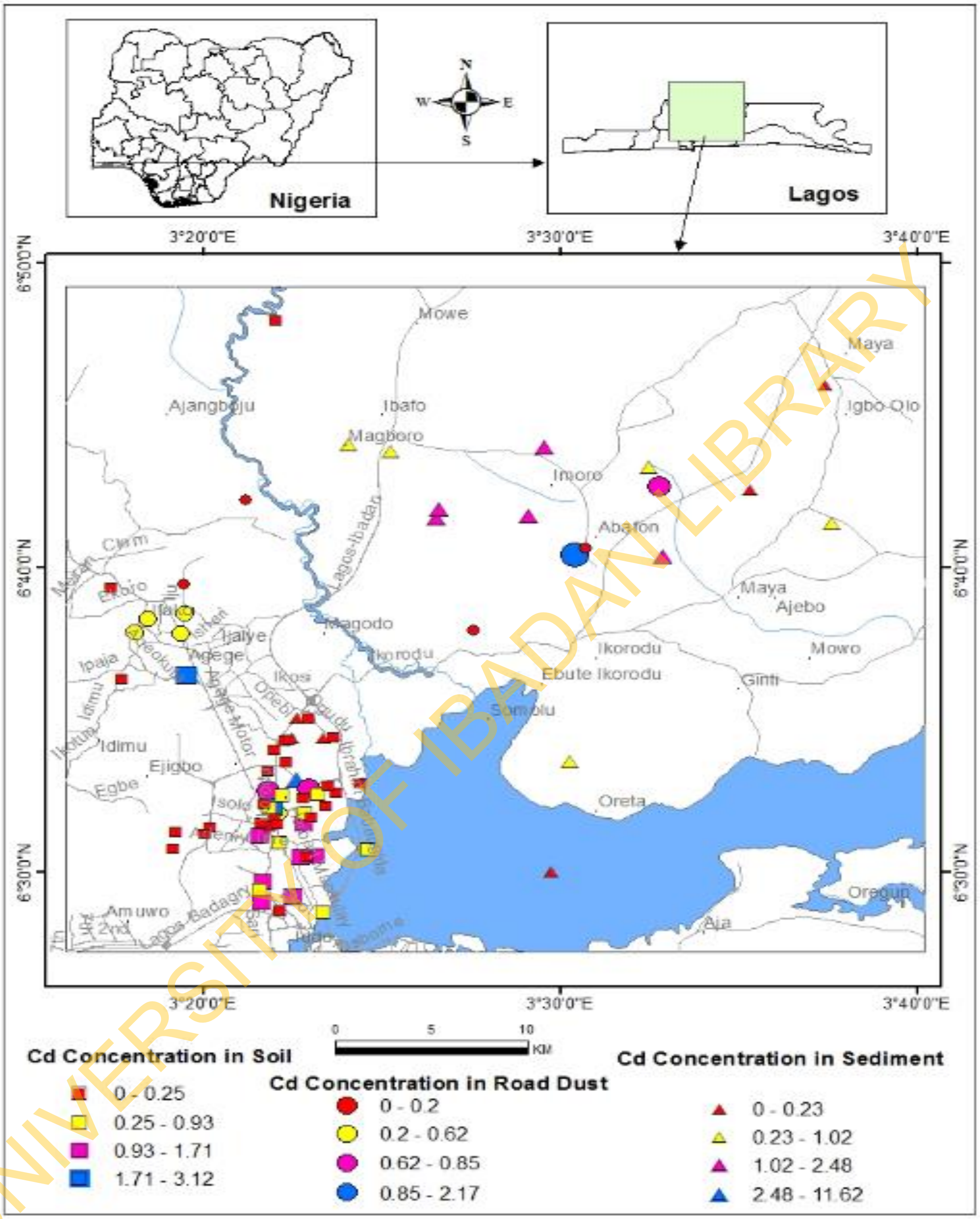


Figure 4.43. Spatial distributions of Cd in the Lagos environmental media

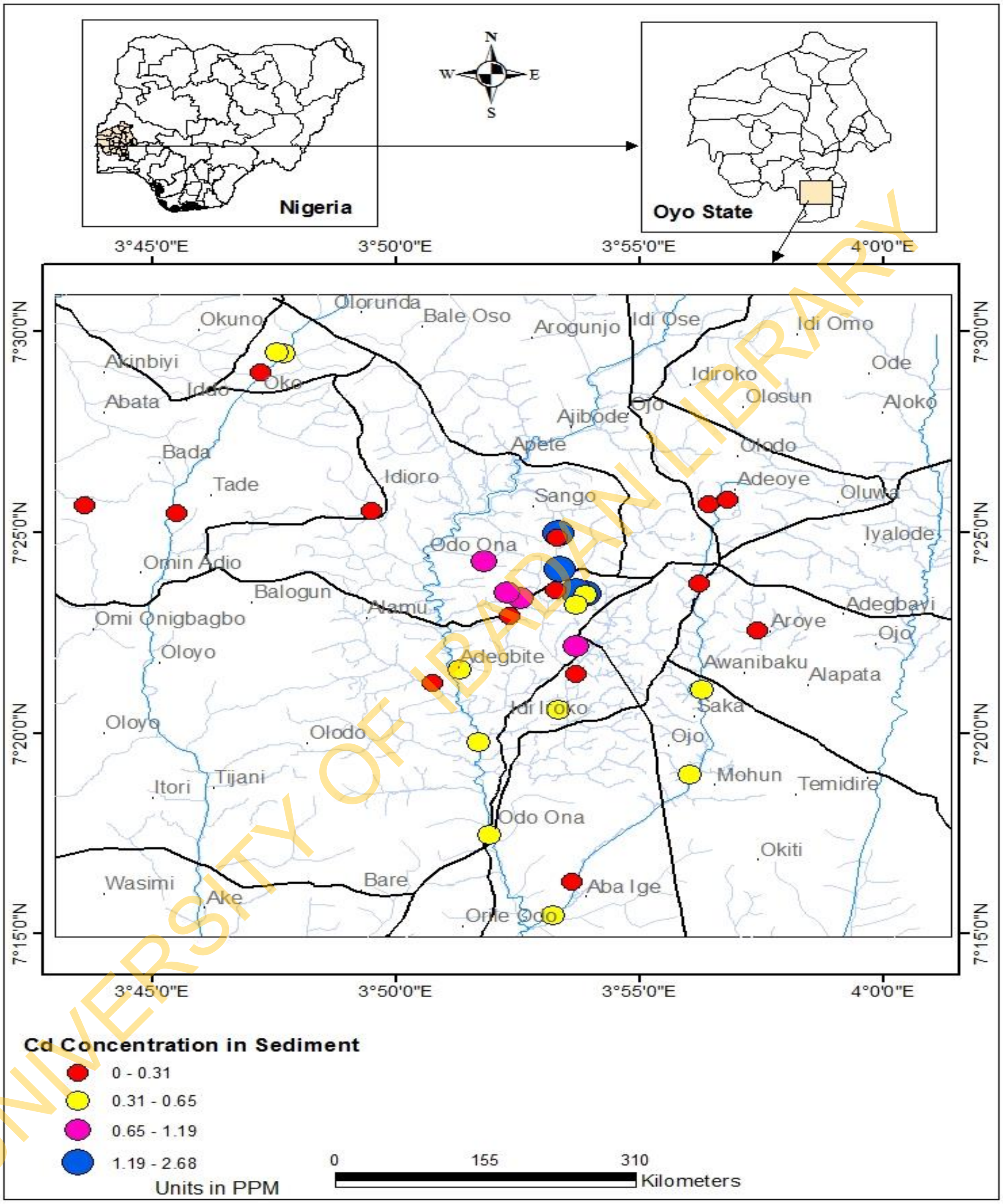


Figure 4.44. Spatial distributions of Cd in the Ibadan media

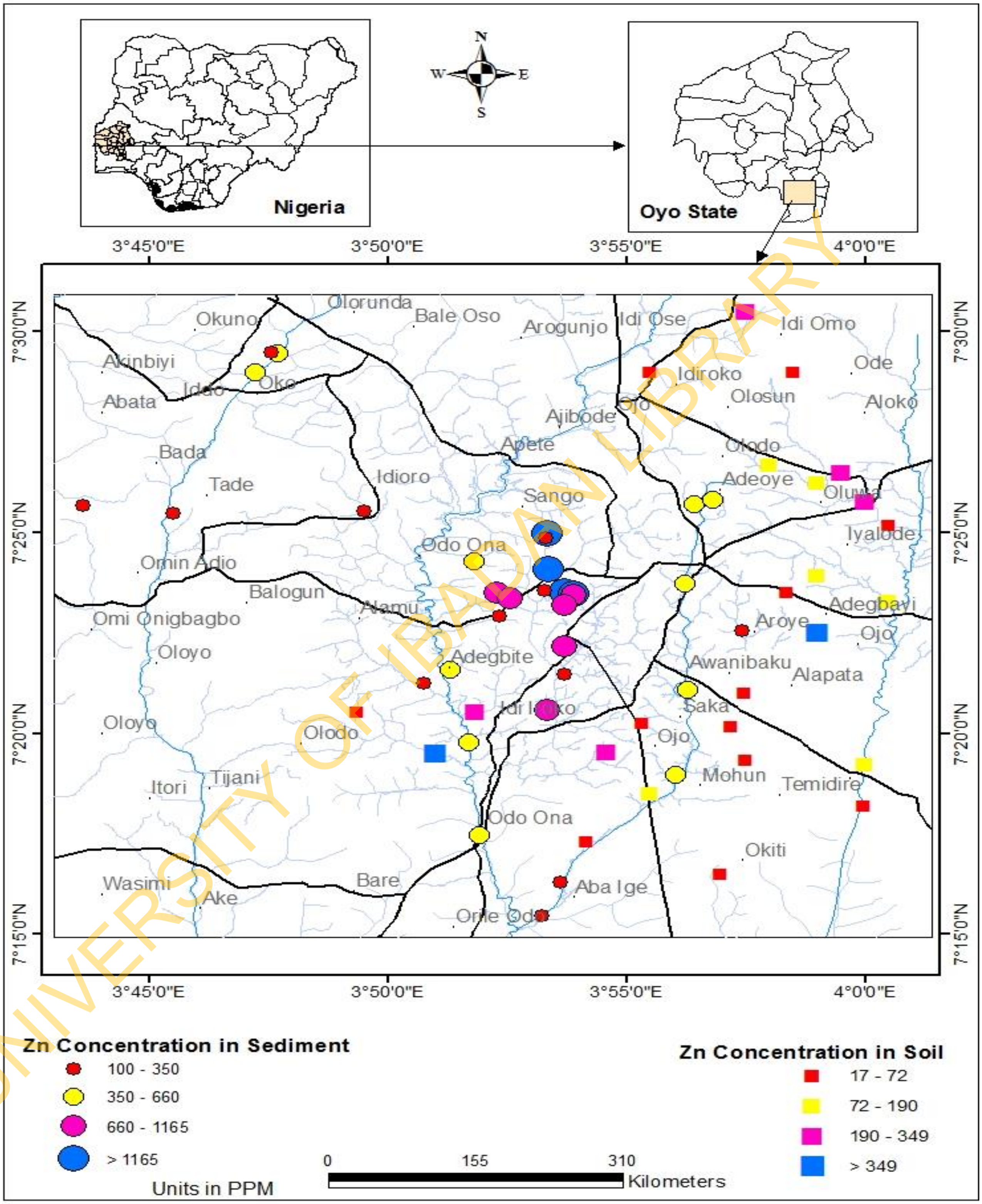


Figure 4.45. Spatial distributions of Zn in the Ibadan media

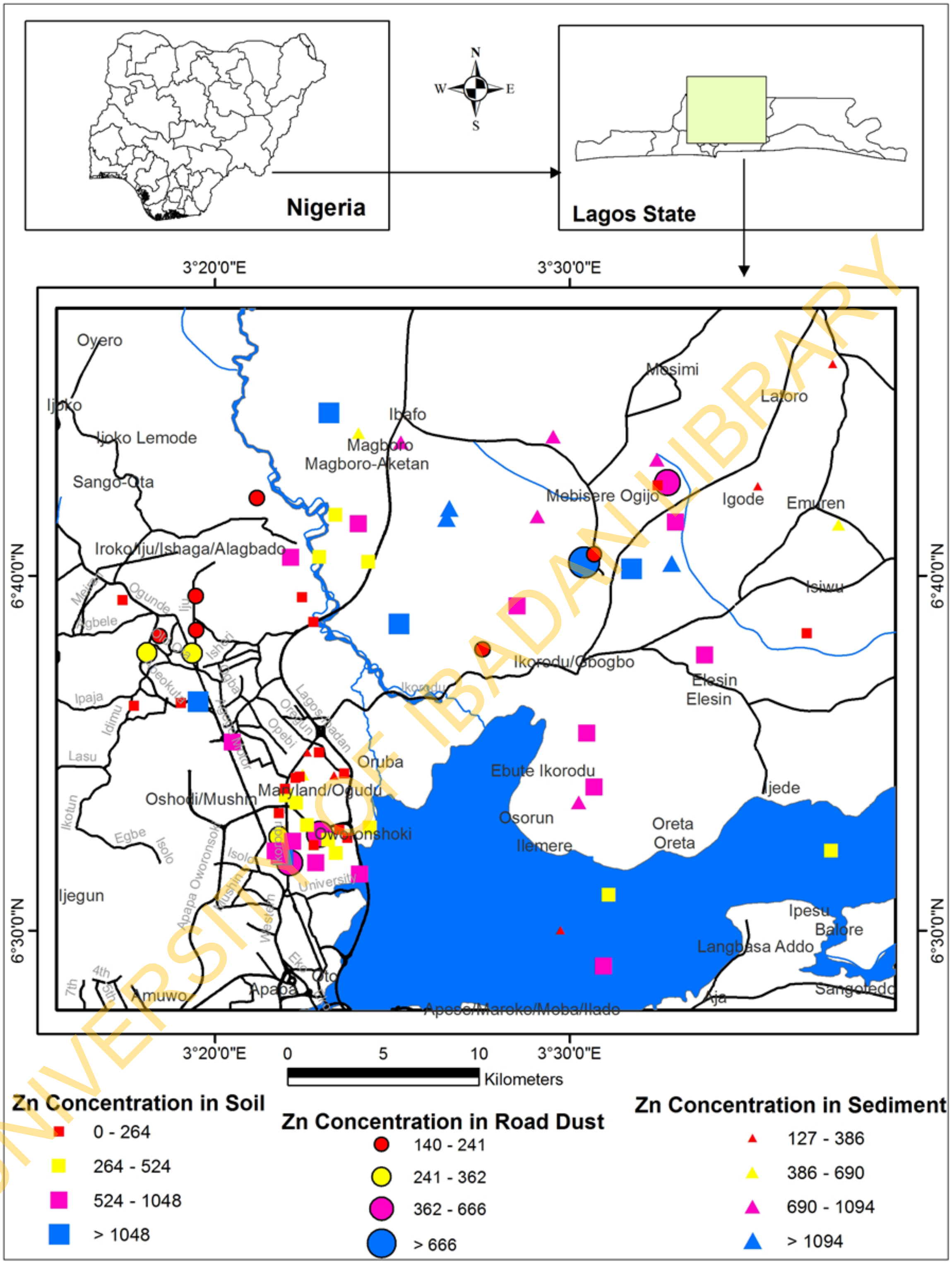


Figure 4.46. Spatial distributions of Zn in the Lagos environmental media

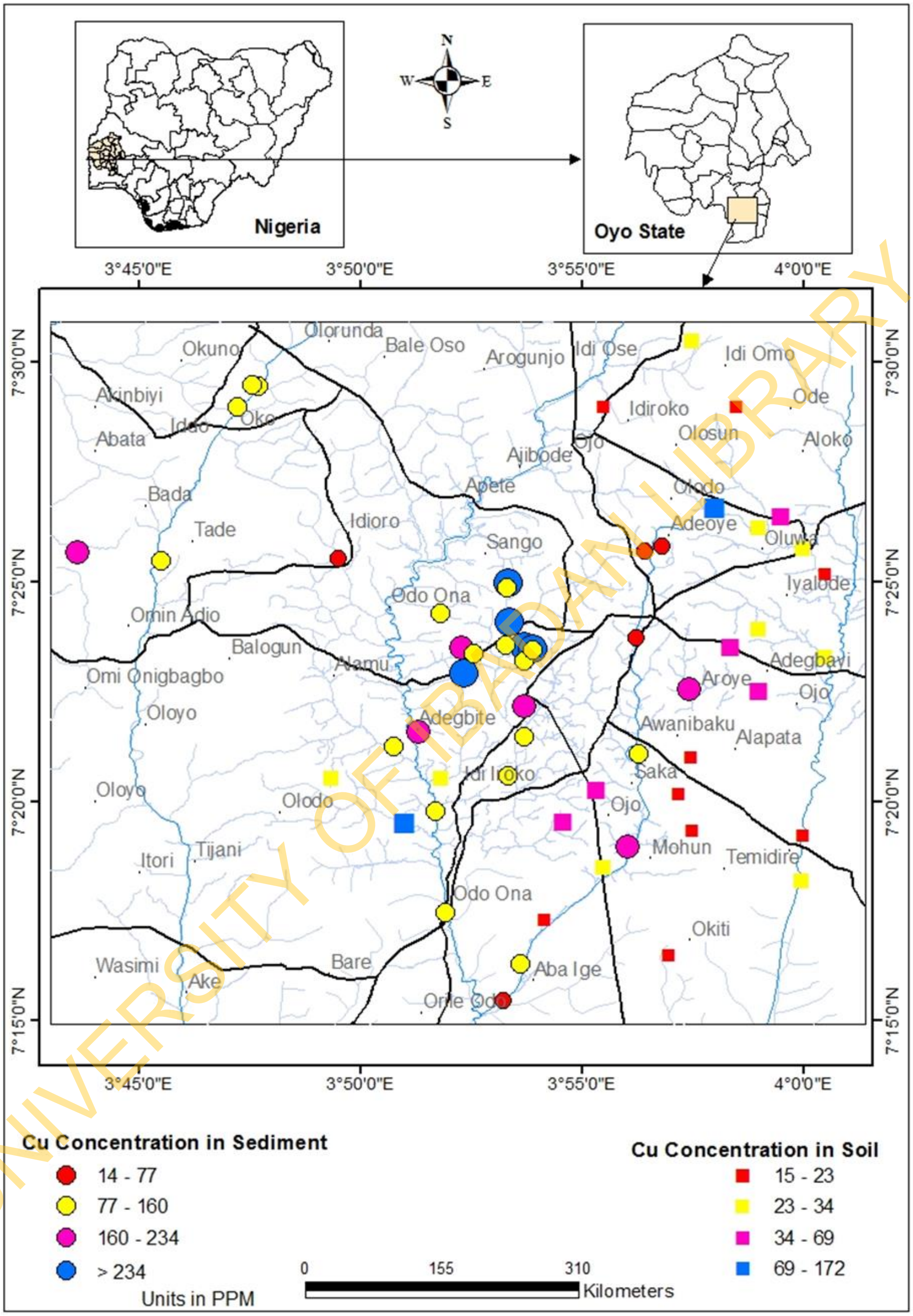


Figure 4.47. Spatial distributions of Cu in the Ibadan media

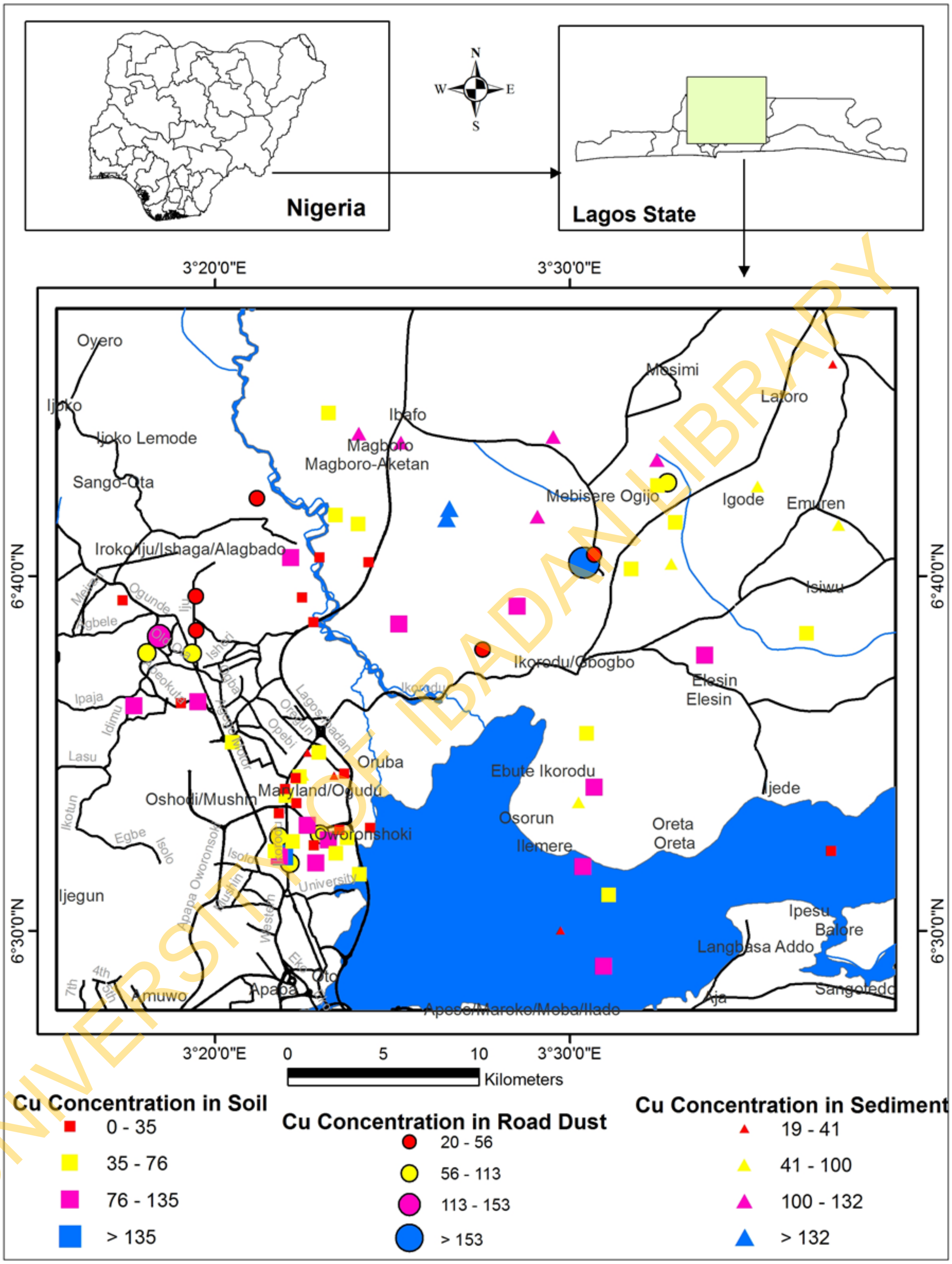


Figure 4.48. Spatial distributions of Cu in the Lagos media

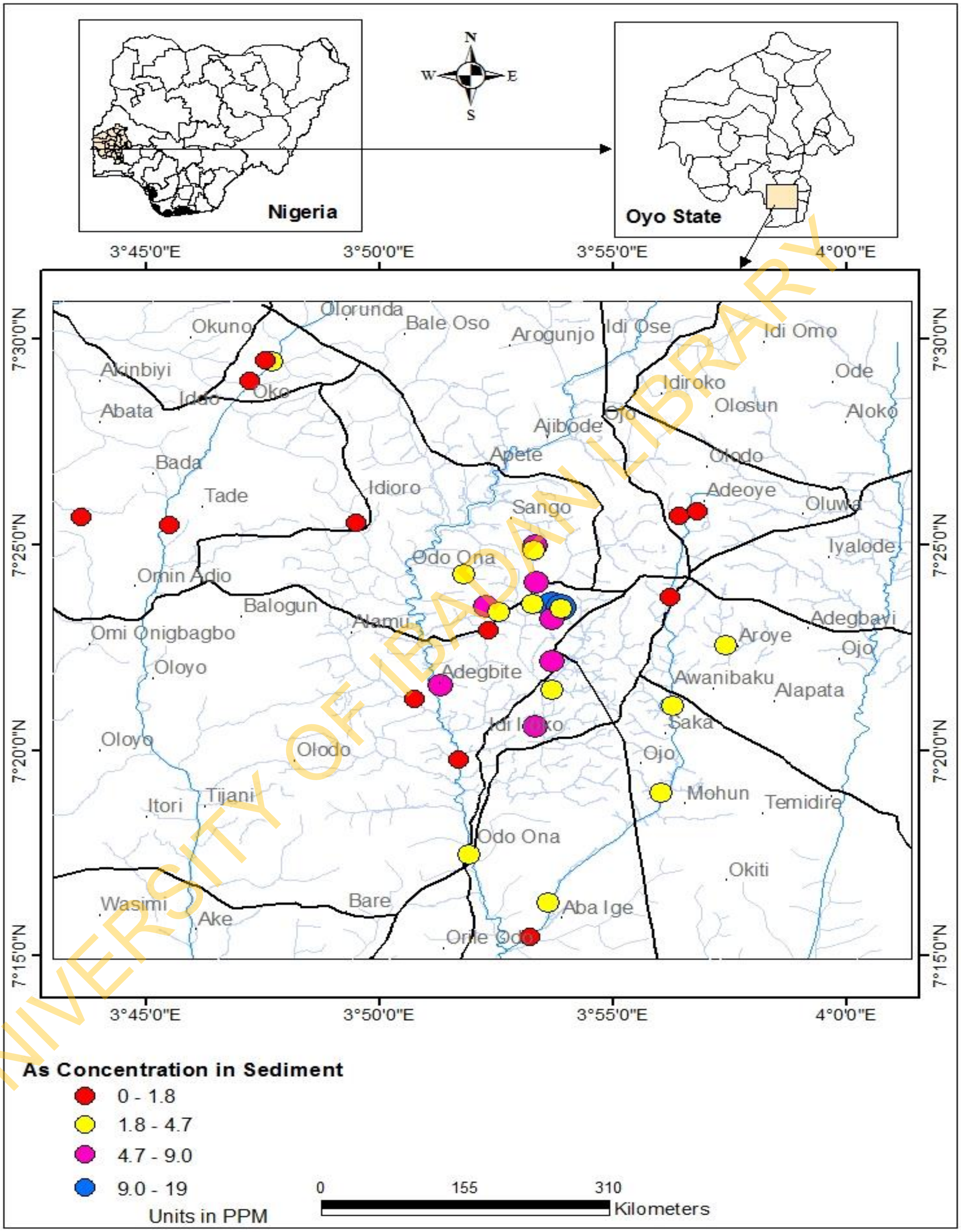


Figure 4.49. Spatial distributions of As in the Ibadan media

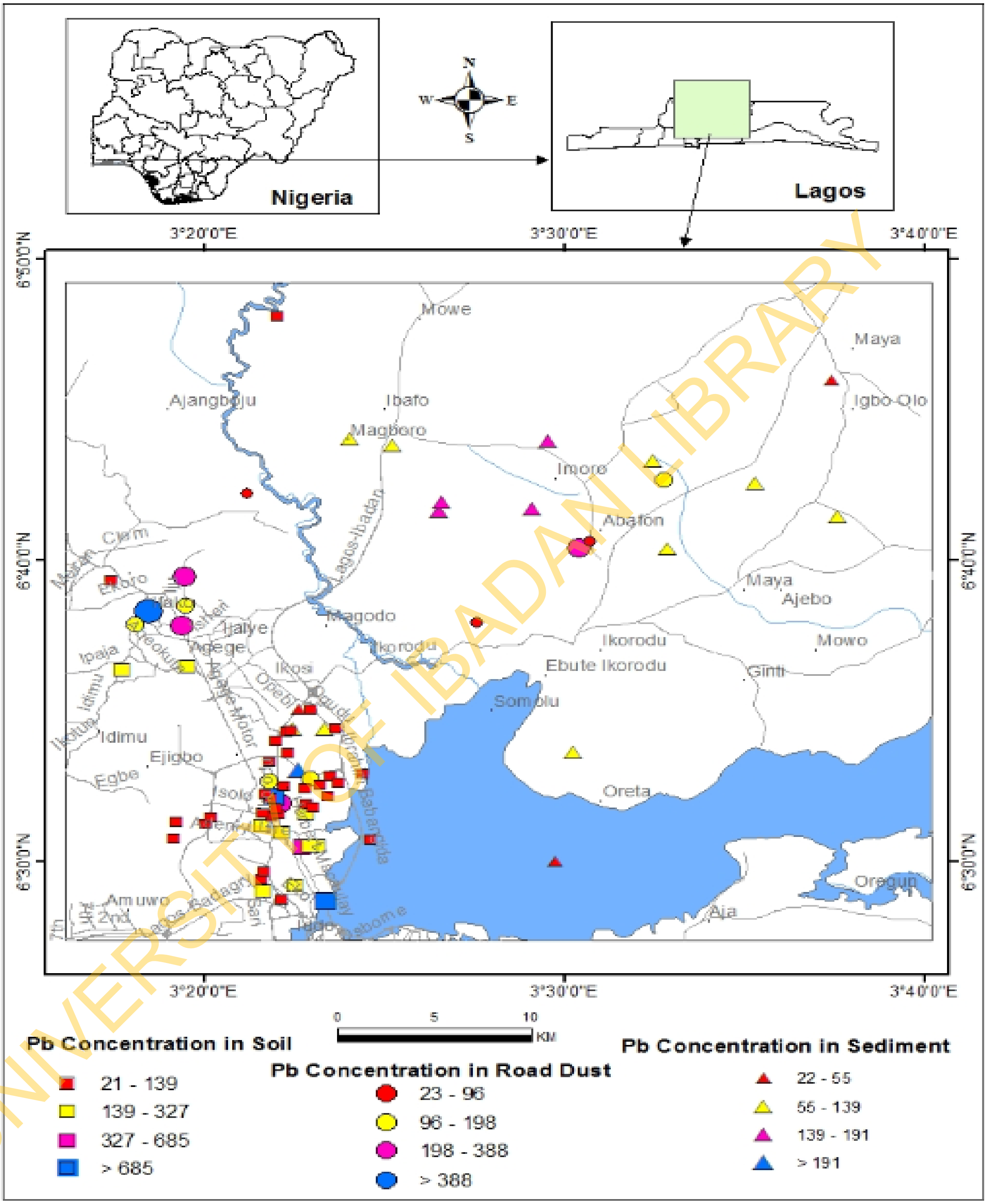


Figure 4.50. Spatial distributions of Pb in the Lagos environmental media

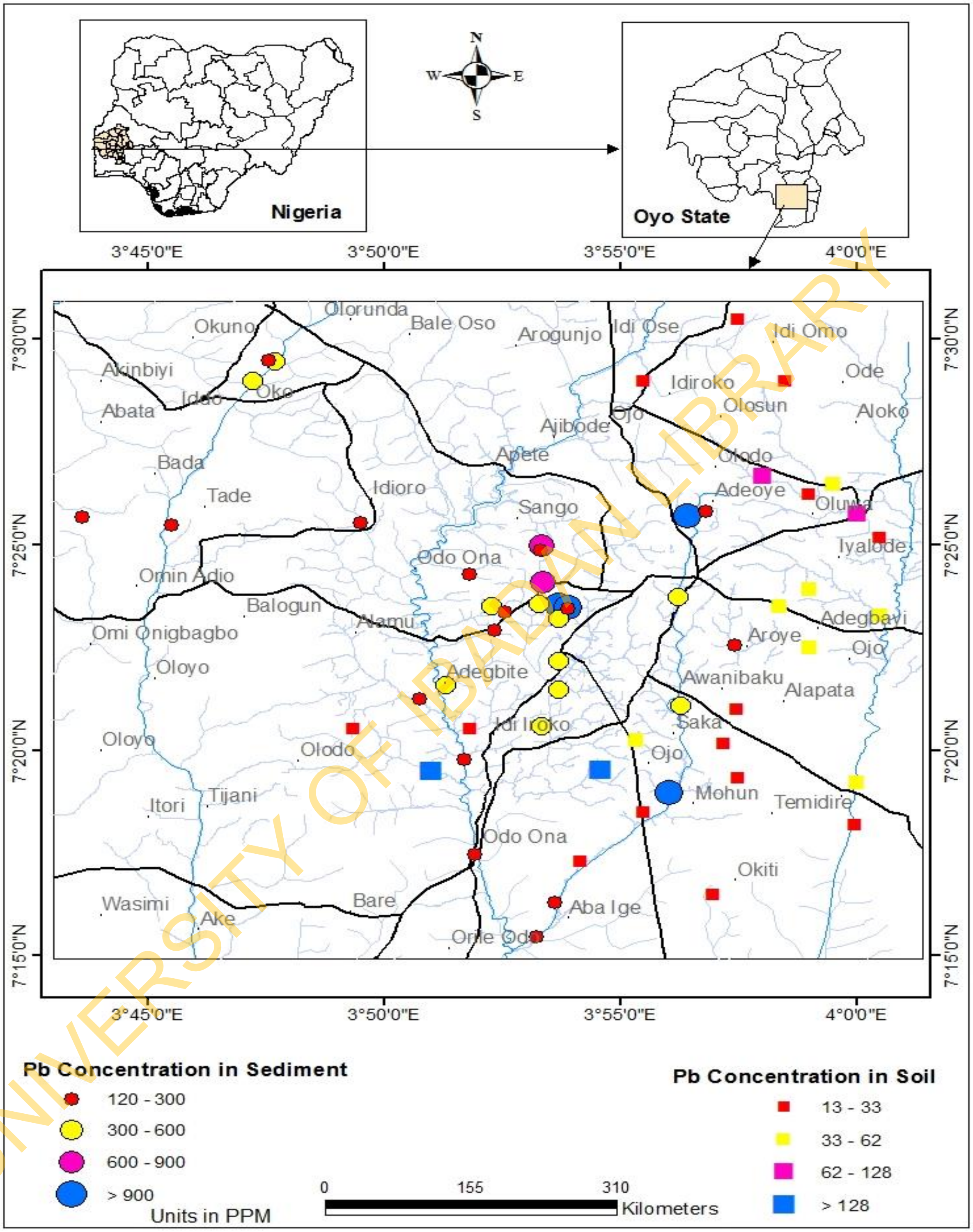


Figure 4.51. Spatial distributions of Pb in the Ibadan environmental media

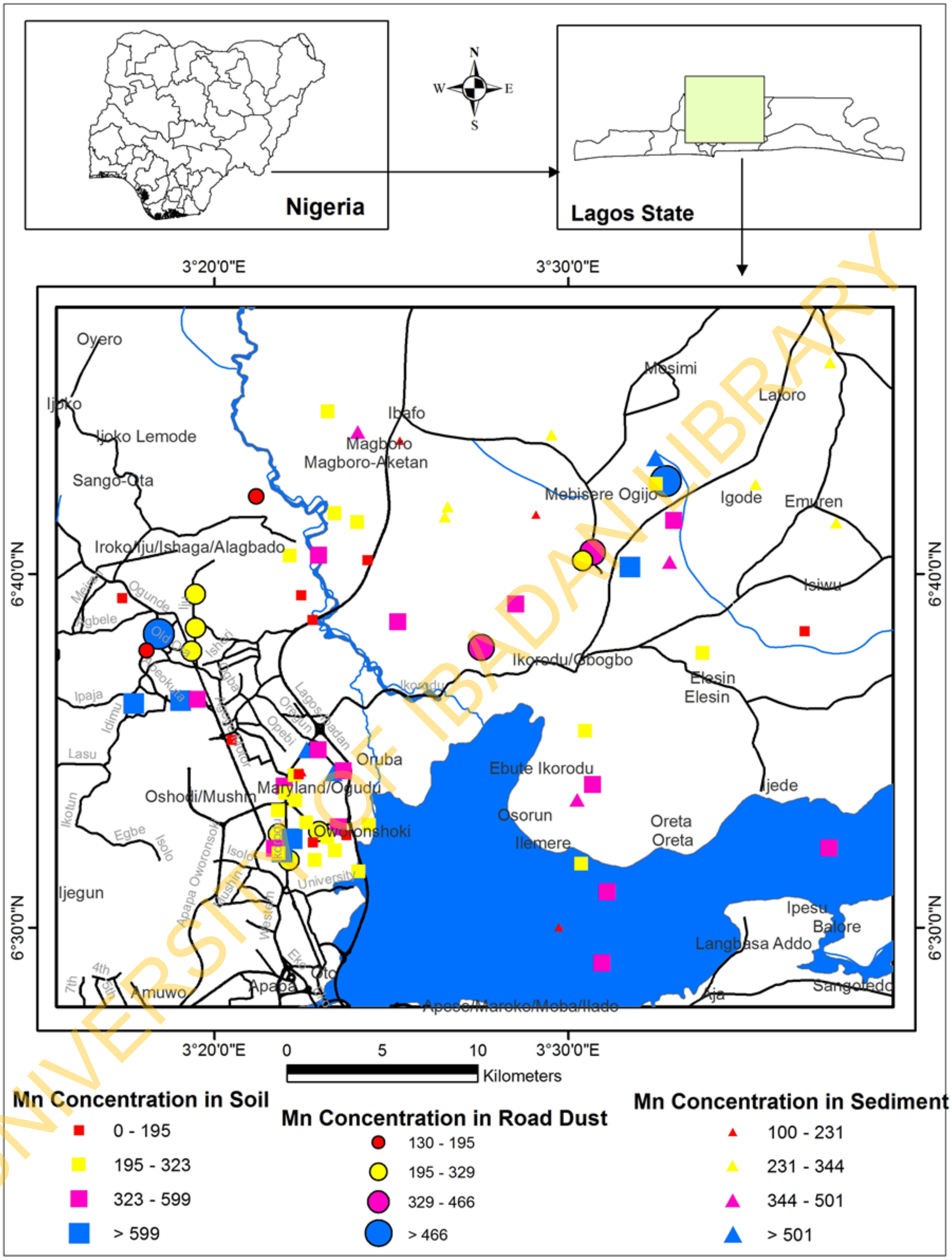


Figure 4.52. Spatial distributions of Mn in the Lagos media

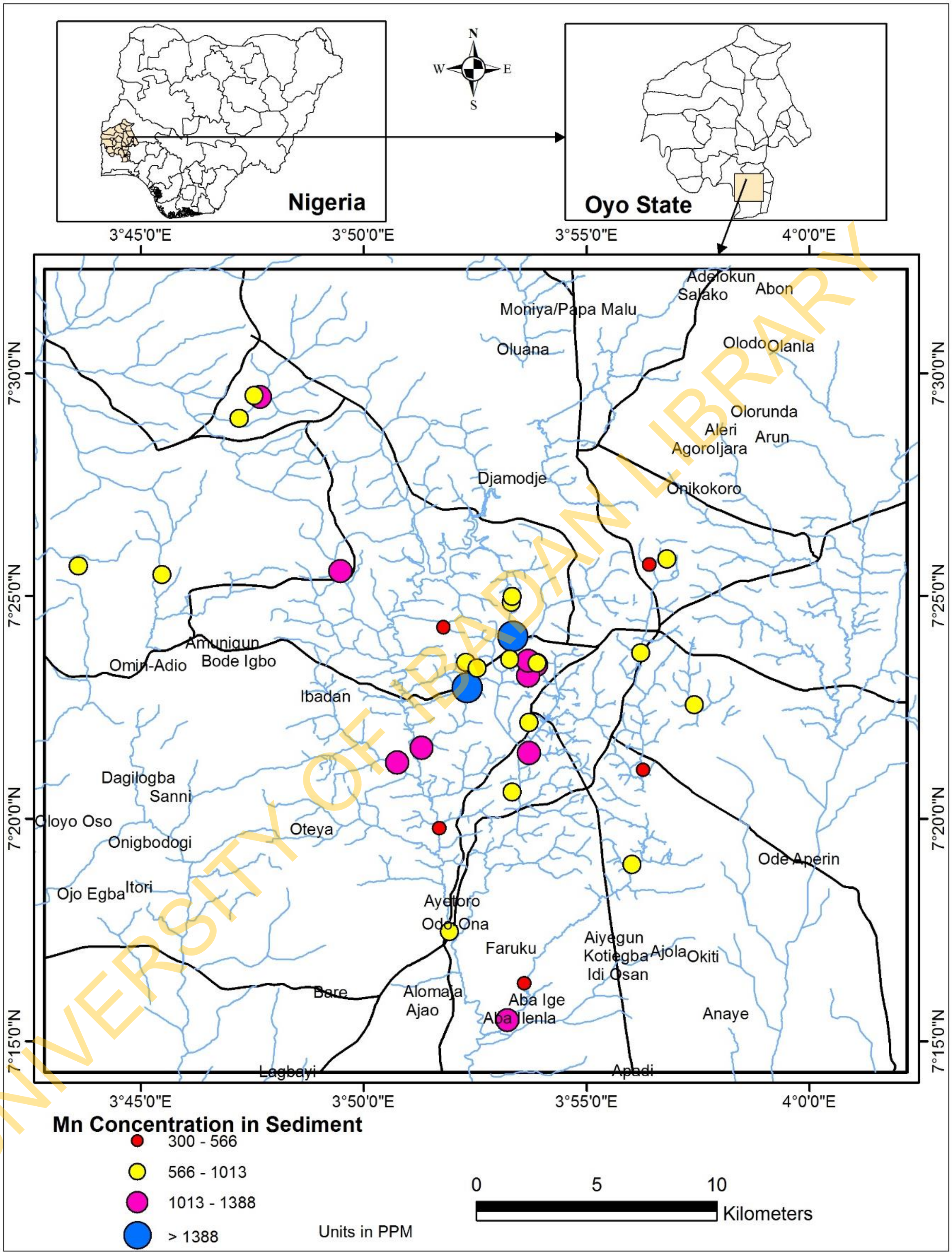


Figure 4.53. Spatial distributions of Mn in the Ibadan media

4.7 Elemental Associations in Lagos Metropolis

The results of chemical analysis of Lagos soils, stream sediments and road dusts were subjected to bivariate analysis using Pearson correlation. R-mode factor analysis was also carried out to reduce the complexity and dimensionality of data sets and also to reveal the underlying factors responsible for the observed variations in the sediments, soils and roadside soils (Reimann et al., 2000). An attempt was made to relate these factors to the actual processes influencing the geochemistry of these media.

4.7.1. Elemental Associations in Lagos Road dusts

4.7.1.1 Correlation Analysis

It was observed that some of the metals showed some levels of relationship (either positive or negative) with one another with the correlation coefficient (r) ranging from 0.98 to 0.50 at 0.01 confidence level (Table 4.11). A significant positive correlation at 0.01 confidence level was observed among these pairs of metals: Pb-Zn (r = 0.69), Pb-Cr (r = 0.73), Pb-Cu (r = 0.35), Zn-Cr (r = 0.53) and Cr-Cu (r = 0.20). Zinc showed very strong positive relationship with metals such as As (0.98), Ni (0.92), Cu (0.92), Co (0.86) and Sr (0.81) (Fig.4.54); moderately associated with Hg (0.68) and W (0.64). This is an indication that these metals have similar sources of input. These were further confirmed by the inter-elemental relationships between copper and some of the other metals Cu/Ni (0.78), Cu/As (0.93), Cu/Co (0.68) and Cu/Th (0.74). Nickel also strengthens this relationship by displaying strong relationship with As (0.93) and Sr (0.82) at both 0.01 and 0.05 confidence levels.

The regression analysis revealed an inter-elemental relationships depending on pollution source and coexisting behavior, whereas it implies to dependent and independent variables. The positive significant correlations were found to be between Zn and As (r=0.98). However, another significant positive correlation was observed between Zn and Cu (r=0.92) (Fig.4.54). It may be attributed to high abundance Zn in the study area.

Table 4.11. Correlation matrix of PHMs in Road Dusts of Lagos metropolis

	Mo	Cu	Zn	Ag	Ni	Co	Mn	Ba	As	U	Au	Th	Sr	Cd	V	Cr	Sc	Hg	Pb	Fe
Mo	1																			
Cu	33	1																		
Zn	**.52**	**.92****	1																	
Ag	.38	.04	.33	1																
Ni	**.54**	**.76***	**.91****	**.47**	**1**															
Co	**.60**	**.69***	**.87****	**.49**	**.92****	**1**														
Mn	**.63**	**.61**	**.50**	**.88**	**.45**	**.50**	1													
Ba	**.86****	**.61**	**.79****	**.52**	**.82****	**.85****	**.63**	1												
As	.40	**.93****	**.98****	**.34**	**.90****	**.89****	.30	**.77****	1											
U	**.96**	**.66**	**.78**	**.59**	**.86**	**.51**	.01	**.88**	**.98**	1										
Au	**.68***	**.83**	**.79**	.45	**.83**	**.66**	**.64**	.12	**.95**	**.82**	1									
Th	**.72**	**-.67***	**-.59**	**.99****	-.44	-.45	**.71**	-.35	**-.65***	.38	.28	1								
Sr	**.57**	**.55**	**.81****	**.64***	**.81****	**.84****	**.95****	**.86****	**.76***	**.74**	.38	-.40	1							
Cd	.30	**.83****	**.81****	**.94**	**.64***	**.69***	**.81**	**.57**	**.83****	**.62**	**.94**	**-.85****	**.61**	1						
V	**.67**	**.98**	**.83**	**.54**	**.85**	**.64**	**.81****	**.56**	**.98**	**.86****	.31	**.53**	.43	**.89**	1					
Cr	.31	**.80***	**.88***	**.97**	.37	.30	**.84****	**.70**	**.69**	**.70***	**.90**	**.73**	**.66**	**.96**	**.72***	1				
Sc	**.70**	1.0	**.97**	**.97**	**.79**	**.69**	.16	**.72**	**.99**	.10	**.76**	.06	**.88***	.32	.15	.42				
Hg	**.69**	.42	**.61**	**.71***	**.54**	**.67***	**.78**	.47	**.64***	**.58**	**.91**	-.49	**.72***	**.54**	-.04	-.08	-.29	1		
Pb	.31	.32	**.89**	**.49**	**.82**	.45	**.61**	**.54**	**.82**	**.75**	.37	**.86**	.39	**.98***	**.79**	**.92**	**.79**	**.62**	1	
Fe	.36	**.93****	**.93****	**.68**	**.89****	**.84****	.49	**.68***	**.95****	**.80***	**.82***	**-.56**	**.60**	**.78****	**.53**	.36	.13	.45	.18	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed

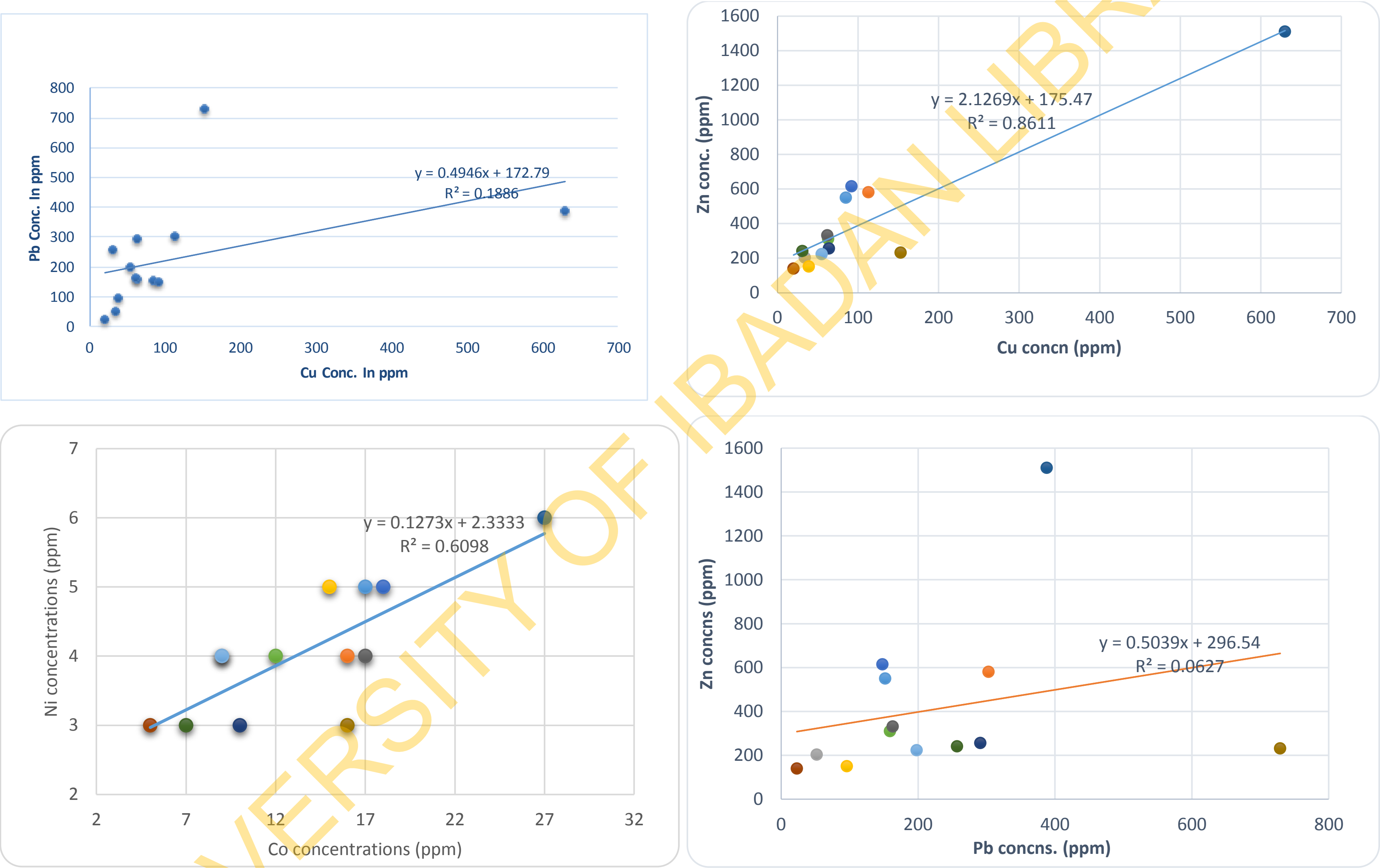


Figure 4.54. Correlation plots of Co, Pb, Ni, Zn and Cu against each other in Lagos Road Dusts

4.7.1.2 Factor Analysis of Road Dusts

For the road dusts, seven components were derived but only the first five has significant data extractions, hence the variables were fractionated into five components which accounted for about 91% of the total variance of the results (Table 4.12).

Factor 1: The First component ***PC-1*** has Eigen value of 8.92 and accounts for about 37.17% of the total variance. The following elements Mo, Cu, Ni, Pb, Zn, As, Co, Sr, Ba, and Hg were strongly loaded in this PC-1 with loading coefficient of variation (*r*) ranging from 0.7 to 0.9 while Ag and Bi display moderate association in this component. In this component Th displays a moderate negative relationship (*r = -0.521)* with others elements. This is an indication that Th has a source that is quite different from other elements. Over 60% of the analyzed variables were strongly and positively loaded in this group suggesting that these metals are governed by the similar geochemical factors.

Factor 2: The second component ***PC-2*** has an Eigen value of 5.11 and accounts for about 21.27% of the total variance with the following elements showing strong association with one another while Th and Tl were moderately associated. Au and La are major components in electronic appliances and therefore were likely contributions from e-wastes.

Factor 3: This factor has significant loadings of the following elements Tl, Sc, Cr, V, Th, U and Mn. These loadings accounted for about 19.14% of the total variance of the data. Mn, U and Cr were strongly fractionated in this component.

Factor 4 and 5 have Eigen values of about 1.70 which accounted for about 7.07% and 6.3% of the total variance. The silver (Ag) and mercury (Hg) have strong loadings in this component and significantly associated with this component. This shows that these two metals are derived from the same source which is no other than anthropogenic source. While factor 5 is only loaded significantly with scandium and this accounted for about of the total variance of data analyzed.

Table 4.12. Result of Principal Component Analysis of PHMs in Lagos Road dusts

PHM	**1**	**2**	**3**	**4**	**5**	**Communalities**
Mo	**.719**	.352	.230	-.312	-.189	.828
Cu	**.707**	-.416	-.265	-.300	-.025	.833
Ag	**.604**	.300	.017	**.708**	-.015	.956
Ni	**.933**	-.318	.005	-.058	-.044	.977
Zn	**.883**	-.292	-.196	-.136	.135	.940
Co	**.902**	-.290	.181	-.020	.223	.980
Mn	.236	**-.536**	**.739**	-.020	-.135	.908
As	**.890**	-.350	-.133	-.092	.023	.942
U	.119	-.200	**.880**	.336	-.154	.964
Au	.394	**.828**	.181	-.252	.070	.941
Th	**-.521**	**.497**	**.572**	.113	.021	.859
Sr	**.913**	.093	-.146	.117	.311	.974
V	-.064	**-.530**	**.804**	.045	-.126	.950
La	.067	**.896**	.387	-.025	.132	.975
Cr	.147	-.327	**.692**	-.154	**-.525**	.908
Sc	-.328	-.042	**.590**	-.250	.592	.870
Tl	.360	**.558**	**.679**	-.086	.116	.922
Ba	**.942**	.169	.029	-.214	.053	.966
Hg	**.765**	-.110	-.074	**.598**	.100	.970
Eigen Value	8.922	5.105	4.594	1.696	1.512	
Cumulative %	37.173	58.445	77.588	84.656	90.957	

Extraction Method: Principal Component Analysis.
a. 5 components extracted.

4.7.2 Metals Associations in Lagos sediments

4.7.2.1 Correlation Analysis of heavy metals in Lagos Sediments

The result of the correlation analysis of the heavy metals compositions of soils showed different trends of elemental associations. The correlation analysis in the sediments showed a significant positive correlation of Pb with some elements as shown in Table 4.13.

The following trends of associations were observed in bivariate analysis of metals in Lagos sediments the first trend observed is Ni-Cu-Pb-Zn-Mn (Fig.4.55) with an average loading value of 0.82; Co-Cu-Pb-Mn with average value of 0.80; Zn-Cu-Pb-Ag is another trend with an average of 0.82; V-Co-Ni-Mn trend with an average of 0.72; As-Cu-Ag-Zn ± Mo with average loading value of 0.73 and Sr-Ba (0.67). These different associations were pointers of generic similarities between these groups of metals.

4.7.2.2 Factor Analysis of Lagos-Sediments

The geochemical results obtained from analyzed sediments collected from Lagos were subjected to factor analysis in order to reduce the dimensionality of the data and integrate the majority of parameters with lesser factors. Table 4.14 displays the factor loadings after varimax rotation. From the result of the PCA analysis, four components were identified and this accounted for about 86% of the total variance in the data extraction.

PCA 1 was dominated by Cu, Pb, Zn, Ag, Ni, Co, Mn and As accounting for 44.21% of the total variance with out-standing positive extractions of 0.98, 0.91, 0.88, 0.86, 0.83 and 0.82 respectively except for Ag and As (Table 4.14). This probably mean that same underlying geochemical factors are responsible for co-precipitations of these elements while As, V and Ag showed strong to moderate but positive loadings in this component. The association of these potentially toxic metals in this component is an indication of common and similar sources which are not farfetched from anthropogenic sources.

Table 4.13. Correlation matrix of some PHMs in Lagos-sediments

	Mo	Cu	Pb	Zn	Ni	Mn	Sr	Cd	V	Co	Cr	Ba	As	U	Au	Sb	Bi	Fe	La	Ag
Mo	1																			
Cu	.86**	1																		
Pb	.53*	.57*	1																	
Zn	.73**	.85**	.44	1																
Ni	.81**	.79**	.40	.79**	1															
Mn	.27	.56	.46	.97	.08	1														
Sr	.63**	.76**	.63**	.59*	.62**	.22	1													
Cd	.72	.69	.73**	.77	.98	.45	.22	1												
V	.79	.27	.78	.25	.48	.52*	-.25	.76	1											
Co	.52	.95	.41	.85	.20	.81**	.51	.56*	.75**	1										
Cr	.34	.61	.92	.59	.42	.68**	.73	.78	.78**	.74**	1									
Ba	.56*	.50*	.54*	.45	.38	.18	.67**	.27	.96	.25	.60	1								
As	.72**	.57	.78	.62*	.91**	.37	.40	-.26	-.40	.88	.89**	.38	1							
U	.84	1.0	.52	.12	.90	.22	.44	.26	.53	.37	.93	.95	.95	1						
Au	.82	.69	.50	.15	.31	.62	.18	.51	.15	.97	.49	.80	.31	.29	1					
Sb	.54	.39	.56	.29	.35	.98	.52	.43	-.45	.27	.95	.^{38}	.19	-.33	.87	1				
Bi	.72	.44	.67	.16	.92	.18	.96	.92	.33	.59	.53	1.00	.89	.23	.08	.47	1			
Fe	.55*	.34	.53	.28	.65**	.78**	.19	.74	.56*	.69**	.91**	.22	.85**	-.^{17}	.89	.20	-.30	1		
La	.34	.39	.23	.40	.60	.84	.36	.91	.43	.84	.58	.51	.58	.74**	.60	.50	.30	.06	1	
Ag	.66	.21	.93	.29	.39	.37	.23	.51	.37	.49	.62	.77	.56	.94	.53	.97	.77	.64	.29	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed)

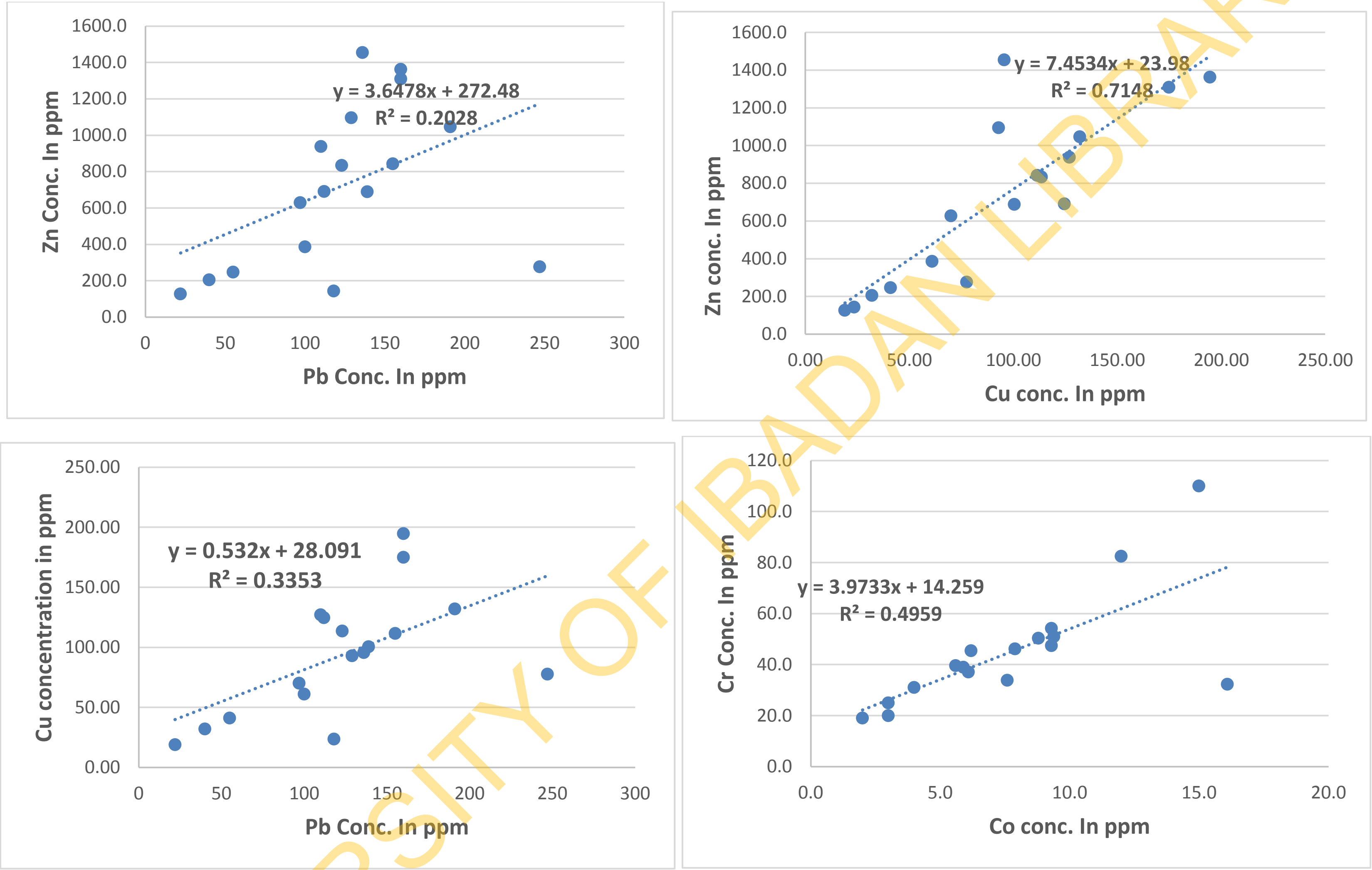


Figure 4.55. Correlation plots of PHMs in Lagos sediments

PCA 2 has an Eigen value of 2.843 and accounted for 20.31% of the total variance. This factor is strongly and positively loaded with Ag, Co, As, V and Cr indicating that their sources is similar to the region of ***PCA 2.*** This implies that ***PCA 1 and 2*** accounted for about 64.5% of the total variance, highlighted the role of industrial and urban activities in contamination of Lagos drain sediments.

PCA 3 has an Eigen value of 1.784 and this accounted for 12.74% of the total variance. It is strongly and positively loaded with Sr and Ba. The result of the correlation analysis also confirmed the significant relationship between Sr and Ba (0.67) as shown in the figure below. These two metals are more lithogenic than anthropogenic and their associations with the rare elements show that they are from the geology of the area.

PCA 4 has an Eigen value of 1.16 and it accounted for about 8.3% of the total variance. This component has Mo and La as the outstanding elements but in reverse order, Mo shows strong to moderate positive loading of 0.63 while La has strong but negative loading of -0.75, this is an indication of substitution reaction between Mo and La.

Table 4.14. Component Matrix of Principal Component Analysis of Lagos sediments

	1	**2**	**3**	**4**	Communalities
Mo	**-.539**	.304	.133	**.631**	.815
Cu	**.910**	-.177	.220	.183	.964
Pb	**.816**	.021	.091	.223	.979
Zn	**.858**	-.401	.219	.036	.968
Ag	**.501**	**-.745**	.240	-.064	.966
Ni	**.984**	.133	.000	-.008	.993
Co	**.831**	**.514**	.002	.140	.989
Mn	**.881**	.392	-.090	.031	.963
As	**.668**	**-.566**	.009	-.203	.870
Sr	-.403	-.033	**.820**	.131	.864
V	**.533**	**.776**	.076	-.163	.964
La	-.181	.310	.270	**-.754**	.855
Cr	.169	**.740**	.277	-.043	.959
Ba	-.167	-.020	**.877**	-.014	.803
Eigen Value	6.189	2.843	1.784	1.163	
% of Variance	44.211	20.307	12.744	8.309	
Cumulative %	44.211	64.518	77.262	85.572	

4.7.3 Heavy Metals Associations in Lagos Soils

4.7.3.1 Correlation

The elemental association in Lagos soils samples showed the following trends of metals associations that were related positively (Table 4.15). Cu-Zn-Ba-Ni have very strong and positive relationship with one another (0.72); Cu-Pb-Zn-Ni showed strong but positive relationship with one another (0.65); Cu-Pb-Zn another positive relationship (0.63) and Ni-Co-V-Ba display strong but positive relationship with one another (0.63) (Fig.4.56). All of these associations are pointers to the fact that these metals have similar sources of input into the environment which is an indication of anthropogenic activities.

4.7.3.2 Factor Analysis of Lagos Soils

The results of the geochemical analysis were further subjected to factor analysis in order to reduce the complexity of the data to a lesser factor and to further confirm the trends that were initially established from the results of the correlation analysis. Seven factors were established within the variables in soil samples which accounted for about 89.2% of the total variance but only four of the factors displayed elemental associations while the remaining three components paraded only one element in their components (Table 4.16).

PCA-1 has more than 50% of the analyzed elements having out-standing positive loading values. This PCA accounted for 36.5% of the total variance with Eigen value of 5.48. The following elements formed the significant association in this component Mo, Cu, Zn, Ni, Co, Ba and also display very strong association; Pb, Sr and Ni display strong to moderate association in this component while Mn, Ag and As were weakly associated. This confirmed the trends that were observed in correlation analysis. This in an indication of anthropogenic input although the degree varies as shown in their loading values.

PCA-2 accounted for about 21% of the total variance with Eigen value of 3.15. Th and V show very strong association in this PCA while Mn and La displayed moderate association but Cr showed weak association (0.45) in this factor (Table 4.16).

Table 4.15. Correlation Matrix of selected PHMs in Lagos Soils

	Mo	**Cu**	**Pb**	**Zn**	**Ag**	**Ni**	**Co**	**Mn**	**As**	**Th**	**Sr**	**La**	**V**	**Cr**	**Ba**
Mo	1														
Cu	**.72****	1													
Pb	**.44****	**.65****	1												
Zn	.33*	**.60****	.37**	1											
Ag	.16	.20	**.97****	.36*	1										
Ni	**.55****	**.74****	**.48****	**.75****	**.50****	1									
Co	**.50****	**.56****	.32*	.36*	.22	**.48****	1								
Mn	**.44****	.29*	.17	.17	**.81****	.35*	**.61****	1							
As	.37**	.34*	.13	.30*	.25	.32*	.21	.12	1						
Th	.27	-.14	-.23	**-.47****	-.12	-.12	.17	**.43****	**.80**	1					
Sr	.26	.35*	.15	**.58****	.37**	.41**	.28	.05	**.50****	-.21	1				
La	**.45****	.13	**.76****	**.63****	.18	.23	.33*	.41**	.15	**.69****	.25	1			
V	.24	**.87****	-.14	-.21	**.78****	**.97****	.44**	**.52****	**.92****	**.63****	-.23	**.41****	1		
Cr	**.51****	**.44****	.11	.14	.10	.28	**.49****	.34*	.29*	.25	.04	.17	**.72****	1	
Ba	**.56****	**.69****	.38**	**.80****	.37	**.74****	**.51****	.12	.30*	-.24	**.48****	.23	-.05	.30*	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed)

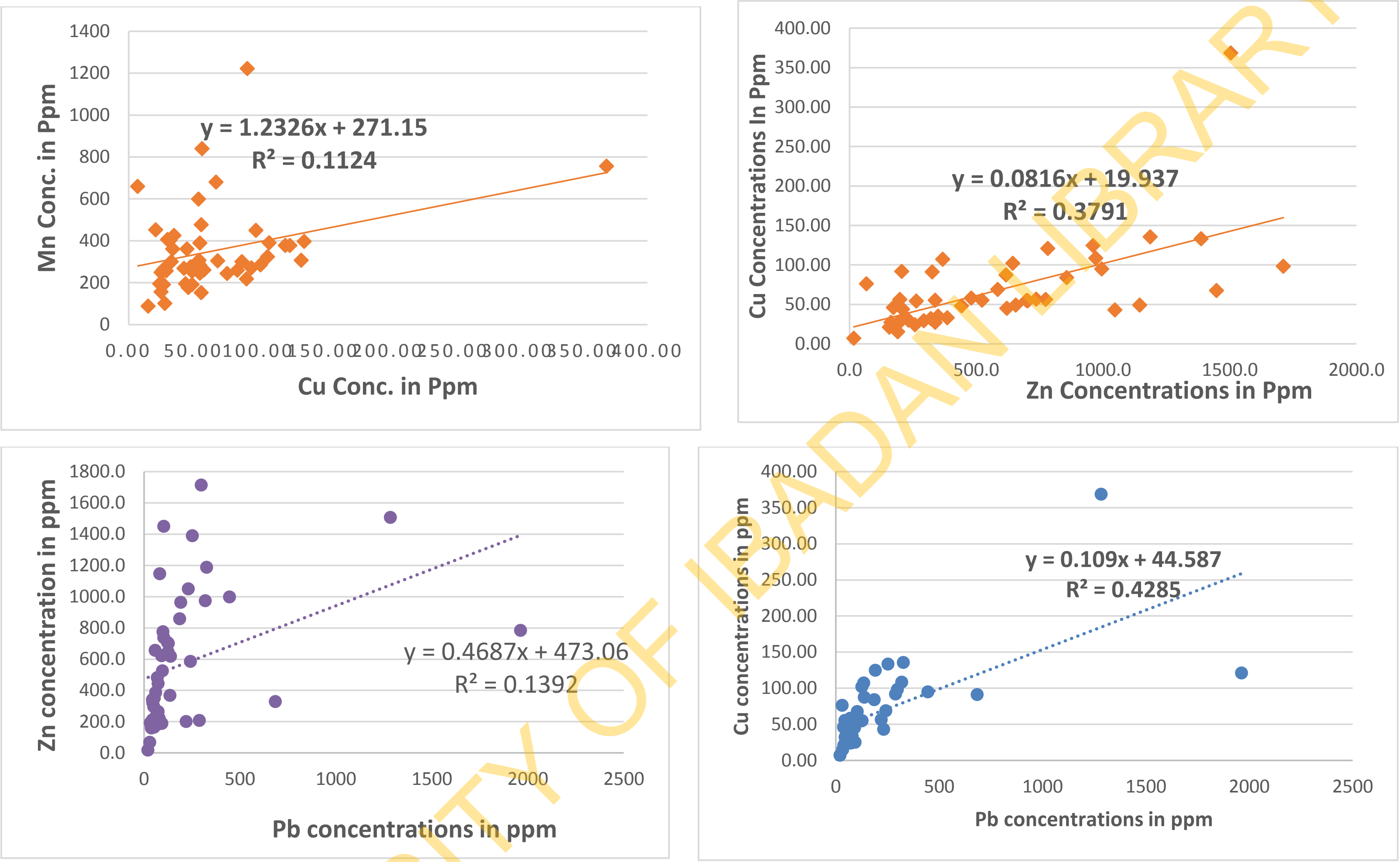


Figure 4.56. Correlation Matrices of some PHMs in Lagos Soils

PCA-3 has an Eigen value of 1.45 and this accounted for about 9.7% of the total variance with Ag and Sr showing strong association while La and Pb displayed moderate association but Pb is negatively associated (Table 4.16). This is an indication that probably points to another source of input other than that accounted for in PCA-1. ***PCA-4*** has La weakly associated (0.45) with Cr showing moderate but negative association with this factor. ***PCA-5, -6 and -7*** have only one element each (Table 4.16). These three components accounted for about 15.12% of the total variance with Eigen value of 2.28. In ***PCA-6 and PCA-7,*** Mn and Ag showed a weak loading values of 0.46 and 0.44 respectively while ***PCA-5*** has only As with outstanding loading value (0.67). These three components actually accounted for the geology of the area reflecting similar weathering process and lithology. Groundwater with high As has been attributed to Holocene sediments which invariably or indirectly saying that Holocene sediments are rich in As (Mitamura *et al*., 2008).

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Table 4.16. Component Matrix of principal component Analysis of selected PHMs in Lagos Soils

	1	2	3	4	5	6	7
Mo	**.775**	.242	-.127	.213	.242	-.260	-.005
Cu	**.849**	-.153	-.330	.053	.125	-.123	.011
Pb	**.524**	-.260	**-.560**	.306	.103	-.034	.290
Zn	**.728**	-.502	.073	-.046	-.191	.117	-.222
Ag	.427	-.169	**.534**	-.315	-.336	-.257	**.442**
Ni	**.849**	-.212	.011	.038	-.219	-.123	.142
Co	**.724**	.300	-.139	-.096	-.207	.326	-.023
Mn	489	**.555**	-.116	.158	-.242	.463	.191
As	.489	-.060	.355	-.142	**.673**	.171	.215
Th	.015	**.886**	.204	.285	.085	-.137	.041
Sr	**.544**	-.353	**.515**	.083	.185	.304	-.135
V	.213	**.857**	-.058	-.369	-.090	-.002	-.038
La	.397	**.557**	.453	.450	-.086	-.156	-.165
Cr	**.529**	.479	-.211	-.558	.216	-.110	-.147
Ba	**.816**	-.297	.032	-.034	-.125	-.167	-.324
Eigen Value	**5.48**	3.15	1.45	1.04	0.96	0.71	0.61
% of Variance	**36.50**	20.99	9.66	6.92	6.37	4.70	4.05
Cumulative %	**36.50**	57.49	67.14	74.06	80.43	85.12	89.17

4.8. Heavy Metals Associations in Ibadan Metropolis

4.8.1 Inter-Elemental Associations in Ibadan Sediments

4.8.1.1 Correlation Analysis of heavy metals in Ibadan Stream Sediments

The result of the Pearson correlation analysis of the elemental compositions of Ibadan sediments is presented in the Table 4.17. From the Table 4.17, the heavy metals in the Ibadan sediments showed significant positive correlation with one another with 'r' ranging from 0.62 to 0.94. This strong positive relationship is a strong indication of the fact that the sources of these metals are related to common anthropogenic inputs rather than the geogenic which most probably could have been inter-dependent on chemical factors such as relative solubility and mobility of respective metals.

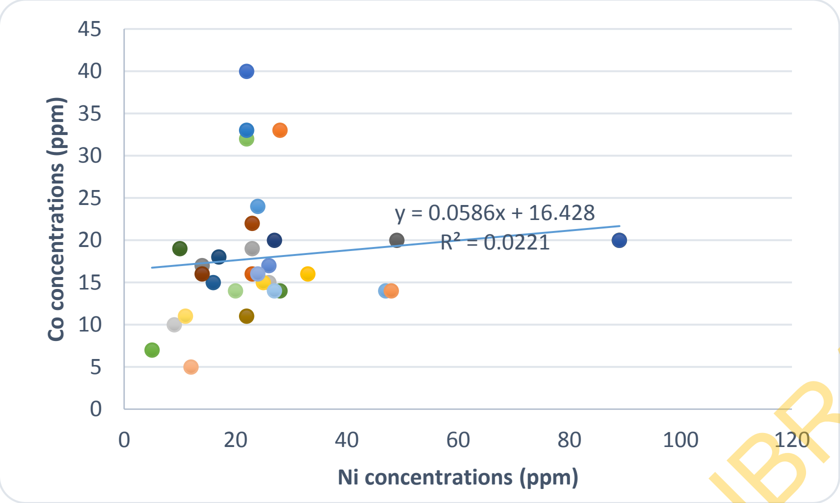
The following trends were however observed based on their relationships with one another, Mo-Cr-Ni-Zn-Cu-Th-V; these metals correlate significantly and positively with one another with the co-efficient of correlation 'r' ranging from 0.62 to 0.94 while it showed weak but positive relationship with Pb, Sr and Ba (Table 4.17). Cu significantly correlates with Ni, Zn, Th, moderate to strong relationship with Cr and weak relationship with Pb. Very weak relationships were observed between Pb and Zn, Cu and Ni (Fig.4.57). This is an indication that Pb has a different source that is quite different from source of Zn, Ni and Cu inputs. The weak association shows that there are still some levels of relationship that exist between these elements which is no other than the fact that they were anthropogenically contributed into the sediments. The strong association between Mn and Co is probably due to agricultural input since these elements are essential components of agrochemicals. The Ni-Sr-V-La-Cr-Ba trend could be attributed to the underlying geology of the study area.

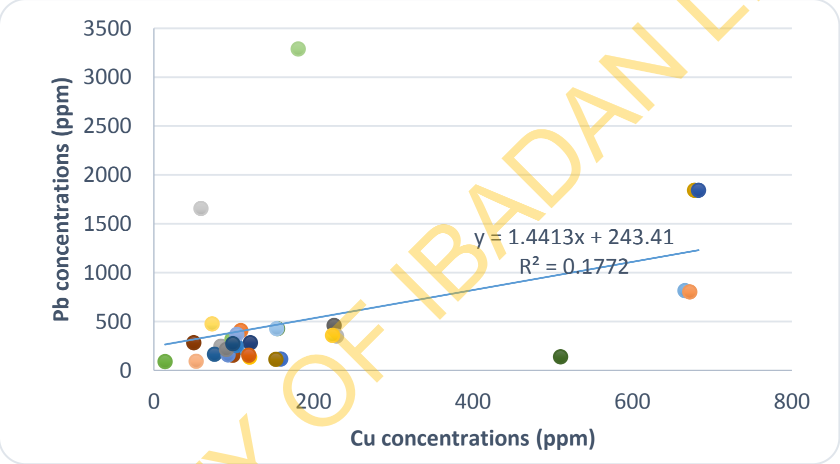
Table 4.17. Correlation matrix of PHMs in Ibadan Stream Sediments

	Mo	**Cu**	**Pb**	**Zn**	**Ni**	**Co**	**Mn**	**Th**	**Sr**	**V**	**La**	**Cr**	**Ba**
Mo	1												
Cu	**.80****	1											
Pb	**.49****	**.42***	1										
Zn	**.85****	**.80****	**.42***	1									
Ni	**.94****	**.78****	**.43***	**.81****	1								
Co	.02	-.01	-.15	-.16	.17	1							
Mn	.02	.16	-.13	-.05	.17	**.64****	1						
Th	**.63****	**.63****	.22	**.58****	**.43***	-.11	-.06	1					
Sr	**.50****	.31	.21	**.65****	**.47****	-.10	.09	.19	1				
V	**.60****	.36*	.21	**.52****	**.52****	.25	.05	**.53****	.36*	1			
La	**-.43***	-.16	-.27	**-.55****	**-.41***	.31	.39*	.01	**-.48****	**-.49****	**1**		
Cr	**.80****	**.53****	.33	**.67****	**.72****	-.02	-.02	**.58****	**.46****	**.87****	**-.57****	1	
Ba	**.44****	.31	.12	.40*	**.50****	.38*	**.59****	.11	**.51****	.23	-.13	.31	1

***. Correlation is significant at the 0.01 level (2-tailed).*

**. Correlation is significant at the 0.05 level (2-tailed).*





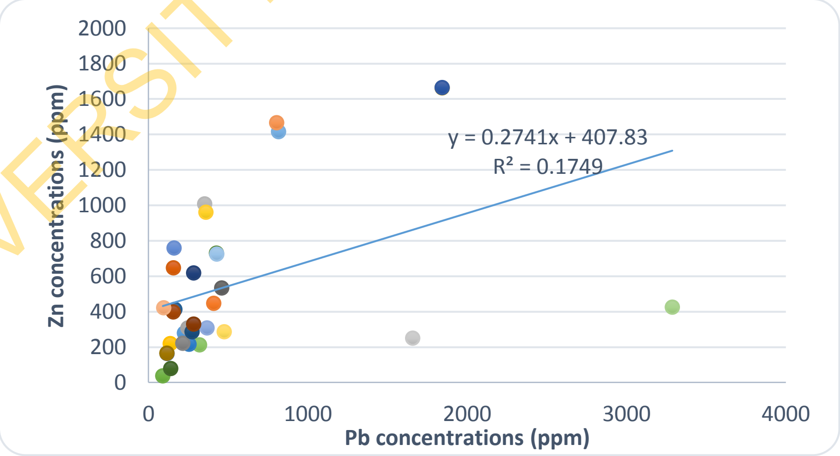


Figure 4.57. Correlation Matrices of PHMs in Ibadan stream sediments

4.8.1.2 Factor analysis of PHMs in Ibadan stream sediments

The geochemical result of the sediment samples from Ibadan were subjected to R-mode analysis and the result of the analysis is presented in Table 4.18. From the Table (4.18), the PCA-1 has about twelve elements showing significant and positive loading values, PCA-2 has four elements that are significantly loaded while PCA-3 and PCA-4 have three elements respectively, PCA-5 has just one metal while PCA-6 no metal showing significant loading. All these together accounted for a total variance of 91.2%.

PCA-1 has an Eigen value of 6.63 and this accounted for a total of 46.63% of the total variance. This PCA is strongly and positively loaded with Mo, Cu, Zn, Ni, Th, Sr, V and Cr and moderately loaded with Pb and Ba as well as La (Table 4.18). This PCA clearly confirmed the trend of relationship that was observed between Mo and Cr, Ni, Zn, Cu, V, Sr and Th in the result of correlation analysis. These elements are major components of industrial and chemical materials.

PCA-2 accounted for over 16% of the total variance with Eigen value of 2.3. It is strongly and positively loaded with Co, Mn and Ba which are major components of agrochemicals. PCA-2 could be likely attributed to agricultural inputs since high concentrations of these elements were mostly recorded in samples collected from the areas of the metropolis where agricultural practices were the major activities.

PCA-3 has an Eigen value of 1.32 and it accounted for about 9.5% of total variance. Th, Sr and La show significant loading values in this PCA (Table 4.18). This PCA could be linked to the geology of the area. ***PCA-4*** has an initial Eigen value 1.23 and accounted for about 8.8% of the total variance. It is weakly loaded with Cu and strongly but negatively loaded with V (Table 4.18). This association is also due to the geology of the area and it shows that Cu has dual sources of inputs into the reservoir. Pb stood out in *PCA-5* and this accounted for 5.74% of the total variance. The significance of Pb and Hg in this PCA shows these metals have a significant source of input that is quite different from every other element in *PCA-1* and *PCA-2*. This could be linked with the atmospheric fallout of Pb from car exhausts.

Table 4.18. Factor Analysis of selected PHMs in Ibadan Stream Sediments

	1	**2**	**3**	**4**	**5**	**Communalities**
Mo	**.946**	-.016	.102	.140	.039	.944
Cu	**.800**	.062	.347	**.402**	-.048	.912
Pb	**.489**	-.237	.078	.316	**.684**	.956
Zn	**.908**	-.155	-.053	.224	-.140	.921
Ni	**.888**	.137	-.012	.191	.119	.933
As	**.982**	-.040	.039	.021	.028	.971
Cr	**.870**	-.103	.000	-.307	-.043	.885
Cd	**.854**	-.179	.222	.206	-.186	.893
Ga	**.748**	.109	.104	-.401	.109	.864
U	**.617**	-.058	-.003	-.544	.163	.857
Th	**.640**	-.088	**.613**	-.046	-.337	.945
Sr	**.619**	-.003	**-.555**	.131	-.282	.918
V	**.747**	.046	.034	**-.612**	.019	.937
Co	.046	**.854**	.046	-.317	.263	.909
Mn	.062	**.909**	-.051	.144	-.046	.856
La	**-.529**	**.488**	**.572**	.198	-.100	.949
Hg	.059	-.273	.172	.260	**.562**	.697
Ba	**.487**	**.609**	-.395	.232	-.089	.832
Eigen Value	6.529	2.301	1.324	1.232	.803	-
% of Variance	46.634	16.433	9.454	8.797	5.735	-
Cumulative %	46.634	63.067	72.522	81.318	87.054	-

4.8.2 Inter-Elemental Associations in Ibadan Soils

4.8.2.1 Correlation Analysis

The results of chemical analysis of soils and stream sediments from Ibadan were subjected to Pearson correlation analysis (Table 4.19). Some of the elements showed some levels of relationship either positive or negative with one another. From table 4.19, Cu has strong positive relationship with elements such as Pb, Zn, Ag, Ni, Co, Cr and V (Fig.4.58) with correlation coefficient (r) ranging from 0.67 to 0.51 while displaying very strong positive association with Th (0.97), Mn (0.78) and Ba (0.78) (Table 4.19). Pb shows very strong association with Zn and Th at r = 0.72 and 0.91 respectively but weakly associated with Ni. The very strong association between Pb and Zn as well as Th is an indication of common source. Pb is produced as radio-nuclei daughter cells during radioactive decay of Th. Zn weakly and positively associated with Co, Cr and Ba but moderately associated with Ni (0.65) and Sr (0.52). While the following associations Ni-Co-Cr-Ba-V-Sr with ***r*** ranges from 0.60 to 0.89 and Mn-Ba-V-La with r varies from 0.42 to 0.84 were also observed in Ibadan soils. Strong correlations signify that each paired element have common contamination source. This is an indication that these metals were probably having similar sources of input. These were further confirmed by the results of the factor analysis in order to establish the observed trends.

4.8.2.2 Factor analysis of PHMs in Ibadan soils

Fourteen selected variables from the geochemical results of soils from Ibadan were subjected to R-mode analysis on the basis of their higher correlation co-efficient in all. The variables were subjected to five components factor analysis of data reductions. These five components accounted for about 90% of the total variance of elements co-precipitated in the soils (Table 4.20).

About 64% of the selected variables were associated with the first principal component (PC-1) with out-standing positive loading values. This PC has Eigen value of 6.22 and it accounted for about 44.46% of the total variance. The following metals were strongly associated in principal component 1 Ni, Ba, Cr, Co, Cu and V while Mn, Sr and Zn were strongly to moderately associated (Table 4.20).

Table 4.19. Correlation matrix of selected PHMs in Ibadan soils

	Cu	Pb	Zn	Ag	Ni	Co	Th	Sr	V	Mn	La	Cr	Ba
Cu	1												
Pb	**.63****	1											
Zn	**.67****	**.72****	1										
Ag	**.56****	.25	.18	1									
Ni	**.63****	**.42**	**.65****	.23	1								
Co	**.53***	.03	**.40**	.20	**.78****	1							
Th	**.97***	**.91***	.40	**.89****	.32	.30	1						
Sr	.22	.26	**.52***	-.08	**.82****	**.63****	**-.46***	1					
V	**.51***	.07	.21	.14	**.53***	**.60****	-.13	.37	1				
Mn	**.63****	.04	.11	.33	**.41***	**.73****	-.11	.12	**.52***	1			
La	.40	.09	.04	**.43**	.21	.33	**.68****	-.18	.11	**.43**	1		
Cr	**.58****	.18	**.49***	.17	**.87****	**.76****	-.31	**.75****	**.79****	**.47***	.05	1	
Ba	**.78****	.29	**.49***	.37	**.70****	**.89****	-.11	**.42**	**.57****	**.84****	**.46***	**.66****	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

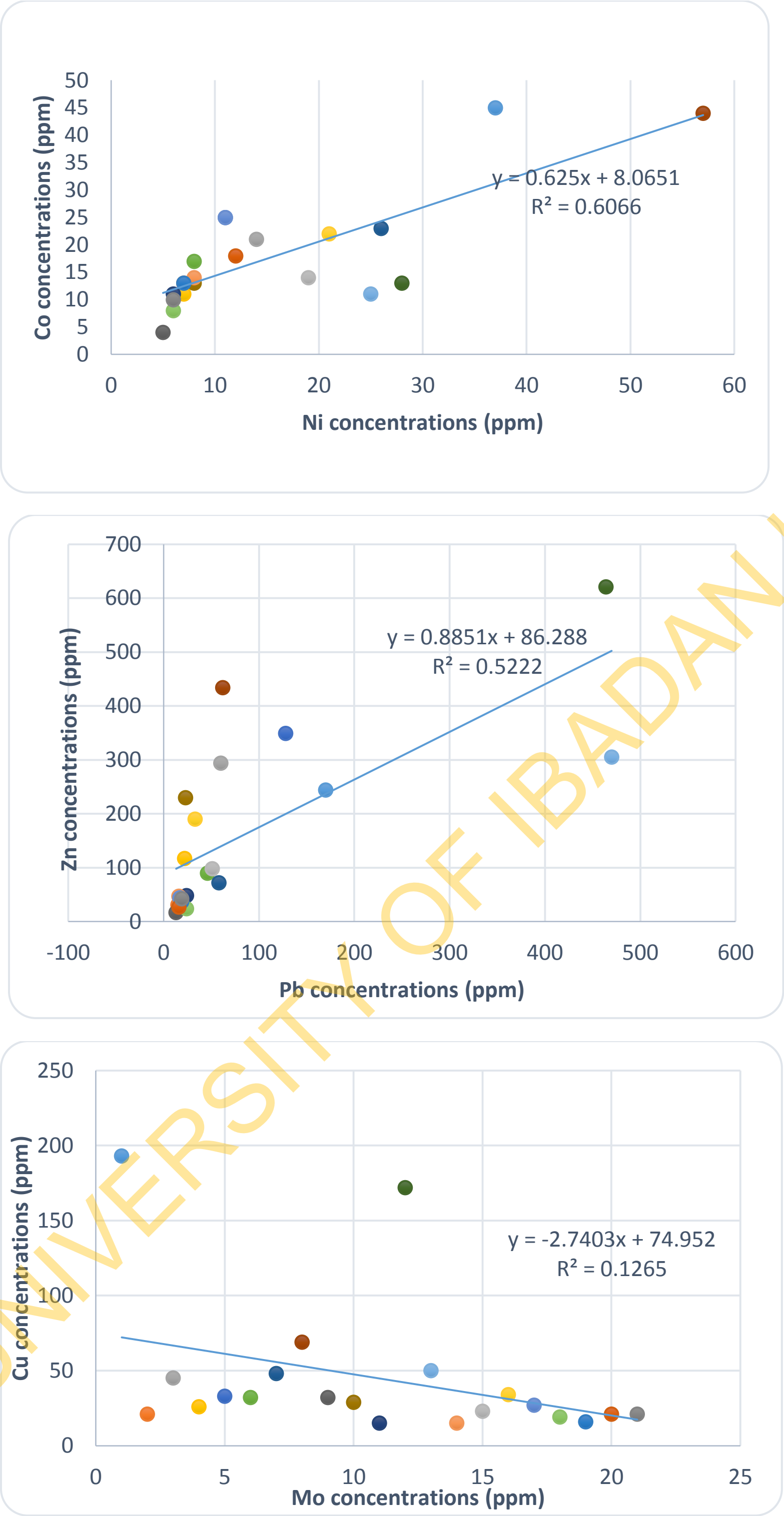


Figure 4.58. Correlation Matrices of some PHMs in Ibadan Soils

Pb displayed weak association with other metals in this PC. These trends were similar to what was previously observed from the result of Pearson correlation analysis. This is an indication of different underlying factors responsible for the introduction of these elements which may be as a result of multiple sources of anthropogenic inputs although the degree of inputs varies as shown in their loading values (Table 4.20).

PC-2 has an Eigen value of 2.35 and accounted for about 16.78% of the total variance. Th and La showed very strong association in this PC while Sr and Ag displayed strong to moderate association but Sr is negatively associated. This PC-2 is solemnly due to the geology of the area (i.e. these elements are geogenically contributed) (Table 4.20). ***PC-3*** has an initial Eigen value of 1.72 which accounted for about 12.29% of the total variance. This component has two is strongly loaded with very important environmental elements Pb and Zn. This PC was strongly loaded with Pb (r = 0.82) and Zn (Table 4.20). This is an indication of similar point source.

PC-4 has two lithogenic metals Th and V that were weakly associated or loaded (r = 0.46 and 0.40) in this PC. This component has Eigen value of 1.38 and accounted for 9.92% of the total variance. The dual associations of V and Th simply suggests that two underlying geochemical factors may be responsible for the co-precipitation of V and Th. ***PC-5*** accounted for about 6.7% of the total variance. It has Ag and Th weakly associated in this PC with loading values of -0.44 and 0.43, respectively. PC-2, 4 and 5 actually accounted for the complexity of the underlying geology of the study area reflecting similar weathering process and lithology.

Table 4.20. Factor Analysis of selected PHMs in Ibadan Soils

Parameter	1	2	3	4	5	Communalities
Cu	**.827**	.323	.312	.015	-.245	.947
Pb	**.433**	.016	**.824**	.086	-.065	.878
Zn	**.645**	-.177	**.631**	-.132	.152	.885
Ag	.371	**.515**	.214	-.175	**-.438**	.671
Ni	**.903**	-.209	.082	.060	.237	.926
Co	**.857**	-.009	-.361	-.230	.213	.964
Mn	**.672**	.375	-.399	-.302	-.183	.876
Th	-.214	**.717**	.069	**.457**	**.430**	.958
Sr	**.648**	**-.612**	.016	-.044	.327	.904
V	**.716**	-.064	-.373	**.404**	-.246	.880
La	.304	**.847**	-.045	.043	.360	.944
Cr	**.880**	-.288	-.189	.157	.009	.918
Ba	**.892**	.249	-.140	-.232	.038	.932
Initial Eigen values	6.224	2.349	1.721	1.388	.932	-
% of Variance	44.460	16.781	12.294	9.917	6.658	-
Cumulative %	44.460	61.241	73.536	83.453	90.111	-

4.9 Assessment of Heavy Metal Contaminations Using Geoaccumulation Index

Geo-accumulation Index proposed by Muller, 1979 (Table 4.21) were calculated for metal composition of individual elements using the under listed equation. The respective average values of the individual elements in the analyzed bedrocks were used as background values for the soils, sediments and road dusts (Tables 4.6 and 4.7).

$$\mathbf{Igeo = Log_2[Cn/1.5\ Bn]}$$

Where Cn and Bn are the measured concentration and the background value of elements n respectively and 1.5 is the background matrix correction factor. In the case of this study, the average local background concentration of element n in the respective underlying bedrocks was used instead of the average crustal value.

4.9.1 Geo-accumulation Indices Assessment of the Environmental Media

The degree of contamination as expressed by geoaccumulation indices, revealed that all the sampled media in Lagos metropolis are extremely to heavily contaminated with Cd, Pb, Zn and Hg, high to moderately contaminated with Cu, Ni and As and practically uncontaminated with respect to Th, U, As, Co, Mo and Ag (Table 4.22). The results also revealed that about 30%, 32% 90%, 71%, 72% and 100% of soils are moderately to extremely contaminated with Cu, Ni, Zn, Pb, Hg and Cd respectively; 65%, 68%, 71%, 77%, 90% and 100% of sediments are moderately to extremely contaminated with Hg, Cu, Cd, Ni, Pb and Zn respectively while 38%, 62%, 76%, 77%, 93% and 100% of the roadside dust sampling sites were moderately to extremely contaminated with Cu, Hg, Mn Cd, Pb and Zn (Table 4.23 and Figs 4.59 – 4.63).

For Ibadan, the pollution levels of the selected metals in both soils and sediments as expressed by their Igeo and the results indicated that the soils and stream sediments varied from uncontaminated to moderately contaminated with Mo, Ag, Sr, Co, Ni, U, As, Th and Cu. They are high to extremely polluted with Cd, Pb and Hg (Table 4.24 and Fig. 4.59 – 4.63).

The overall implication based on the average Igeo is that the dusts are most impacted or affected with Pb followed by the soils and then the sediments. The wider variability in the compositions of Pb in soils and sediments is due to the facts that Pb is relatively immobile. More variability was observed in soils than any other samples (Table 4.22). This agreed with the findings of Nriagu (1988) which observed or concluded that the order of magnitudes of most metals input into environmental media increases from air to water to soil (soil>water>air) while the least were observed in sediment samples.

For Ibadan metropolis, eight metals (Cu, Zn, Pb, Ag, Cd and Hg) showed varied degree of contaminations in sediments and five metals (Cu, Zn, Pb, Cd and Hg) in soils while the remaining metals fell in classes 1 and 0 (Table 4.23). The calculated Igeo showed that the sediments are moderately contaminated to extremely contaminated with Hg, Cd, Ag, Pb, Zn and Cu while soils are moderately contaminated to heavily contaminated with Pb, Zn and Cd (Table 4.22 and 4.24). Hence, the contamination with Pb and other pollutants if left unattended to may increase with time and cause Pb and Cd hazards outbreak in the nearest future in the metropolis. The general outlook of percentage distributions of the PHMs into various Igeo classes is presented in Table 4.24. The overall Igeo showed that the degree of contamination was far higher in sediments than the soils which could be attributed to different characteristics of the drainages catchment areas.

Table 4.21. Geoaccumulation (Igeo) index Values classification ***(After Muller 1979)***

Class	Value	Sediment Quality Classification
0	Igeo≤0	Practically uncontaminated
1	0<Igeo<1	Uncontaminated to moderately contaminated
2	1<Igeo<2	Moderately contaminated
3	2<Igeo<3	Moderately to heavily contaminated
4	3<Igeo<4	Heavily uncontaminated
5	4<Igeo<5	Heavily to extremely contaminated
6	5<Igeo	Extremely contaminated

Table 4.22. Summary of Geo-Accumulation Indices of selected PHMs in Lagos and Ibadan environmental media

ELEMENT	Lagos Soils		Lagos Road dusts		Lagos Sediments		Ibadan Soils		Ibadan Sediments	
	Range	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Mo	0.1 -1.0	0.29	0.2 - 0.5	0.34	0.2 -0.6	0.34	0.2 - 0.4	0.34	0.2 -3.1	0.63
Cu	1.0 - 8.2	2.26	0.7 - 15.0	3.18	0.52 - 4.3	2.52	0.3 -1.4	0.69	0.4 -5.4	1.68
Zn	4.0 - 30.0	16.9	5.0 -32.0	10.3	3.0 - 29.0	17.9	0.7 - 1.4	1.0	0.2 - 5.0	1.4
Pb	4.0 - 79.0	15.0	6.0 - 29.0	11.0	4.0 -10.0	6.0	3.0 -10.0	8.0	3.0 - 40.0	12.0
Ag	0.0 - 6.0	1.0	0.0 -1.0	0.4	0.0 - 19.0	4.0	0.1 - 0.5	0.3	0.1 -5.2	1.0
Cd	5.0 - 63.0	21.0	4.0 - 44.0	15.0	5.0 -233.0	41.0	5.0 -32.0	19.0	3.0 - 54.0	15.0
Ni	2.0 - 8.0	3.2	2.0 -5.0	2.7	1.6 - 8.3	3.8	0.1 - 0.4	0.3	0.1 - 1.3	0.4
Co	0.4 - 1.1	0.6	0.3 - 0.7	0.4	0.5 - 1.4	0.8	0.3 -0.6	0.4	0.3 - 1.1	0.5
As	0.1 - 0.2	0.1	0.0 - 0.3	0.1	0.0 - 0.3	0.1	0.4 - 1.3	0.7	0.2 - 5.4	1.3
U	0.01 - 0.3	0.09	0.1 - 0.33	0.12	0.1 - 0.2	0.10	0.1 - 0.11	0.1	0.05 - 0.2	0.12
Th	0.0 - 0.1	0.1	0.0 - 0.1	0.1	0.0 - 0.1	0.1	0.0 -0.1	0.1	0.0 - 0.2	0.1
Hg	1.3 - 22.0	9.1	0.2 - 9.0	2.7	1.0 - 76.0	19.8	1.0 - 4.0	2.0	0.6 - 42.0	4.5

0: unpolluted; 1: unpolluted to moderately polluted; 2: moderately polluted; 3: moderately polluted to high polluted; 4: highly polluted; 5: highly polluted to very highly polluted; 6 and above: very highly polluted. (Muller, 1979)

Table 4.23. Proportion of Elements in different classes of Geo-Accumulation Index for Lagos Media

Class		Quality	Percentage of the Element						
			Hg	**Ni**	**Cd**	**Ag**	**Pb**	**Zn**	**Cu**
Igeo≥0	Soils	Practically	0	0	0	73	-	2	6
	Dusts	Uncontaminated	23	0	23	69	0	0	8
	Sediments		29	29	29	41	0	0	12
0<Igeo<1	Soils	Uncontaminated	4	21	0	23	7	2	63
	Dusts	to Moderately	15	23	0	31	8	0	54
	Sediments	Contaminated	6	0	0	29	6	0	18
1<Igeo<2	Soils	Moderately	19	48	0	0	23	0	23
	Dusts	Contaminated	31	23	0	0	8	0	15
	Sediments		0	12	0	6	12	0	41
2<Igeo<3	Soils	Moderately to	0	12	0	2	19	6	6
	Dusts	Heavily	8	46	0	0	0	15	15
	Sediments	Contaminated	6	12	0	6	0	12	15
3<Igeo<4	Soils	Heavily	10	13	0	2	13	16	0
	Dusts	Contaminated	0	0	8	0	8	15	0
	Sediments		6	41	0	6	24	6	12
4<Igeo<5	Soils	Heavily to	5	2	10	0	8	6	0
	Dusts	extremely	15	8	0	0	0	23	0
	Sediments	Contaminated	0	12	6	0	24	12	0
5<Igeo	Soils	Extremely	62	4	90	0	31	67	2
	Dusts	Contaminated	8	0	69	0	77	46	8
	Sediments		53	0	65	12	35	70	0

Table 4.24. Proportion of Elements in different classes of Geo-Accumulation Index of Ibadan Sediments

Class		Quality	Percentage of the Element					
			Hg	Cd	Ag	Pb	Zn	Cu
Igeo≥0	Sediments	Practically Uncontaminated	0	0	55	0	0	9
	Soils		>80	60	70	0	0	68
0<Igeo<1	Sediments	Uncontaminated to Moderately Contaminated	27	0	24	0	61	42
	Soils		15	0	30	57	90	32
1<Igeo<2	Sediments	Moderately Contaminated	24	0	15	6	21	36
	Soils		4	0	0	24	0	0
2<Igeo<3	Sediments	Moderately to Heavily Contaminated	6	10	0	12	6	0
	Soils		0	0	0	5	10	0
3<Igeo<4	Sediments	Heavily Contaminated	21	0	0	15	6	0
	Soils		0		0	10	0	0
4<Igeo<5	Sediments	Heavily to extremely Contaminated	9	0	6	6	6	3
	Soils		0	10	0	0	0	0
5<Igeo	Sediments	Extremely Contaminated	12	90	0	>60	0	12
	Soils		0	20	0	0	0	0

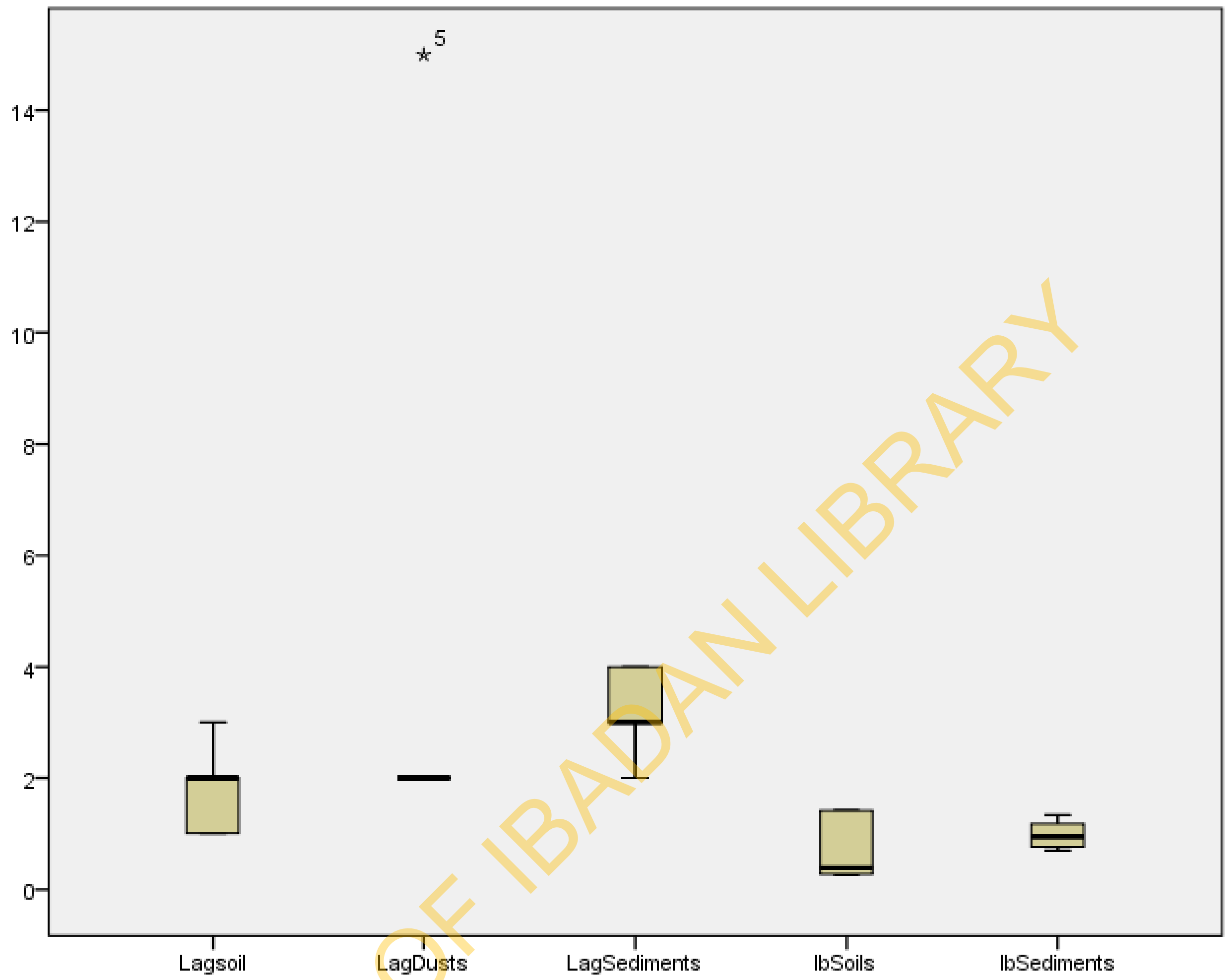


Figure 4.59. Geo-accumulation Indices of Cu in the study areas

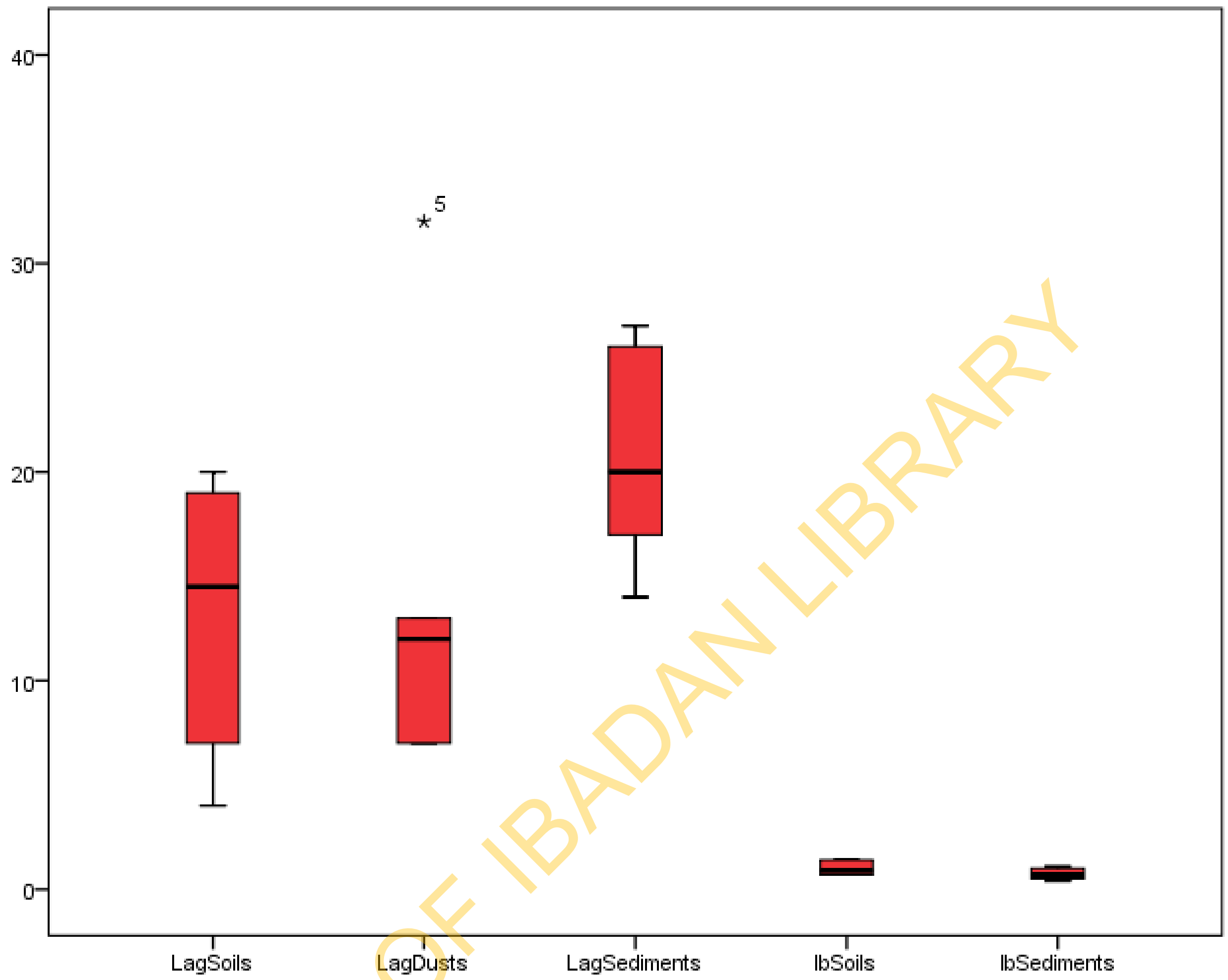


Figure 4.60. Geo-accumulation Indices of Zn in the study areas

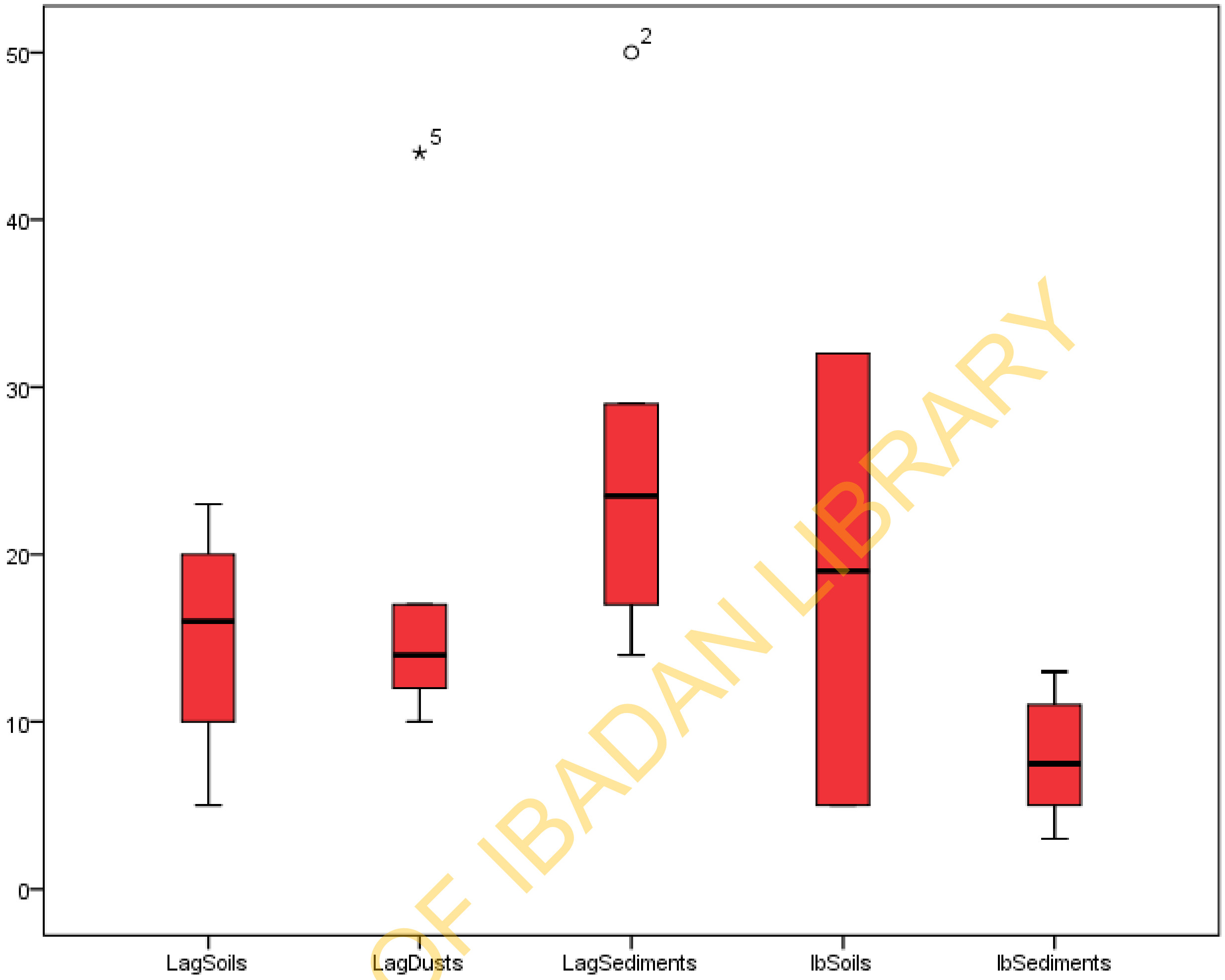


Figure 4.61. Geo-accumulation Indices of Cd in the study areas

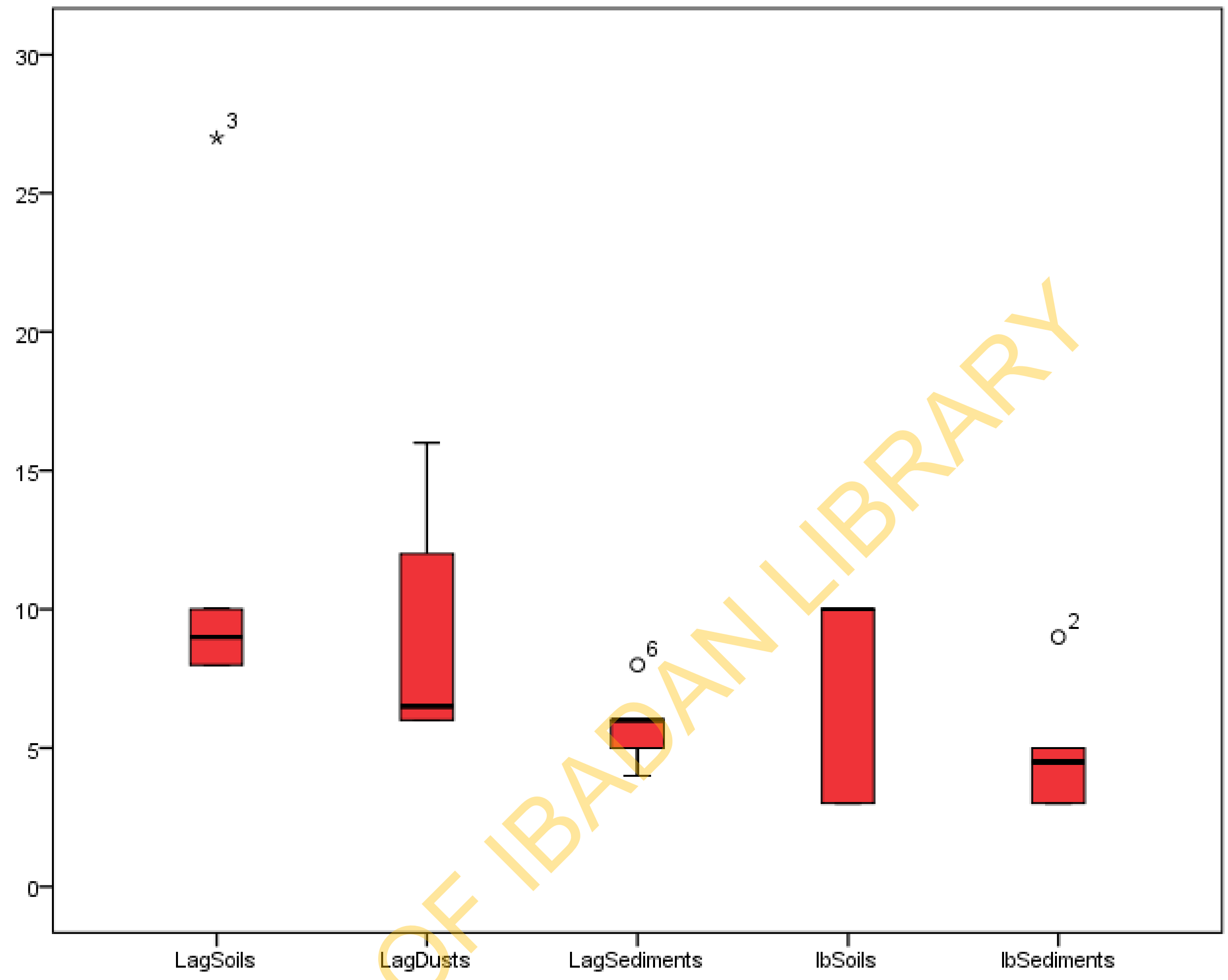


Figure 4.62. Geo-accumulation Indices of Pb in the study areas

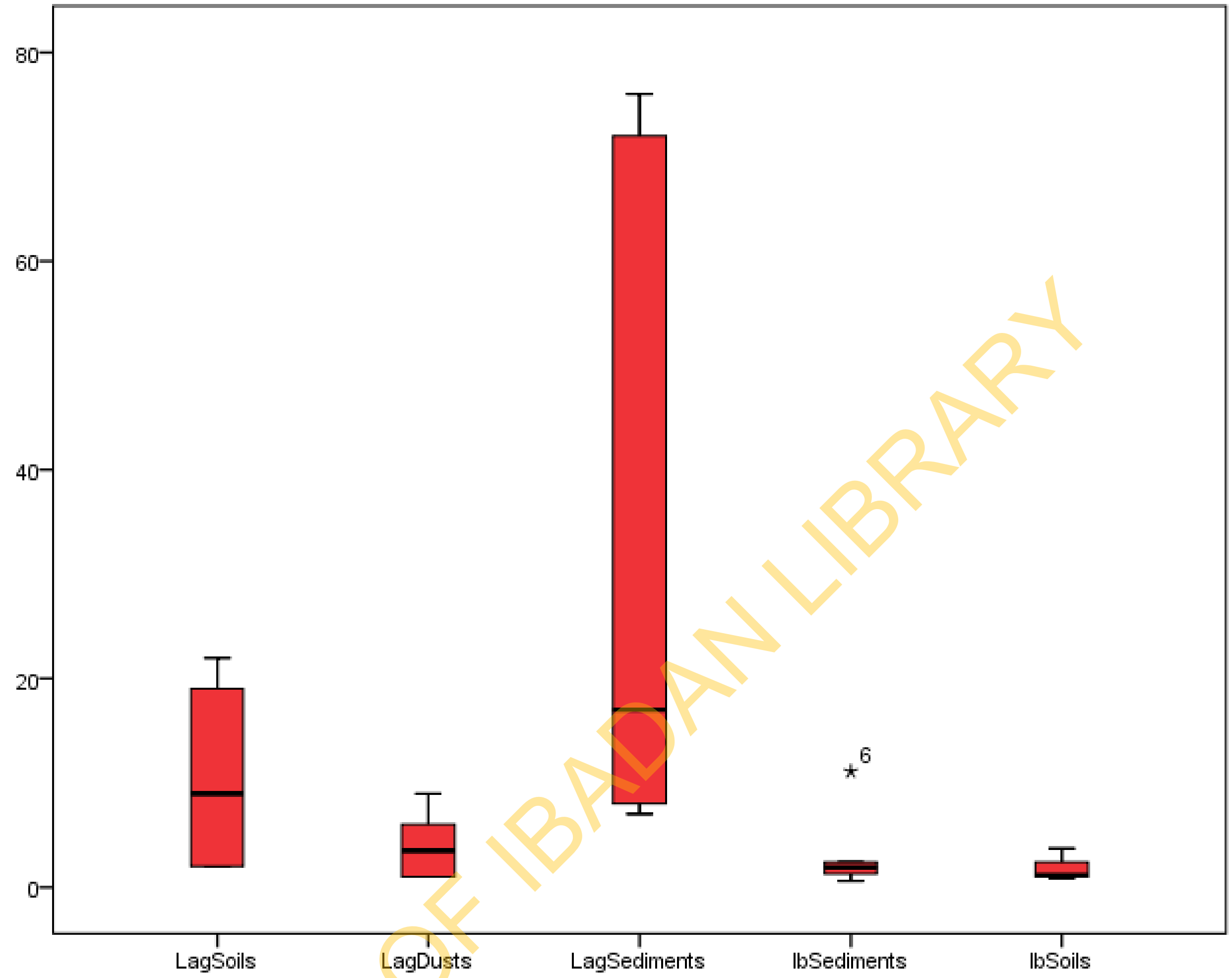


Figure 4.63. Geo-accumulation Indices of Hg in the study areas

4.10. Lead (Pb) Isotopes Geochemistry

4.10.1 Lead (Pb) Isotopes Geochemistry of Lagos Environments

In Pb-Isotopes environmental geochemistry, there are two different types of lead. These are primordial lead (lead that has been around since the formation of the earth at a fixed isotopic composition) and radiogenic lead (lead produced by the decay of uranium and thorium). The uranogenic Pb-206 and Pb-207 (i.e. Pb isotopes that are derived as daughter cells from disintegration or decay of uranium as parent cell) as well as the thoriogenic Pb-208 (i.e. Lead isotope derived as daughter cell from disintegration of thorium as parent cell) are normalized with the non-radiogenic isotope Pb-204. Pb isotopes are generally represented as $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$. Four Pb isotopes were analyzed in this work and these were Pb-204, Pb-206, Pb-207 and Pb-208. The summary of these Pb isotopes in the three media sampled in Lagos metropolis as well as the Coastal Plain sands and their isotopic ratios (IRs) are presented in Table 4.25.

The concentration of Pb-204 ranged from 1.43 to 31.00 ppm in soils with mean value of (5.78 ± 7.12) ppm. Pb-206 ranged from 25.26 to 509.74 ppm with a mean value of (97.37 ± 115.6) ppm (accounts for 24.9% of the total Pb in soils). This is almost twenty folds of the non-radiogenic stable isotope (Pb-204) while Pb-207 and Pb-208 ranged from 21.96 to 446.22 ppm and 52.61 to 1089.93 ppm with mean values of (85.05 ± 100.8) ppm and (203.36 ± 246.88) ppm, respectively (Fig. 4.64).

The results of Pb isotopes in sediment samples from Lagos (Table 4.25) and their relative percentage distributions are presented in Fig.4.65. The concentration of primeval lead isotope (Pb-204) ranged from 1.87 to 3.54 ppm with mean value of (2.36 ± 0.48) ppm while the radiogenic isotopes, Pb-206 ranged from 33.3 to 61.6 ppm with a mean of (41.6 ± 2.4) ppm; Pb-207 ranged from 29.0 - 53.7 ppm with mean value of (36.3 ± 7.2) ppm and Pb-208 concentrations ranged from 69.3 to 126.9ppm with a mean value of (87.1 ± 16.8) ppm (Table 4.25).

Pb-204 in road dusts ranged from 2.3 to 11.8 ppm with a mean of (4.91 ± 3.02) ppm, Pb-206 from 39.79 to 196.3 ppm with a mean of (84.9 ± 49.3) ppm; Pb-207 ranged from

(35.3 to 169.2) ppm with a mean of (73.8 ± 42.4) ppm while the Pb-208 concentration ranged from (84.4 to 421.7) ppm with mean of (177.1 ± 106.6) ppm (Table 4.25). The percentage distributions (relative abundance) of these four Pb isotopes (Pb-204, -206, -207 and -208) varied significantly (Fig.4.65).

The Recent Alluvial and Coastal Plain sands underlying Lagos metropolis were characterized by low concentrations of Pb and Pb isotopes (Pb-204, Pb-206, Pb-207 and Pb-208) (Table 4.25 and Fig. 4.65). The concentrations of Pb isotopes in these samples also showed that Pb-204 ranged from (0.03 - 0.06) ppm, Pb-206 ranged from (0.56 - 1.21) ppm, Pb-207 ranged from (0.47 - 1.01) ppm and Pb-208 ranged from (1.22 - 2.57) ppm. The concentrations and variations of Pb isotopes in these Coastal Plain sands were used as background values for Pb isotopes in the secondary materials.

The percentage mean distributions of the four Pb isotopes in the sampled media and the Coastal Plain sands remained fairly constant and were within the percentage distribution presented by Komarek et al., (2008). The concentrations of the three radiogenic Pb isotopes (Pb-206, Pb-207 and Pb-208) in the sampled media from Lagos metropolis (soils, sediments and roadside dusts) were normalized with their respective primordial lead (Pb-204) concentrations (Table 4.25), in order to remove the effect of the stable isotope lead (Pb-204).

The normalized data, (Table 4.25) showed that Pb-206 ranged from 16.22 - 17.95 with mean of 17.33 and accounting for 25.3% of the percentage distribution of total Pb isotopes, Pb-207 ranged from 14.01 - 15.81 with mean of 15.14, accounting for 22.1% of total Pb isotopes while Pb-208 ranged from 33.74 - 37.98 with mean of 35.91 (52.6%). It was observed that the relative percentage distributions of the three radiogenic isotopes remained fairly constant after normalization. The evaluated results of the three isotopes in the three media showed that soils have the highest radiogenic Pb (Pb-206, Pb-207 and Pb-208) isotopes, followed by roadside dusts while sediments have the least (i.e. soils > dusts > sediments) (Table 4.25 and Fig. 4.66). This could be explained by different mobility of Pb in the three media.

Table 4.25. Summary of Pb Isotopes and Their IRs in Lagos Media

	SOILS		**RDS**		**SEDIMENTS**		**COASTAL PLAIN SANDS**	
PARAMETER	RANGE	MEAN	RANGE	MEAN	RANGE	MEAN	RANGE	AV.
Pb-204	1.43 - 31.00	5.78 ± 7.12	2.25 - 11.75	4.91 ± 3.02	1.87 - 3.54	2.36 ± 0.48	0.03 - 0.06	0.05
Pb-206	25.26 - 509.74	97.37 ± 115.60	39.79 - 195.26	84.92 ± 49.30	33.3 - 61.63	41.61 ± 8.30	0.56 - 1.21	0.89
Pb-207	21.96 - 446.22	85.05 ± 100.88	35.28 - 169.23	73.84 ± 42.44	29.03 - 53.66	36.32 ± 7.17	0.470 - 1.01	0.74
Pb-208	52.61 - 1089.93	203.36 ± 246.88	84.36 - 421.66	177.07 ± 106.06	69.28 - 126.88	87.09 ±16.83	1.22 - 2.57	1.90
^{206}Pb/^{204}Pb	16.22 - 17.95	17.33 ± 0.52	16.62 - 18.02	17.54 ± 0.44	17.41 - 17.95	17.64 ± 0.19	18. 67 - 20.17	19.417
^{207}Pb/^{204}Pb	14.01 - 15.81	15.14 ± 0.46	14.40 - 15.90	15.30 ± 0.5	15.16 - 15.62	15.40 ± 0.15	15. 67 - 16. 83	16.25
^{208}Pb/^{204}Pb	33.74 - 37.98	35.91 ± 1.30	34.80 - 37.86	36.48 ± 1.1	35.84 - 37.56	36.95 ± 0.47	40.67 - 42.83	41.75
^{206}Pb/^{207}Pb	1.11 - 1.19	1.15 ± 0.02	1.12 - 1.17	1.15 ± 0.2	1.12 - 1.17	1.15 ± 0.01	1.192 - 1.198	1.195
^{207}Pb/^{206}Pb	0.84 - 0.90	0.87 ± 0.01	0.85 - 0.89	0.87 ± 0.01	0.85 - 0.89	0.873 ± 0.01	2.124 - 2.179	2.151
^{208}Pb/^{206}Pb	1.97 - 2.14	2.07 ± 0.05	2.20 - 2.16	2.08 ± 0.05	2.06 - 2.11	2.10 ± 0.02	0.835 - 0.839	0.837
^{208}Pb/^{207}Pb	2.234 -2.443	2.372 ± 0.045	2.334 - 2.454	2.392 ± 0.065	2.363 - 2.456	2.399 ± 0.021	2.545 - 2.596	2.570

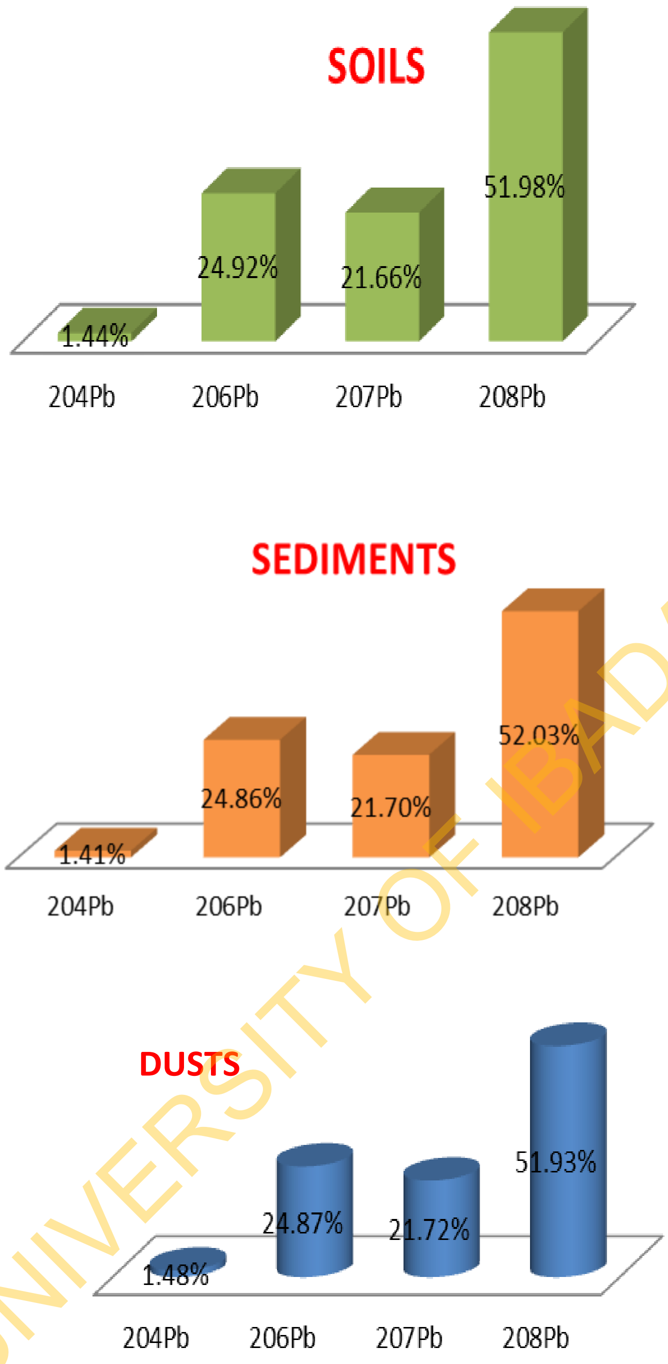
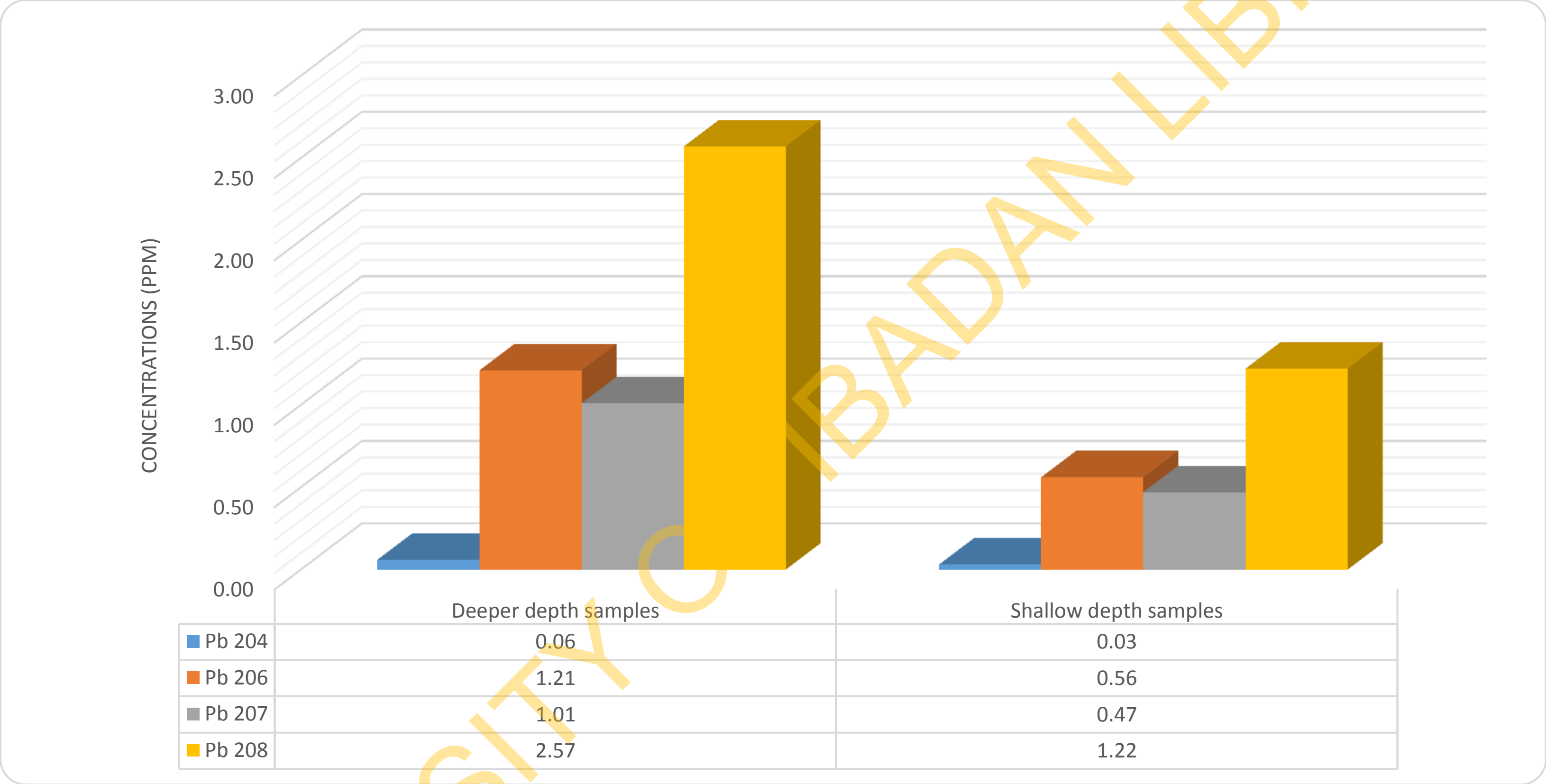
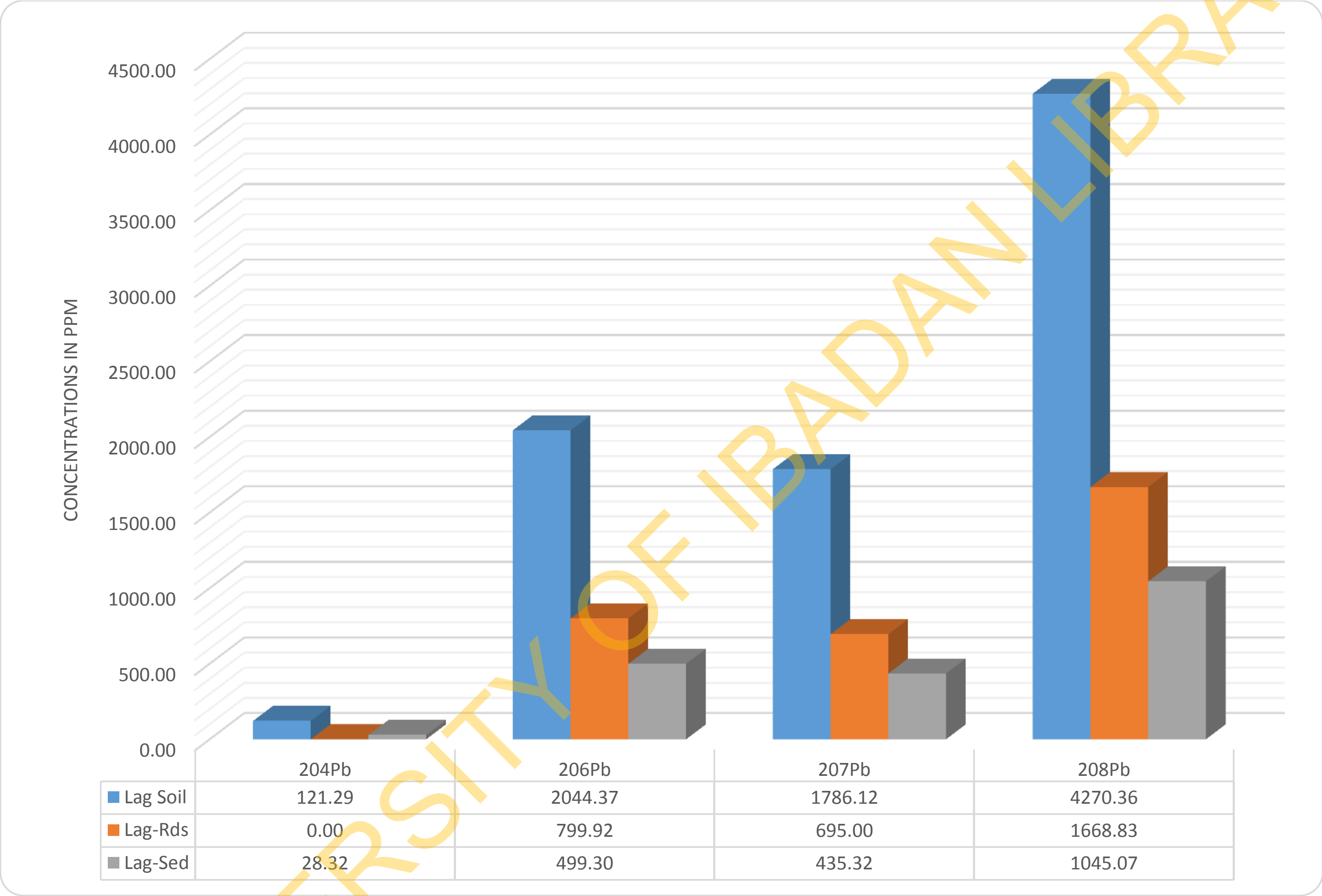


Figure 4.64. Relative % Distributions of Pb Isotopes in Lagos Media



	Deeper depth samples	Shallow depth samples
🟦 Pb 204	0.06	0.03
🟧 Pb 206	1.21	0.56
⬜ Pb 207	1.01	0.47
🟨 Pb 208	2.57	1.22

Figure 4.65. Relative distributions of Pb Isotopes in Coastal Plain sands of Lagos metropolis



	204Pb	206Pb	207Pb	208Pb
🟦 Lag Soil	121.29	2044.37	1786.12	4270.36
🟧 Lag-Rds	0.00	799.92	695.00	1668.83
⬜ Lag-Sed	28.32	499.30	435.32	1045.07

Figure 4.66. Summary of Total Pb Isotopes of the three environmental compartments in Lagos

4.10.2 Lead (Pb) Isotopes Geochemistry of Ibadan Rocks, Sediments and Soils

The Pb isotopes of the rock samples from Ibadan were used as the background values for Pb isotopes in soils and sediments from Ibadan metropolis (Table 4.26 and Fig.4.67). The concentrations of Pb-204 in the rock units ranged from 0.02 to 0.1ppm with an average value of 0.05ppm, Pb-206 concentrations ranged from 0.06 to 2.33ppm with an average value of 1.25ppm, Pb-207 ranged from 0.38 to 1.56ppm with an average value of 0.83ppm while Pb-208 ranged from 1.19 to 4.13ppm with an average value of 2.37ppm. The relative abundance of these isotopes agreed with the natural abundance of Pb isotopes presented in Komarek et al., 2008.

The concentrations of the four isotopes in Ibadan sediments varied from sample to sample and a larger scale of variability was observed from one isotope to another (Table 4.27). The concentrations of non-radiogenic lead (Pb-204) ranged from 1.72 to 47.4ppm with a mean value of (7.58 ± 9.58) ppm while the radiogenic Pb, Pb-206 ranged from 30.7 to 779.7ppm and mean value of (127.0 ± 154.7) ppm. Similarly, Pb-207 concentrations ranged from 27.0 to 664.5ppm with a mean value of (109.1 ± 132.1) ppm while the concentration of thoriogenic derived Pb isotope (Pb-208) ranged from 65.8 to 1642.3ppm with a mean of (263.0 ± 327.0) ppm (Table 4.27). The relative abundance of the four Pb isotopes in the Ibadan sediment samples showed that they remained fairly constant with the relative natural abundance recommended by Komarek, et al, 2008 (Fig. 4.68).

The stable Pb isotopes ratios in Ibadan sediments were plotted against one another and a positive linear relationship was observed between the three isotopes. The significance of this relationship decreases from ^{206}Pb/^{207}Pb through ^{208}Pb/^{207}Pb to ^{208}Pb/^{206}Pb as observed in their coefficient of variation 'r' which decreases from 0.90 to 0.71 (Fig.4.68). This is an indication of a close similarity in Pb contents. The difference in 'r' could probably be linked to the fractionation of Pb-isotopes during Pb formation as Pb-208 is a precursor or daughter cell of the decay of Th-232 while Pb-206 and Pb-207 isotopes are daughter cells of the decay of U-238 and U-235 respectively.

Table 4.26. Pb Isotopes of the Ibadan MGC and their Isotopic Ratios (in ppm)

	Pb 204	Pb 206	Pb 207	Pb 208	^{206}Pb/^{207}Pb	^{207}Pb$^{/206\text{Pb}}$	^{208}Pb/^{206}Pb	^{208}Pb/^{207}Pb
G. Gneiss	0.10	2.33	1.56	4.13	1.494	0.670	1.773	2.648
G. Gneiss	0.07	1.66	1.14	3.39	1.456	0.687	2.042	2.974
B. Gneiss	0.05	1.20	0.74	2.33	1.622	0.617	1.942	3.149
B. Gneiss	0.04	1.14	0.65	2.04	1.753	0.570	1.789	3.139
A. Gneiss	0.02	0.60	0.38	1.19	1.579	0.633	1.983	3.132
S. Amphib.	0.04	0.92	0.63	1.80	1.460	0.685	1.957	2.857
Amphibolite	0.04	0.89	0.55	1.68	1.618	0.618	1.888	3.055

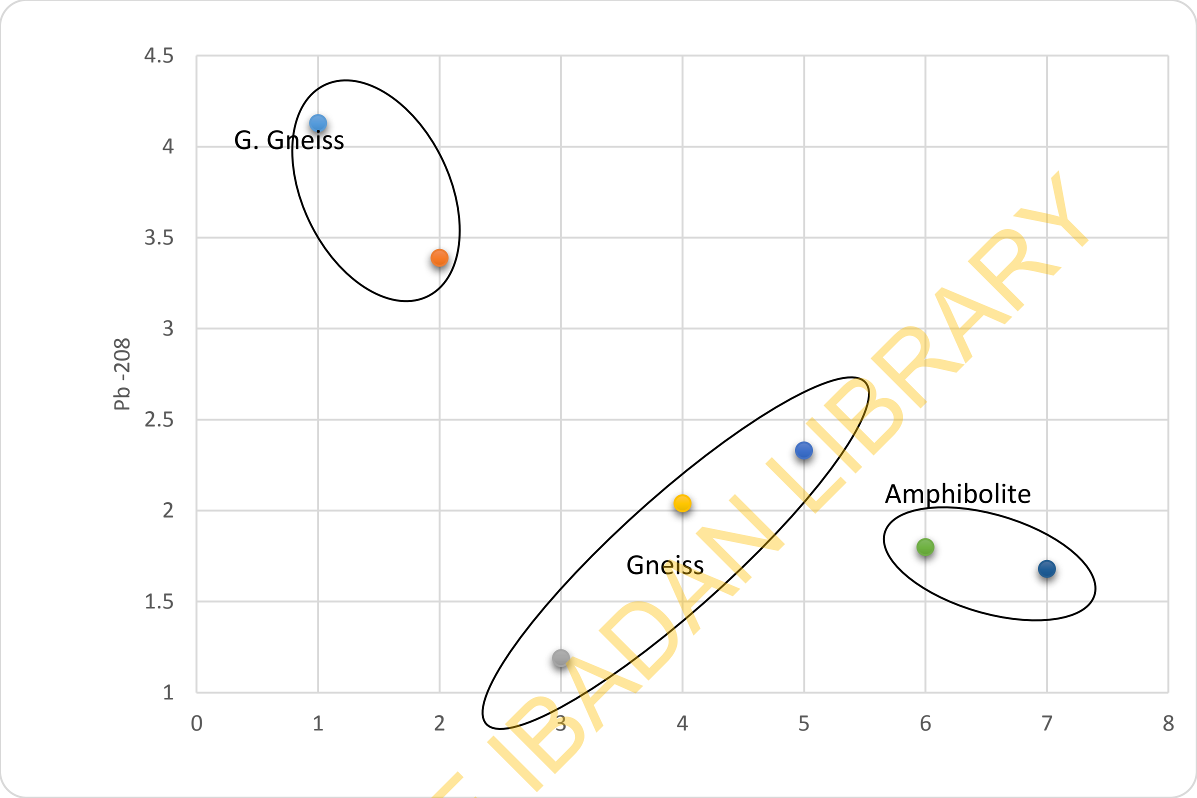
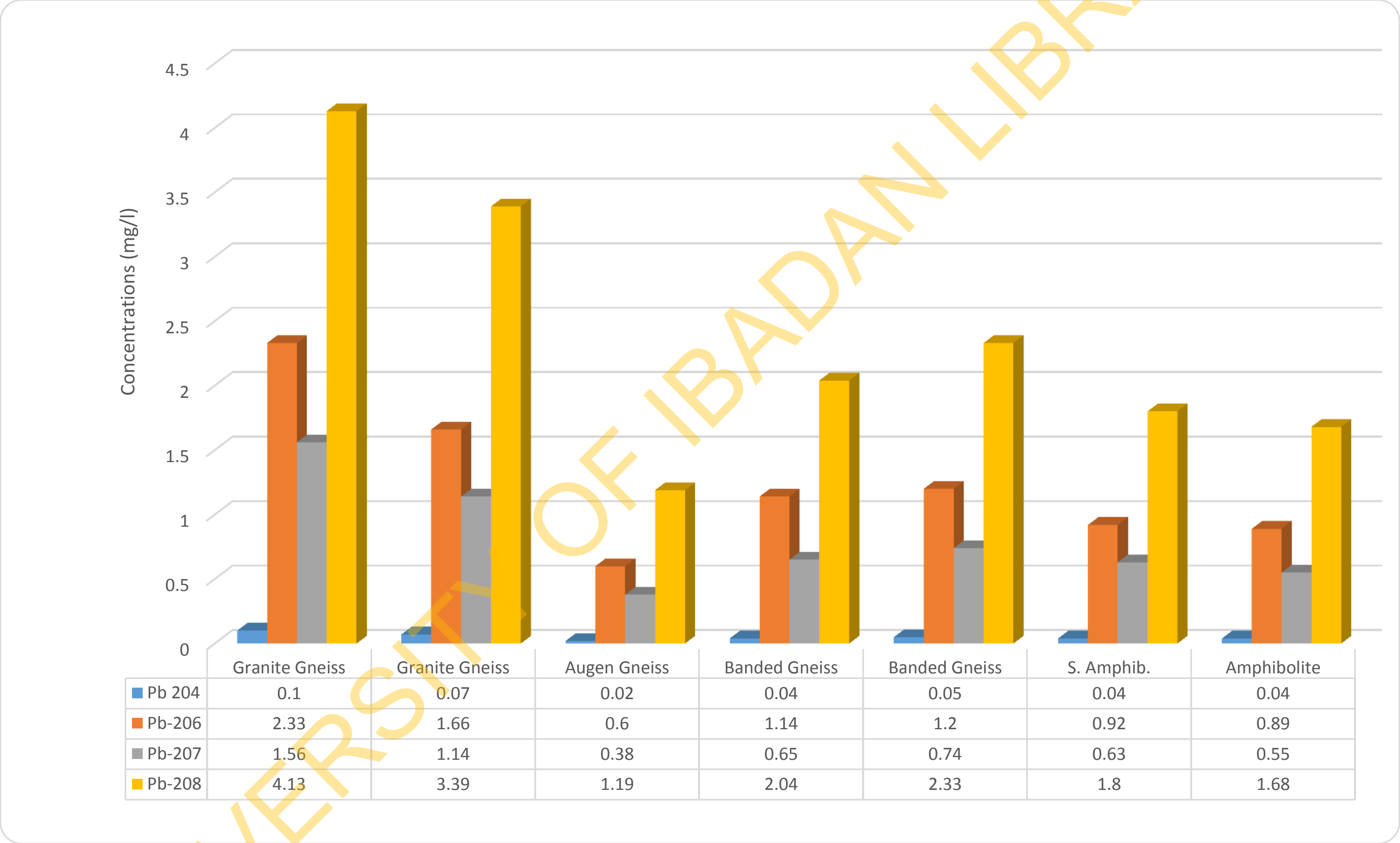


Figure 4.67a. Variations of Pb-Isotopes in Ibadan Rock Units



	Granite Gneiss	Granite Gneiss	Augen Gneiss	Banded Gneiss	Banded Gneiss	S. Amphib.	Amphibolite
Pb 204	0.1	0.07	0.02	0.04	0.05	0.04	0.04
Pb-206	2.33	1.66	0.6	1.14	1.2	0.92	0.89
Pb-207	1.56	1.14	0.38	0.65	0.74	0.63	0.55
Pb-208	4.13	3.39	1.19	2.04	2.33	1.8	1.68

Figure 4.67b. Relative Compositions of Pb Isotopes in Ibadan Rock Units

Table 4.27. Summary of Lead (Pb) Isotopes and Their Isotopic Ratios in Ibadan Environments

	IBADAN SEDIMENTS		**IBADAN SOILS**		**IBADAN MGC**	
	Range	**Mean ± S.D.**	**Range**	**Mean ± S.D.**	**Range**	**Average**
Pb-204	1.72 - 47.41	7.58 ± 9.58	1.89 - 6.97	4.79 ± 5.89	0.02 - 0.10	0.05
Pb-206	30.69 - 779.68	127.04 ± 154.74	33.14 - 118.29	82.58 ± 104.56	0.6 - 2.33	1.25
Pb-207	27.00 - 664.46	109.05 ± 132.07	28.54 - 102.97	71.13 ± 90.54	0.38 - 1.56	0.81
Pb-208	65.67 - 1642.27	262.99 ± 326.95	69.76 - 238.62	165.95 ± 258.43	1.19 - 4.13	2.37
^{206}Pb/^{204}Pb	16.00 - 18.12	17.33 ± 0.58	16.95 - 17.91	17.54 ± 0.56	22.25 - 30.00	24.966
^{207}Pb/^{204}Pb	13.60 - 15.97	14.91 ± 0.57	14.77 -17.02	15.284 ± 0.61	13.75 - 19.00	15.919
^{208}Pb/^{204}Pb	33.64 - 38.43	35.55 ± 1.37	33.99 -37.573	35.421 ± 1.22	41.30 - 59.70	47.689
^{206}Pb/^{207}Pb	1.13 - 1.20	1.16 ± 0.02	1.137 - 1.187	1.164 ± 0.01	1.456 - 1.753	1.570
^{208}Pb/^{206}Pb	1.93 - 2.14	2.05 ± 0.06	1.933 - 2.105	2.02 ± 0.05	1.789 - 2.042	1.910
^{207}Pb/^{206}Pb	0.83 - 0.89	0.86 ± 0.01	0.843 - 0.897	0.86 ± 0.01	0.570 - 0.685	0.640
^{208}Pb/^{207}Pb	2.281 - 2.507	2.387 ± 0.05	2.141 - 2.444	2.320 ± 0.04	2.647 - 3.149	2.990

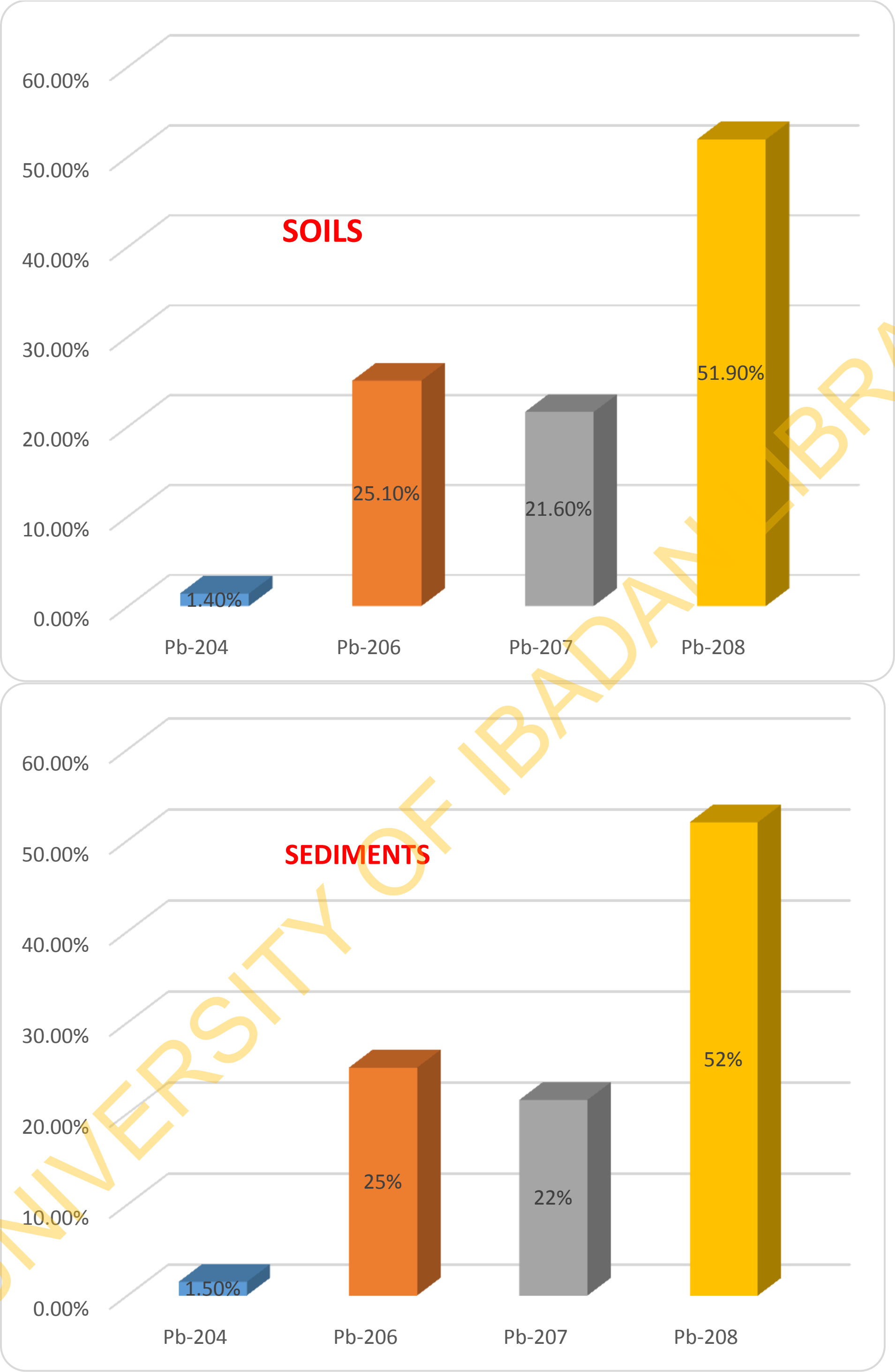
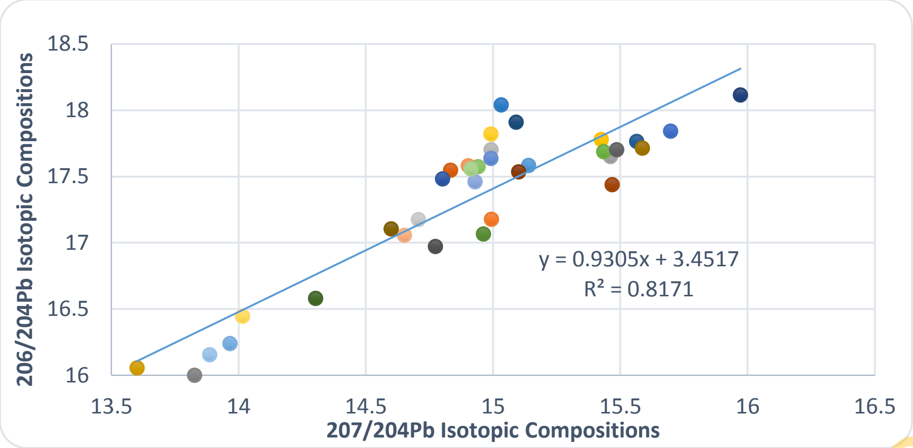
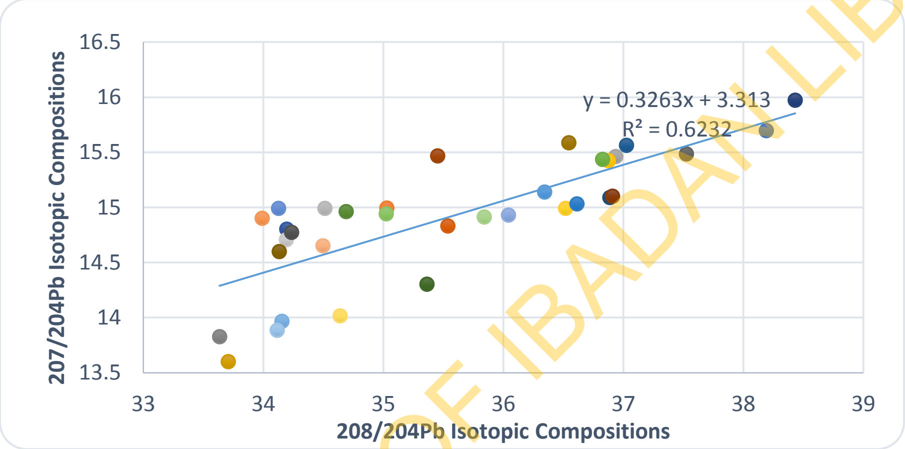


Figure 4.68. The Relative Percentage Distributions of Pb Isotopes in soils and sediments of Ibadan Metropolis



a.



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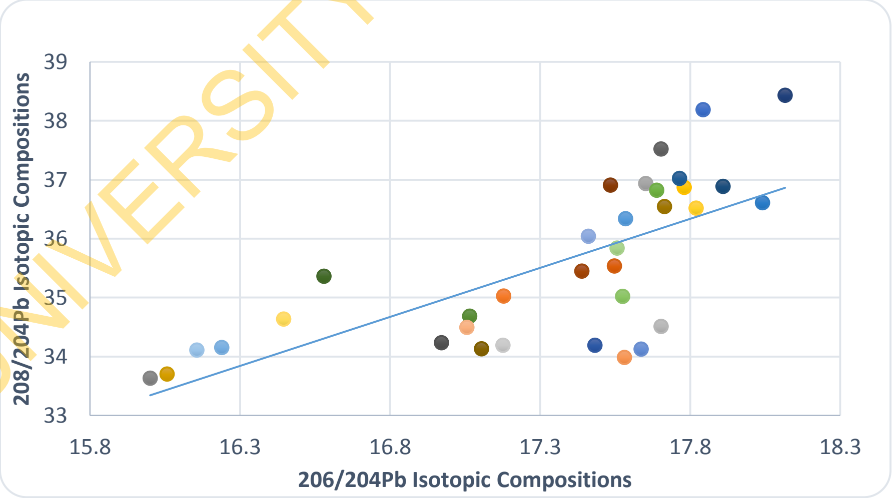


c.

Figure 4.69. Correlation Matrices of some Pb IRs in Ibadan Sediments

The Pb isotopes data obtained from Ibadan soils (Table 4.27) showed that the concentrations of Pb-204 ranged from 1.89 to 6.97ppm with an average value of 4.42ppm, Pb-206 ranged from 33.14 to 118.3ppm with an average of 76.0ppm while Pb-207 and Pb-208 ranged from 28.54 to 102.97ppm and 69.76 to 238.62ppm with average values of 65.3ppm and 153.9ppm respectively.

The average values of the four isotopes in soils and sediments were compared with each other and subsequently with the background values in the rock units. Stream sediments showed 2-folds enrichments over the soils isotopic compositions. A comparison of the range of values of the four isotopes in Ibadan sediments with their respective ranges in Ibadan rocks showed that Ibadan sediments were significantly enriched (over 100-folds). Pb-204 isotope in sediment samples was over 100-fold enriched while soils showed 88-fold enrichment. Pb-206 isotope in sediments was 100-fold enrichment over its value in rocks and 60-fold in soils. Pb-207 and Pb-208 isotopes data also display similar trends of enrichments in both soils and sediments with respect to their respective background values.

4.10.3 Lead (Pb) Isotopic Ratios (LIRs) of Lagos Media

It is a common tradition to plot different lead isotope ratios against one another such as (^{206}Pb/^{204}Pb)/(^{207}Pb/^{204}Pb) against (^{207}Pb/^{204}Pb)/ (^{208}Pb/^{204}Pb) which is often expressed as ^{206}Pb/^{207}Pb versus ^{208}Pb/^{207}Pb. Selection of the type of isotope ratios to be plotted against each other is subjective (Duzgoren-Aydin and Weiss, 2008). However, Bird, (2011); Bird et al., (2010) and Bollhofer, (2003) suggested the use of ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios for environmental studies while ^{207}Pb/^{206}Pb ratio is used in the field of geochronology. Source identification requires a distinction between natural and anthropogenic Pb and ^{206}Pb/^{207}Pb ratios has been widely used in identifying Pb pollution (Sun et al., 2011; Cheng and Hu, 2010).

The calculated LIRs of the Recent Alluvia/Coastal Plain sands underlying Lagos metropolis (Table 4.25) showed that the ratios of ^{206}Pb/^{207}Pb varied from 1.192 to 1.198 with an average of 1.195, this range of ratios is almost equal to the average global ratio of

1.2 obtained from the analysis of the upper continental crust and marine sediments from various regions of the globe although some regional variations have been recorded in the literatures such as the Swedish Lake sediments (Renberg et al., 2002) and sediments from pre-Cambrian provinces (Zhu, 1995). ^{207}Pb/^{206}Pb ratios varied from 0.835 to 0.839 with an average ratio of 0.837; ^{208}Pb/^{207}Pb ratios ranged from 2.545 to 2.596 with an average of 2.571 while ^{208}Pb/^{206}Pb ratios ranged from 2.124 to 2.179 with an average of 2.152 in the Coastal Plain sands.

The LIRs of soils revealed that the ratios of ^{206}Pb/^{207}Pb varied from 1.11 to 1.19 with a mean of (1.15 ± 0.02); ^{208}Pb/^{206}Pb ranged from 1.96 to 2.14 with mean of 2.07 while ^{207}Pb/^{206}Pb ranged from 0.84 to 0.90 with mean of 0.87 Table 4.25. Likewise, the calculated LIRs of sediments showed that ^{206}Pb/^{207}Pb varied from 1.12 to 1.17 with a mean of (1.15 ± 0.01); ^{208}Pb/^{206}Pb ranged from 2.06 to 2.11 with mean of (2.10 ± 0.02); Pb-207/206 from 0.85 to 0.89 having a mean of 0.87 while ^{208}Pb/^{207}Pb ranged from 2.363 to 2.456 with an average of 2.399 (Table 4.25). For the IRs of roadside dusts, ^{206}Pb/^{207}Pb varied from 1.12 to 1.17 with a mean of (1.15 ± 0.018); Pb-208/206 ranged from 2.02 to 2.16 with mean of (2.08 ± 0.05); ^{207}Pb/^{206}Pb from 0.85 to 0.89 having a mean of (0.87 ± 0.01) while ^{208}Pb/^{207}Pb ranges from 2.334 to 2.492 with a mean of (2.392 ± 0.04) Table 4.25.

A comparison of the LIRs in the three media with one another showed that soils, sediments and roadside dusts compared favorably with one another. This is an indication of similarities of sources which may be as a result of several factors, especially the increasing dominance of recycling in global Pb production and the international transportation of Pb-ore concentrates and refined Pb, can cause unpredictable changes in the isotopic signatures of industrial sources, with a long-term trend towards homogenization. Further evaluation of the results with the mean values obtained from the underlying Recent alluvial sands, revealed that the Recent alluvial sands is characterized by higher Pb isotopic ratios (^{206}Pb/^{207}Pb (1.195) and ^{208}Pb/^{206}Pb (2.15)) while the sampled environmental media (soils, sediments and roadside dusts) were characterized by low LIRs. This result agreed with Monna et al., (1999) who concluded that the geochemical background Pb have higher LIRs especially (^{206}Pb/^{207}Pb ratios) while the Pb derived from recent industrial sources (anthropogenic Pb) have low LIRs. This trend of higher LIRs in the local background implied that the Pb in soils, sediments and roadside dusts of Lagos metropolis were not derived from the underlying geology of Lagos metropolis. This is also an indication that the underlying Recent alluvial sands contained less radiogenic Pb (with distinct Pb signature) than the three sampled media since lower IRs is typical of more radiogenic Pb (Monna et al., 1999).

4.10.3.1 Lead (Pb) Isotopic Ratios (LIRs) Plots of Lagos Media

In order to ascertain the sources and similarities in Pb concentrations of the various media, the LIRs of the background materials were plotted against those from the media (Fig. 4.70). The plots revealed the two distinct fields with the LIRs in the environmental media clustering together while that of the background clustered separately. This clearly showed that Pb in Lagos soils was unrelated to the underlying bedrocks. This is similar to the plots of Philips, (2007) who crossed plotted the isotopic values of saturated and aromatic fractions of Pb together. He concluded that samples related to one another plotted very close to each other while those that are not related plotted totally in different field. This is an indication that Pb in the environmental media were of different sources from those of the background. Similar scenarios were observed for the plots of road dusts and sediments but with reduced variability in sediments and wide variability in road dusts samples (Figs. 4.70 - 4.72). It is obvious that the Pb types in soils, sediments and roadside soils were characteristically different from the type in the underlying bedrocks and were far from being derived and controlled by the underlying geology of Lagos metropolis (Figs. 4.70- 4.72).

In addition, the Pb isotope ratios of soils, sediments and dusts showed a wide range of variation within the same sampling sites which corresponded with the wide range of Pb concentrations in these media. However, the range of Pb isotopic composition was broadly comparable among the different locations. These results can be attributed to the fact that Pb concentrations of road dusts actually represent the direct accumulation from the automobile emissions and break lining while Pb in soils and drainage sediments represent mixed products of industrial discharges and emissions, vehicular exhausts and a host of other anthropogenic sources.

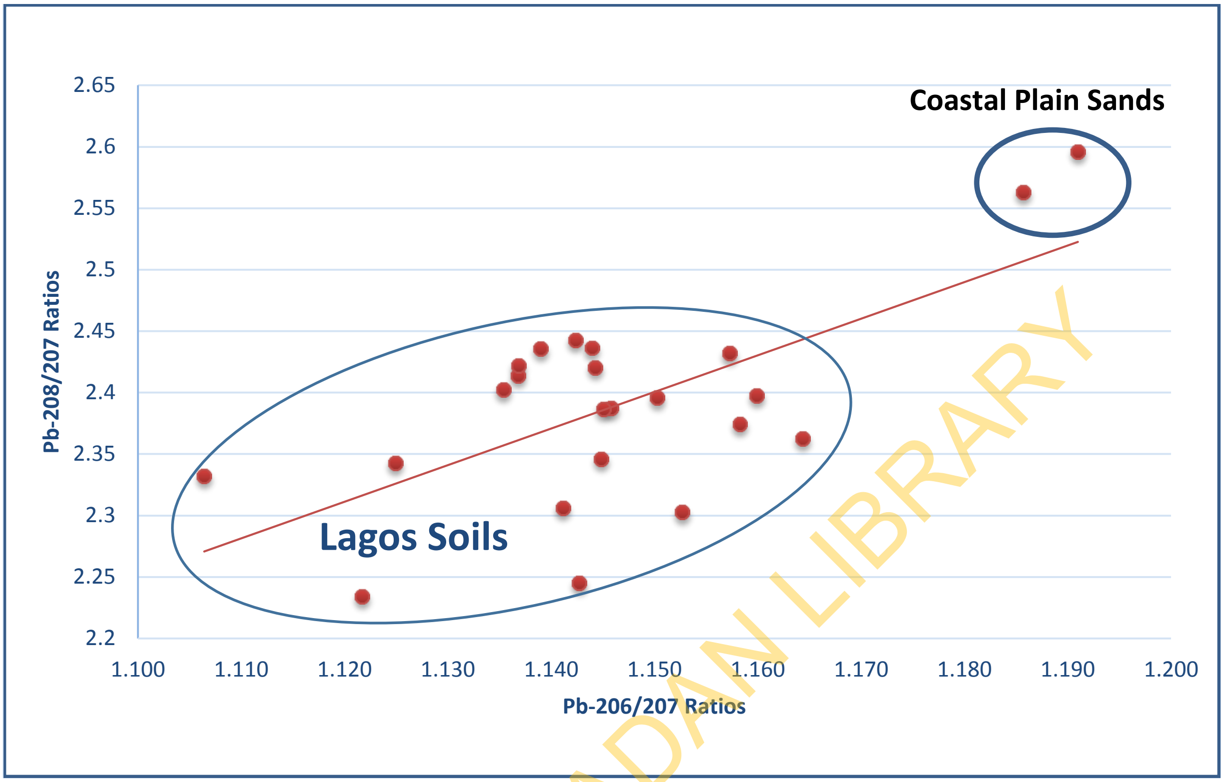


Figure 4.70. Plot of ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb in Coastal Plain Sands and Soil Samples from Lagos Mainland

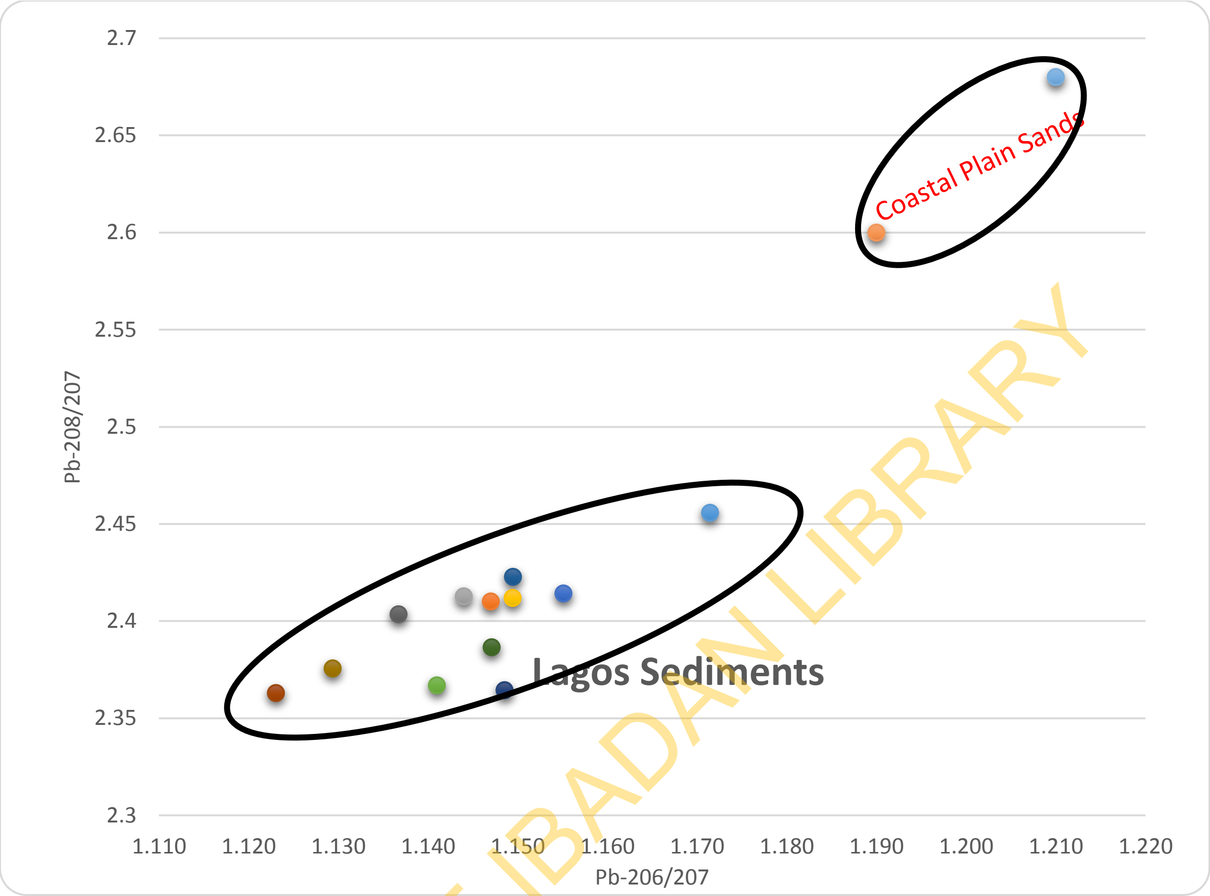


Figure 4. 71. Plot of ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb in Coastal Plain Sands and Sediment Samples from Lagos metropolis

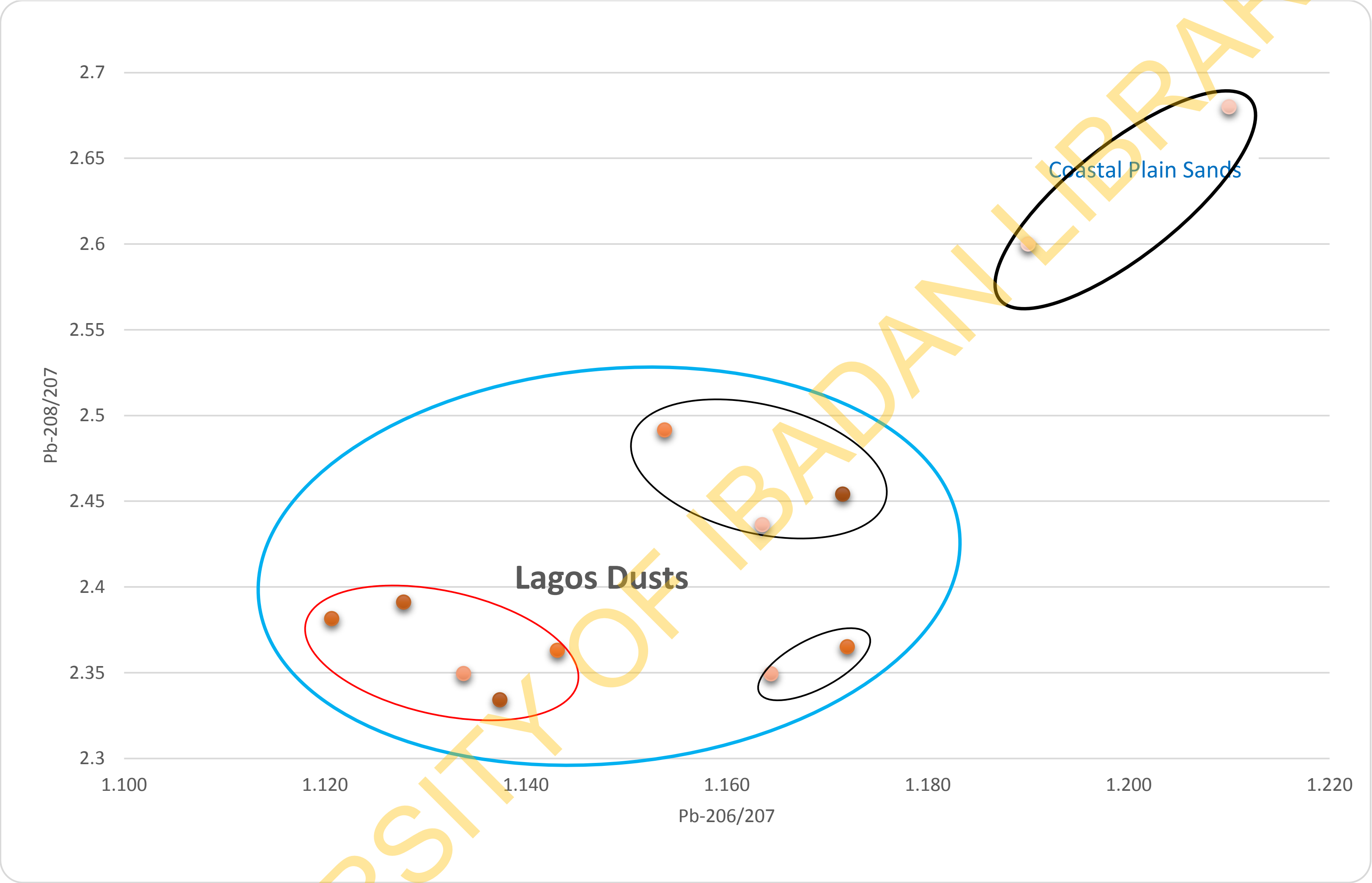


Figure 4.72. Plot of $^{208}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ in Coastal Plain Sands and Road dusts of Lagos Metropolis

4.10.4 Lead Isotopic Ratios (LIRs) of Ibadan Environments

The Pb isotope ratios of the rock, soil and sediment samples collected within Ibadan metropolis were calculated using ^{206}Pb/^{207}Pb, ^{208}Pb/ ^{207}Pb, ^{208}Pb/ ^{206}Pb and ^{207}Pb/^{206}Pb (Table 4.27). The calculated IRs of the sediment and soil samples were compared with the isotopic ratios of the bedrocks from the study area and it was observed that the bedrock materials have higher IRs than the Ibadan sediment and soil samples a similar trend observed for Lagos samples (Table 4.27). A cross plot of these LIRs revealed that the rocks samples plotted in a cluster around the same area while there is a close association with plots from the same type rocks but little variations among rock types (Fig.4.73). This could be an indication of mineralogical differences and variations in rock types as well as their geochronological discrepancies.

The LIRs of stream sediments within Ibadan displayed distinct IRs. Samples from Rivers Omin and Ona were characterized by lower ^{206}Pb/^{207}Pb ratios ranging from 1.127 - 1.153 while samples from Rivers Ogbere and Ogunpa were characterized by higher ^{206}Pb/^{207}Pb ratios ranging from 1.160 - 1.200 with Ogunpa River sediments showing higher IRs than sediments from River Ogbere. These disparities displayed by these rivers are reflections of different catchments drained by the river channels. Rivers Omin and Ona drain areas that are mostly dominated by agricultural practices while Rivers Ogunpa and Ogbere drain the city centre where industrial and commercial activities predominate. The variability of Pb isotopes ratios of Ibadan sediments appeared to indicate the influence of anthropogenic lead from different sources.

A plot of the LIRs of rocks and sediments (Fig. 4.73) revealed that LIRs of stream sediments plotted at lower ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb ends while the bedrocks isotopic ratios plotted at higher ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb ends. These plots revealed that there is no relationship between Pb in bedrock samples and Pb in sediment samples an indication that the Pb were sourced from other origins other than the bedrocks. Furthermore, the clustering of LIRs observed in Ibadan sediments showed similarity in the origins and sources of the various Pb contents in the sediments. A similar trend was also observed between the LIRs of bedrock and soils (Fig. 4.74). It is well known that soils from areas exposed to a rapid and uncontrolled urbanization are highly modified due to the intense human activities.

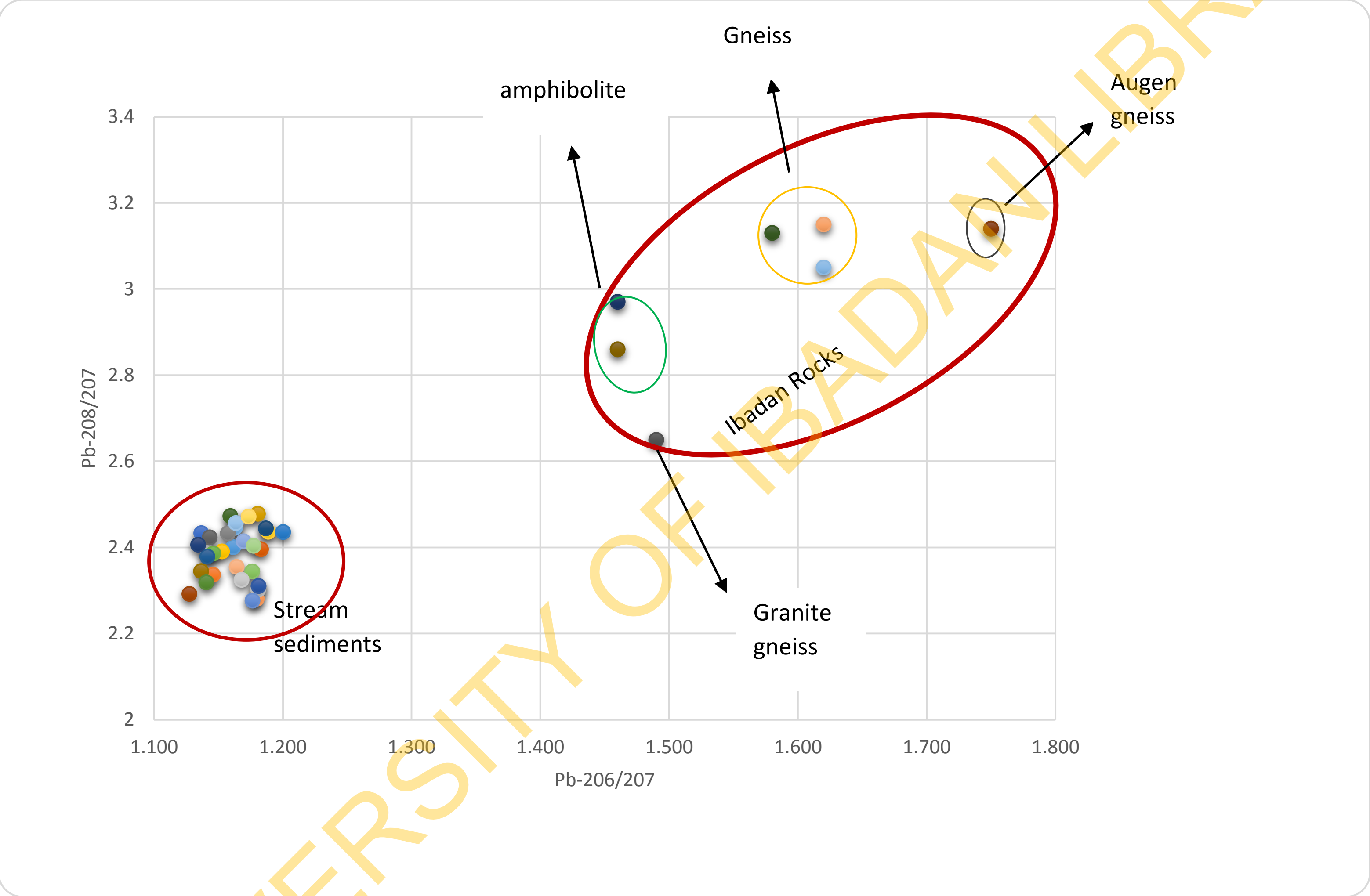


Figure 4.73. Plot of ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb in Ibadan rock units and Stream sediments of Ibadan Metropolis

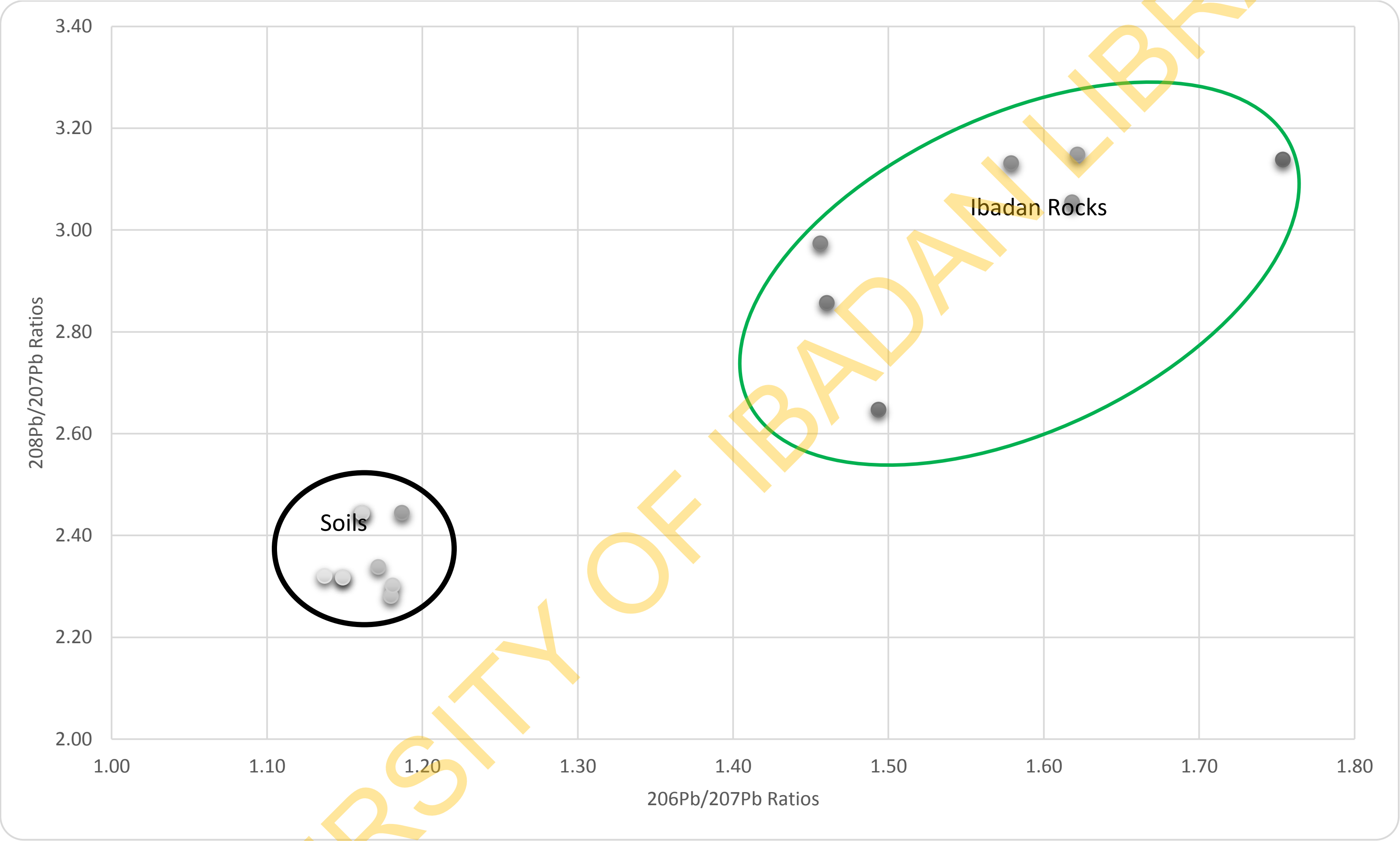


Figure 4.74. Plot of $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ in Ibadan rock units and Soils from Ibadan Metropolis

4.10.5 Quantification of Source inputs using Pb Isotope Ratios

Important Pb sources are commonly identified on the basis of bivariate plots using the ratios of the three normalized isotopes such as ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb (Bird, 2011). Using these plots, various authors such as Ettler et al., (2006); Geraldes et al., (2006); Miller et al., (2002) and Bird *et al*., (2010) have established linear trend of isotopic signatures defining a mixing line between two sources or types of Pb. One of these is usually formed by a significant source of anthropogenic Pb (usually referred to as anthropogenic end-member) while the other is called natural end-member as established by Erel et al., (1997). The anthropogenic end-member defines a significant source of anthropogenic Pb while the natural end-member defines natural source of Pb. If two or more sources of lead exist in a medium, the resulting Pb IRs would be mixed and would reflect the combined IRs of the mixed sources.

In order to determine the natural and anthropogenic end-members, Pb isotopes of five Pb derived sources (galena (2), coal, vehicle exhaust and battery cell) were analysed and their LIRs were evaluated. The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios were plotted with the soils, sediments and dusts samples. The distributions of the samples showed a significant linear relationship with the coefficient correlation (r^2) ranging from 0.5 to 0.7. In Lagos media, the plots showed linear trends where the galena samples plotted in between the natural and the anthropogenic fields while samples of coal, vehicle exhaust and battery cell plotted within the anthropogenic field (Fig.4.75 – 4.77). Thus forming two end-members as established by Erel et al., (1997) while Bird et al., (2010) described this type of trend as suggestive soils or sediments composed of Pb derived from different sources (i.e. diffuse sources) with the linear trend defining a mixing line. Similar trend was also observed in Ibadan stream sediments but the galena samples plotted very close to the anthropogenic field (Fig. 4.78). The similarities of Pb isotopic ratios of galena and other samples with the LIRs of soils, sediments and dusts from study areas (Lagos and Ibadan) showed that Pb in these media were derived from anthropogenic activities since Pb ores either processed or unprocessed do not change their isotopic signatures.

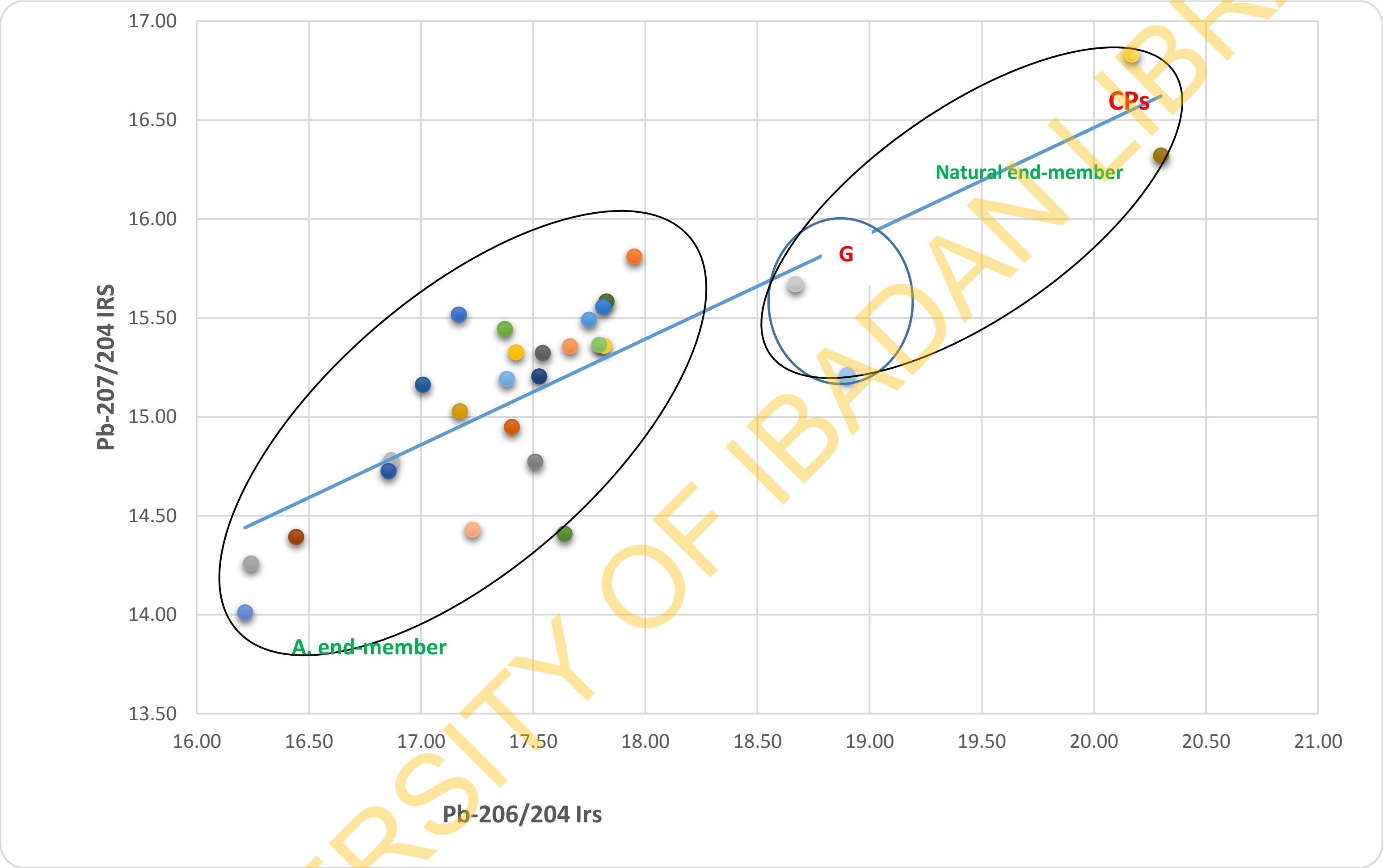


Figure 4.75. Plot of Pb IRs in Lagos soils, Costal Plain sands (CPs), galena(G), Vehicle Exhaust, Coal and battery cell (BC

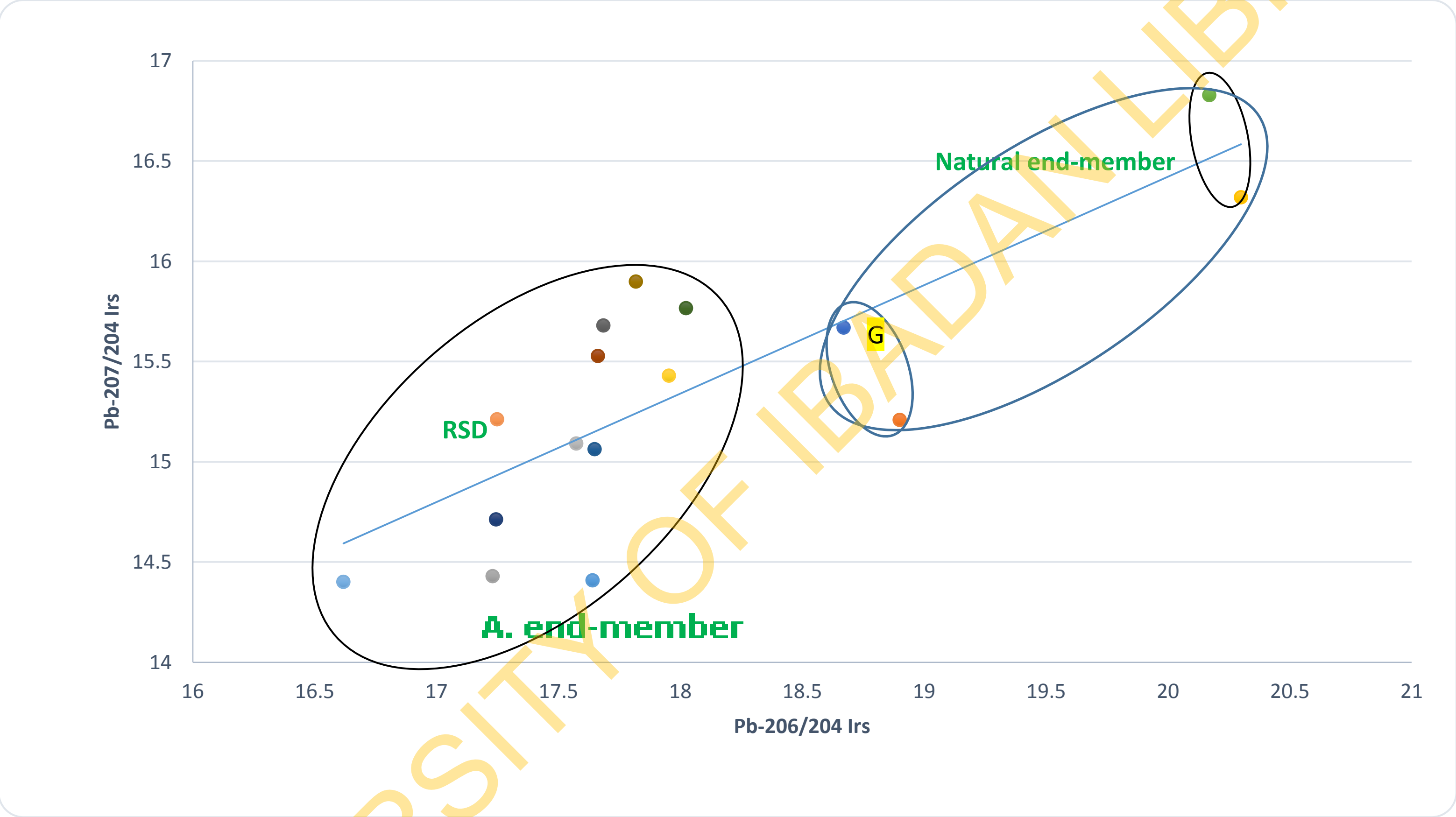


Figure 4.76. Plot of Pb IRs in road dusts (RSD), Costal Plain sands (CPs), galena, aerosol, coal and battery cell (BC)

Figure 4.77. Plot of Pb IRs in Lagos sediments (Sed), Costal Plain sands (CPs), galena, aerosol, coal and battery cell (BC)

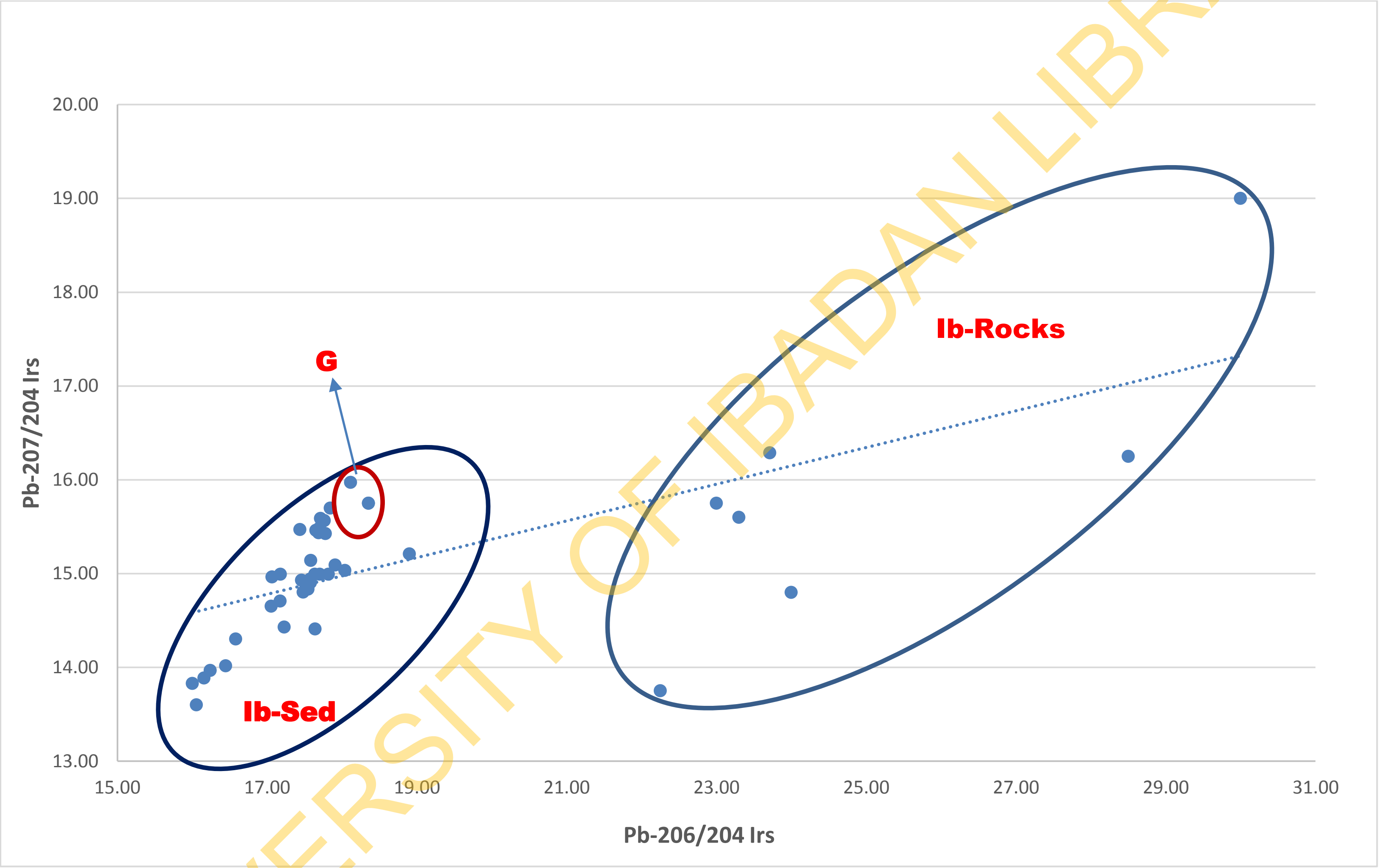


Figure 4.78. Plot of Pb IRs in Ibadan sediments (Ib-Sed), Ibadan rocks (Ib-rocks), galena (G), Vehicle exhaust, coal and battery cell

4.10.6 Differentiation of Lead Species Using the three Isotopes Plots

Bollhofer, (2003) has differentiated between different species of Pb based on decay factor into uranium rich- and thorium rich-LIRs. He concluded that if the Pb is derived solemnly from more uranium parent, the LIRs will be plotted along line AC while thorium derived Pb will plots along CB. However, if a mixing of the two sources of Pb species with different lead isotopes ratios occurs, the Pb isotopic compositions of the mix will lie somewhere on/along the line AB. If three sources mix, the mixture will have an isotopic composition somewhere within the triangle, ABC (Fig. 4.79). This is derived from the fundamental principle that Th-rich materials tend to have higher Pb-208/Pb-207 ratios as Pb-208 is produced from the decay of Th-232 while U-rich materials will head towards the top left corner of a three isotopes plot, as Pb-208/Pb-207 ratios are relatively low and Pb-206/Pb-207 ratios increase as there is relatively more Pb-206 produced than Pb-207.

Plotting these ratios against each other in soils, dusts and sediments from Lagos metropolis showed no particular trend but rather can be seen as being plotted within the Bollhofer triangle, an evidence that Pb in these media were derived from multiple sources. Meanwhile, in Ibadan sediments, two trends were observed, some clustered towards the top left corner of the isotopes plot while others plotted within the triangles. This showed that some the Pb were actually derived from Uranium rich materials while majority of the data set were derived from multiple sources (Figs. 4.80 - 4.83).

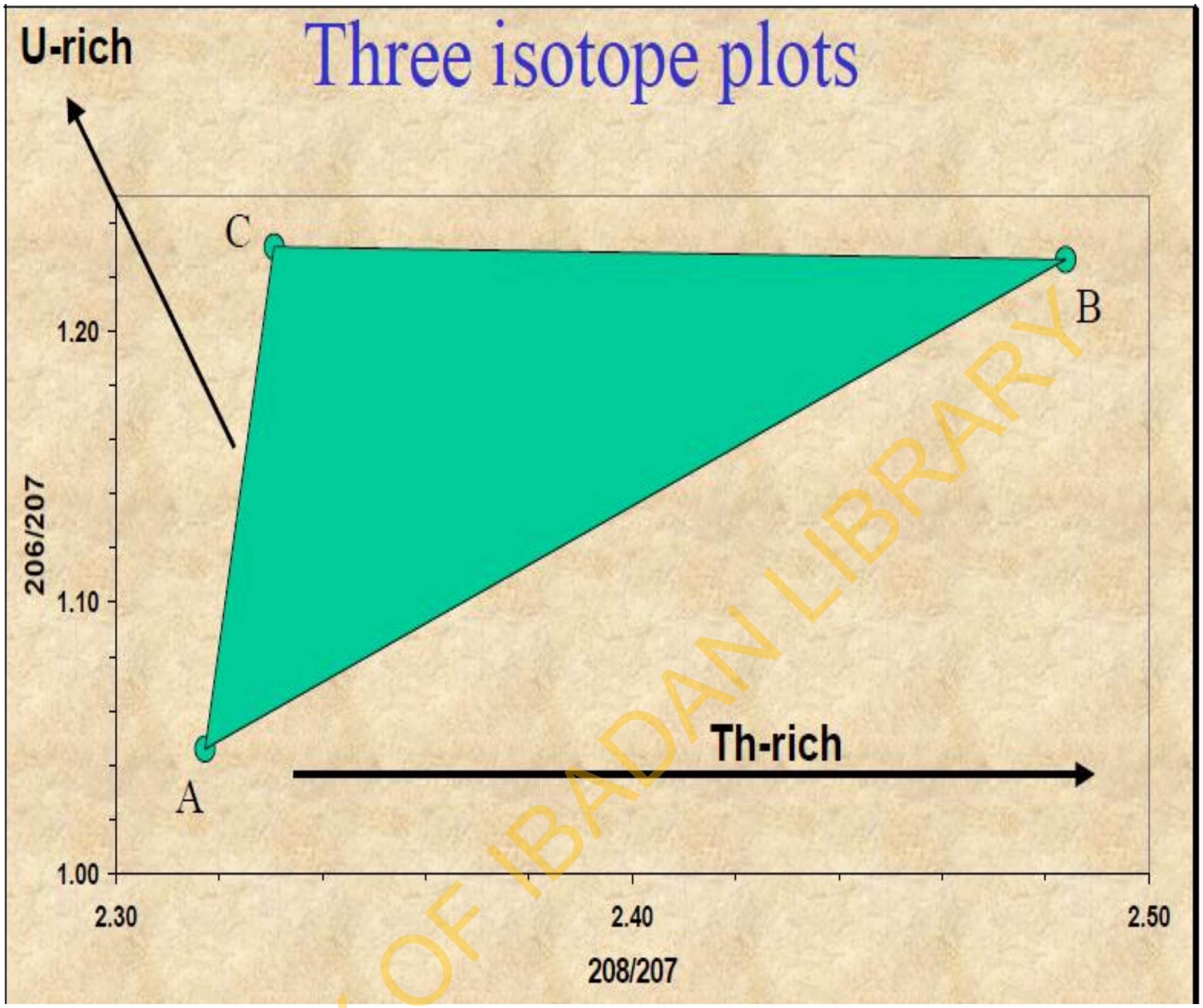


Figure 4.79. Three IRs plot for source identification (after Bollfoher, 2003)

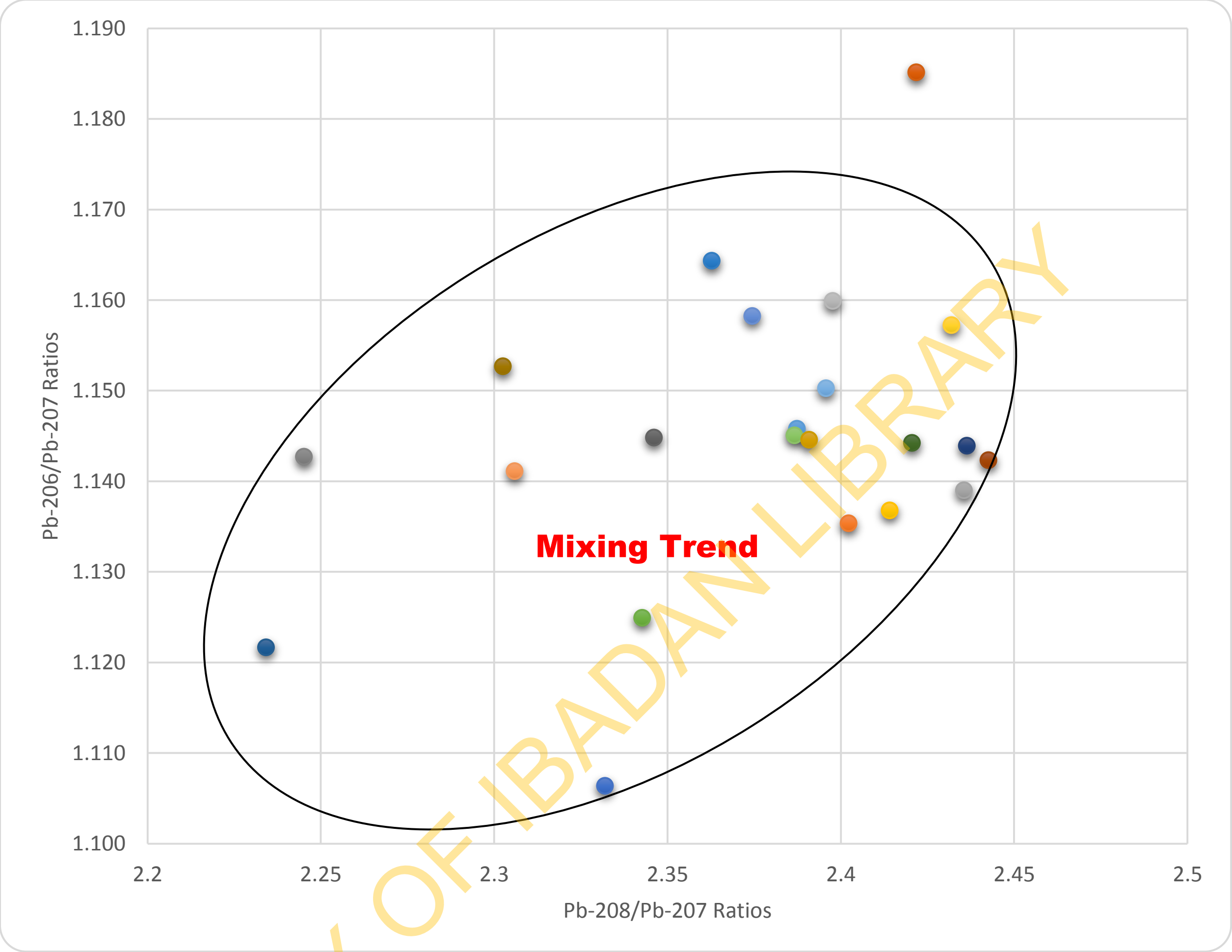


Figure 4.80. Three isotopes plots of Lagos soils

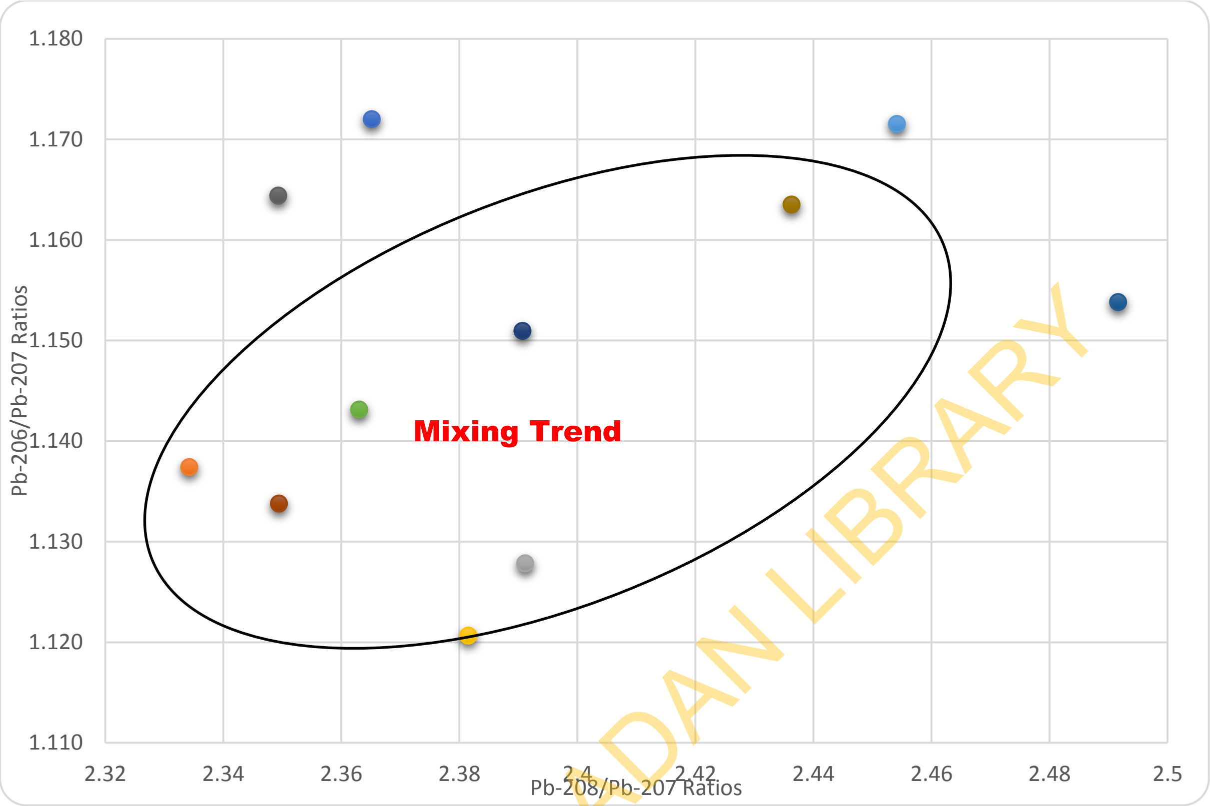


Figure 4.81. Three isotopes plots of Lagos dusts

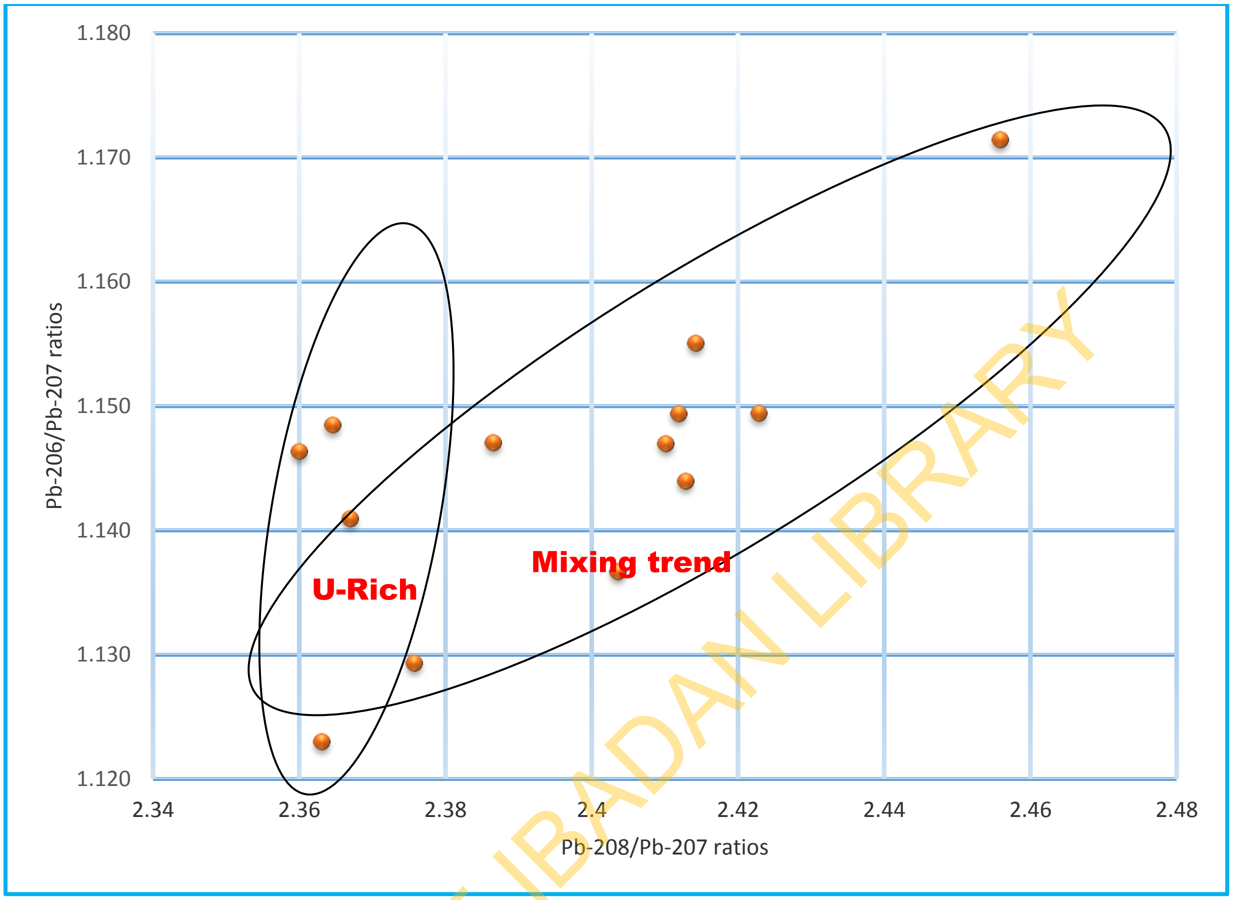


Figure 4.82. Three isotopes plots of Lagos sediments

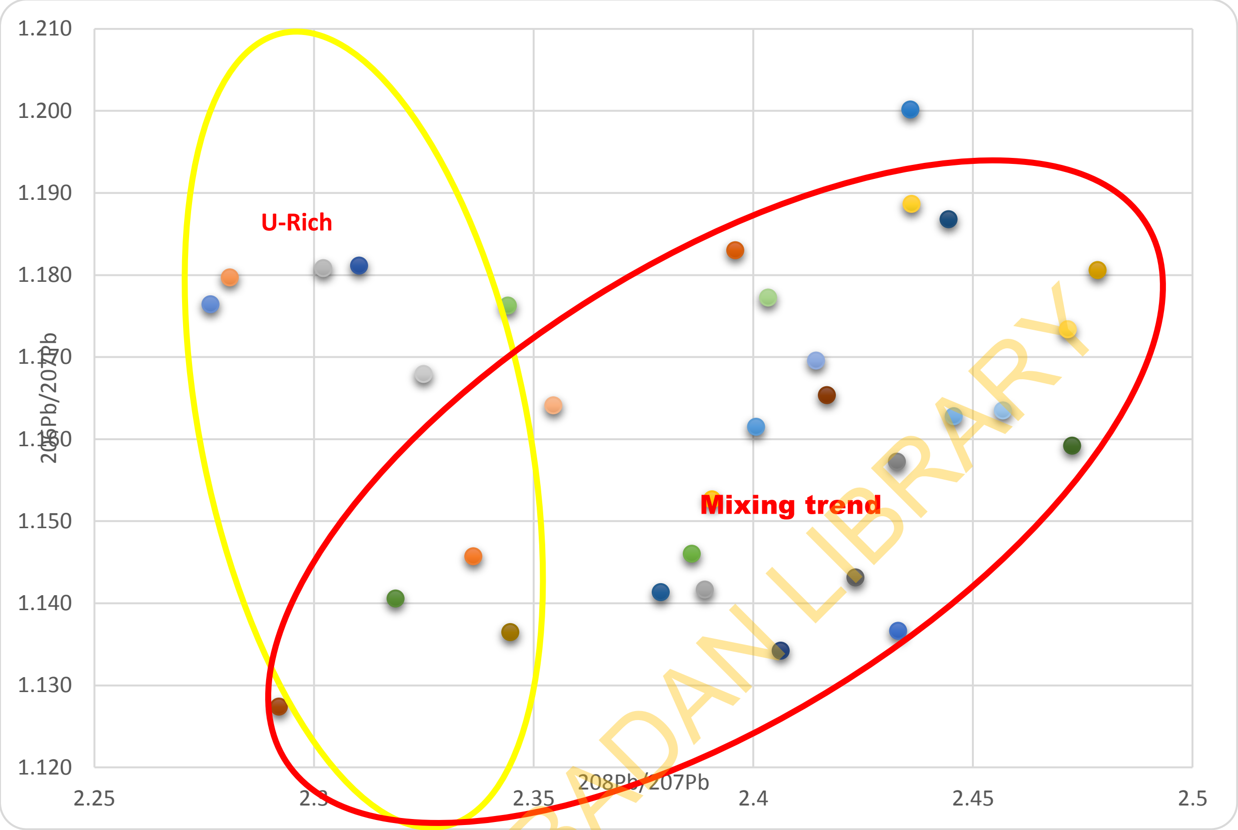


Figure 4.83. Three isotopes plot of Ibadan sediments

4.10.7 Determination of Pb Origins using $^{206}Pb/^{207}Pb$ Isotopic Ratios

A comparison of LIRs of Lagos and Ibadan with some IRs of some cities and world Pb-ore deposits showed that the IRs $^{206}Pb/^{207}Pb$ of soils, sediments and roadside dusts compared favorably with most of the IRs of Pb derived from various parts of the world with exception of USA Pb ores (MVT and Missouri) and Ontario Pb ores (Canada). The ranges of values obtained in Lagos and Ibadan soils, sediments and roadside dusts were within the ranges or means values of Pb ores from Yereva; Chinese Pb ores; European ores; Durango ores (Mexico); New Brunswick (Canada); Altay Kazakhstan (Russia) and Broken Hills Pb ores (Australia) (Table 4.28). This is an indication that the Pb in the environmental media of Lagos and Ibadan may have links with these mines, since industrial processes do not apparently change the isotopic compositions of Pb but retain the IRs of the ore from which its originated.

Using the relative abundance of $^{206}Pb/^{207}Pb$ Ratios, the relative age of Pb ore bodies can be determined. Old Pb ore bodies such as Mont Isa Pb-ores have relatively low $^{206}Pb/^{207}Pb$ Isotopic Ratios while younger Pb-ores have relatively higher ratios. In this study, the relative ratios of Pb-206/207 in Mont Isa (Older Pb ore bodies) and that of MVT Ores (Younger ore bodies) were used to differentiate and characterised the generations of Pb found in soils, sediments and dusts of the study areas. Almost all the sampled media collected from Lagos and Ibadan metropolises have relatively low $^{206}Pb/^{207}Pb$ ratios (ranged from 1.106 to 1.200) (Table 4.28), a comparison with the $^{206}Pb/^{207}Pb$ ratios of the known sources provided strong evidence that the excessive Pb concentrations in Lagos and Ibadan metropolises originated from Pb-ore bodies with low $^{206}Pb/^{207}Pb$ ratios such as Mont Isa, Australian and Canadian Pb ores. This suggests that the Pb in Lagos and Ibadan soils, sediments and dusts were sourced from older Pb ore bodies. It can therefore be concluded that Pb in Nigerian cities belong to the older generations and are older than the Mississippian Valley Types.

The mean contents recorded in soils, sediments and roadside dusts were compared with previous studies in other parts of the world. The results showed that soils, sediments and dusts from Hong Kong, Shanghai, Russia, Mexico, Czech Republic, Scotland, Switzerland and north western parts of France have similar IRs to those of Ibadan and Lagos (Table 4.29).

4.11 Nature of Potentially Harmful Elements

The results of the partitioning of some selected PHEs in the sediments, soils and roadside dusts (<75µm) are presented in Table 4.30. The phases determined were Exchangeable, Carbonate, Reducible, Organic-sulphide and Residual phases. The sequential chemical distributions of the soil, sediments and dust samples showed distinctive differences in the mobility, solubility and potential bioavailability of PHMs between Lagos and Ibadan metropolises. The sequential chemical distribution of selected PHMs in the sediments, soils and road dusts from Lagos and Ibadan metropolises showed that a larger percentage of these heavy metals resided in the non-residual fractions (Table 4.30 and Fig. 4.84).

4.11.1 Exchangeable Phase

Metals in the exchangeable portions can be from authigenic as well as anthropogenic sources. Elements in this fractions are the most mobile and readily available for biological uptake in the environment (Gadde and Laitinen, 1974). In the Lagos sediments, soils and dusts; the heavy metals associated with this phase are relatively very low especially Zn, Cd and As (Table 4.30). The low concentration of this exchangeable phase is suggestive of poor elemental availability in these media. This may be linked to relatively high pH of these media (av.6.96) since alkaline conditions tend to induce a decrease of availability of metals by reducing their solubility and thus the capacity to form chelates (Copeland and Ayenrs, 1972; Forstner and Wittmann, 1983; Singh, *et al.*, 1999). The relative percentage order of mobility of the selected PHMs in this faction for Lagos environment is: Soils, Cu > As > Zn > Cd > Pb; Sediments, Cd > Cu > Zn > As > Pb; and Road Dusts, Cu > As > Zn > Cd > Pb. For Ibadan: Soils, Zn >>>> Cu >> As >> Th > Pb > Cd and for Sediments, Cu > As > Cd = Th > Zn > Pb.

Table 4.28. $^{206}Pb/^{207}Pb$ isotopic ratios of Pb derived from major Pb ore deposits in the world

Pb Origin	Range of $^{206}Pb/^{207}Pb$	Mean	Reference
Ibadan Soils	1.137 - 1.187	1.164 ± 0.01	Current study
Ibadan Sediments	1.127 - 1.200	1.163 ± 0.02	Current study
Lagos Soils	1.106 - 1.185	1.145 ± 0.02	Current study
Lagos Sediments	1.123 - 1.171	1.145 ± 0.012	Current study
Lagos Road Dusts	1.121 - 1.172	1.149 ± 0.2	Current study
Av. Chinese Ores		1.08225	
Yereva		1.16	
European Ores		1.17	
Broken Hill Types	1.03 - 1.10	1.037	Vanhaecke, et al., 1999; Komarek, et al., 2008
MVT (USA)	1.31 - 1.35		
World (range) ore	1.19 - 1.25		
Durango (Mexico)		1.192	Vanhaecke, et al., 1999
Trepan (Yugoslavia)		1.195	
Ontario (Canada)		0.920	
New Brunswick (Canada)		1.160	
Idaho (USA)		1.052	
Missouri (USA)		1.385	
Altay, Kazakhstan (Russia)		1.131	

Table 4.29. ^{206}Pb/^{207}Pb isotopic ratios of soils, sediments and dusts in some parts of the world

Country (Location)		**Range of values**	**Mean ± S.D.**	
Current study (Ibadan)	Soils	1.137 - 1.187	1.164 ± 0.01	
	Sediments	1.127 - 1.200	1.163 ± 0.02	
Current study (Lagos)	Soils	1.106 - 1.185	1.145 ± 0.02	
	Sediments	1.123 - 1.171	1.145 ± 0.012	
	Road Dusts	1.121 - 1.172	1.149 ± 0.2	
United Kingdom		1.059 - 1.079	1.067 ± 0.007	Monna et al. 1997
France (NW)		1.060 - 1.100	1.083 ± 0.015	Veron et al, 1999
France		1.069 - 1.094	1.084 ± 0.009	Monna et al., 1997
Switzerland(Geneva)		1.081 - 1.132	1.113 ± 0.015	Chiaradia and Cupelin, 2000
Switzerland (Milchbuck) (Dusts)		1.109 - 1.118	1.114 ± 0.004	Hansmann & Koppel, 2000
Switzerland (Milchbuck) (Dusts)		1.086 - 1.125	1.107 ± 0.012	Hansmann & Koppel, 2000
Czech Rep.		-	1.110 ± 0.016	Noyak et al., 2003
Czech Republic (Prague)		-	1.135 ± 0.001	Ettler et al., 2004
Israel (Jerusalem)		1.094 - 1.119	1.109 ± 0.007	Erel et al, 1997
Mexico		1.202 - 1.204	1.203 ± 0.001	Sanudo-Wilhelmy & Flegal, 1994
USA		1.040 - 1.390	1.183 ± 0.103	Sturges and Barrie, 1987
Canada		0.920 - 1.190	1.105 ± 0.086	Sturges and Barrie, 1987
Russia		1.134 - 1.149	1.142 ± 0.008	Mukai et al., 2005
China (Shanghai)		1.098 - 1.116	1.110 ± 0.005	Chen et al., 2005
European (Gasoline)		1.12 - 1.15	-	Komarek et al., 2008

4.11.2 Carbonate Phase

Heavy metals in the carbonate fraction of soils or sediments may either be authigenic or detrital lot of trace elements have carbonate species which are relatively stable at pH and Eh conditions (Stumm and Morgan, 1981). In this study, about 50% of Zn and Cd partitioned into this phase in all the sampled media in Lagos while Cd in both soils and sediments from Ibadan, and Zn and Pb in sediments have about 50% or more of their total concentrations in carbonate fraction. All other selected heavy metals have their relative percentage less than 30% in this phase. The overall relative percentage mobility and bioavailability of heavy metals in this phase are: Zn > Cd > Pb > Mn > Cu > As in Lagos and Cd > Zn > Pb > Mn > As > Cu > Th for Ibadan.

4.11.3 Reducible Phase

The Fe and Mn oxide (the reducible phase) of the soils and sediments under oxidizing conditions constitutes a significant sink in both terrestrial and aquatic environments (Gibbs, 1977). This phase accumulates metals from aqueous system by adsorption and co-precipitation. These processes are very sensitive to change in redox potential and minor variations from medium to medium which can affect the relative amounts of heavy metals within this phase. It is the most significant among the labile phases in soils, sediments and roadside dusts from the study areas. The relative percentage concentrations of heavy metals in this phase ranged from 0 to 97% in Ibadan while in Lagos it ranged from 10 to 59%. Majority of the heavy metals in Ibadan sediments and soils have their highest concentrations partitioned into this phase with the exceptions of Pb and Cd and to certain extent As. It is the major phase of portioning for Cu and As in soils, sediments and roadside dusts from Lagos metropolis. Singh et al., (1999) established that colloids of Fe-Mn oxides act as efficient scavengers for many of the heavy metals. Hence, the relatively high percentage of Cu, Zn, Th, As in Ibadan can be traced to the adsorption of these metals by the Fe-Mn colloids. The order of metals apportment in this phase are for Lagos media Cu>As>Pb>Zn>Cd>Mn and Ibadan Th>>Cu>Zn>As>Pb>Cd.

4.11.4 Organic-Sulphide Phase

The association of heavy metals with the organic substances and their decomposition products is of great importance for behavior of trace substances most especially in aquatic systems (Singh et al., 1999). Organic matters play a significant role in the distributions and dispersions of heavy metals in secondary environments by chelation and cation exchange mechanism (Filipek et al., 1982). This phase was observed to be an important scavenger for Pb and Mn in both Lagos and Ibadan (Tables 4.30). About 43 - 83% and 57 - 70% of Pb and Mn respectively in soils and sediments from Ibadan and 51 - 74% and 67 - 76% of Pb and Mn were bound to this fraction in Lagos soils, sediments and roadside dusts which indicated that there are more organic Pb than inorganic Pb. This may be bioavailable when there is slight change in redox conditions of the environments. Considerable portions of Cd, Zn and As in Ibadan soils and sediments were also partitioned into this phase. The relative order of metals in this phase are Mn > Pb >> Cd > Zn > Cu > As and Mn > Pb > Cd > As > Cu > Zn > Th for both Lagos and Ibadan media respectively.

4.11.5 Migration Patterns of Pb and Selected PHMs

Pb in the soils, sediments and dusts from Lagos exhibited similar trend in their distribution patterns where the organic-sulphide fraction was most dominant (51.0 to 74%) followed by the carbonate and reducible fractions (12.5 - 27.6% and 13.5 to 27.2% respectively), with less significance in exchangeable fraction. Pb in Ibadan sediment is associated with carbonate and organic-sulphide fractions with less in reducible and exchangeable fractions but preponderantly associated with organic-sulphide fraction (>80%) in soil (Table 4.30 and Fig.4.85). The distribution of Pb in the five fractions appeared to be relatively similar for the Lagos and Ibadan environmental media, despite their difference in total Pb concentrations. However, it was observed that Pb in the carbonate fraction of Ibadan sediments was higher than that of Lagos sediments. This could be an effect of relative low pH in Ibadan sediments resulting in increased solubility and potential bioavailability of Pb in the river channels and that acid dumping could alter the geochemistry of the aquatic system.

The chemical distribution of Zn in the soils, sediments and dusts from Lagos was noticeably different from that of Ibadan. Zn in the selected soil, dust and sediment samples from Lagos were dominantly associated with the carbonate fractions (54 - 68%) and the organic fractions (24.7-30.3%) while Zn in the exchangeable and Fe–Mn oxides fractions were less significant. Zn in Ibadan soils was dominated by reducible fraction (57.2%) and exchangeable fractions (24.3%) and slightly with the carbonate fraction (18.5%) but in sediments, it showed strong association with both carbonate (53.1%) and organic-sulphide fraction (35.3%) but with little significance in exchangeable and reducible fractions (Table 4.30 and Fig. 4.84).

In soils, dusts and sediments, Cd in both Lagos and Ibadan environments were strongly associated with carbonate and organic-sulphide phases (46.2 -55% and 30.4 - 45%). The observed associations in Ibadan soils and sediments were similar to its chemical distributions of Pb. In Lagos samples, the distribution of Cd showed a relatively strong association with carbonate and organic-sulphide fractions (46.4 - 52.5%), organic-sulphide fraction (30.4 - 32); Fe–Mn oxides fraction (10.7 - 12.9%), residual (5.6 - 8.6%) and exchangeable phase 0.2 - 2.1%) (Table 4.30 and Fig.4.84).

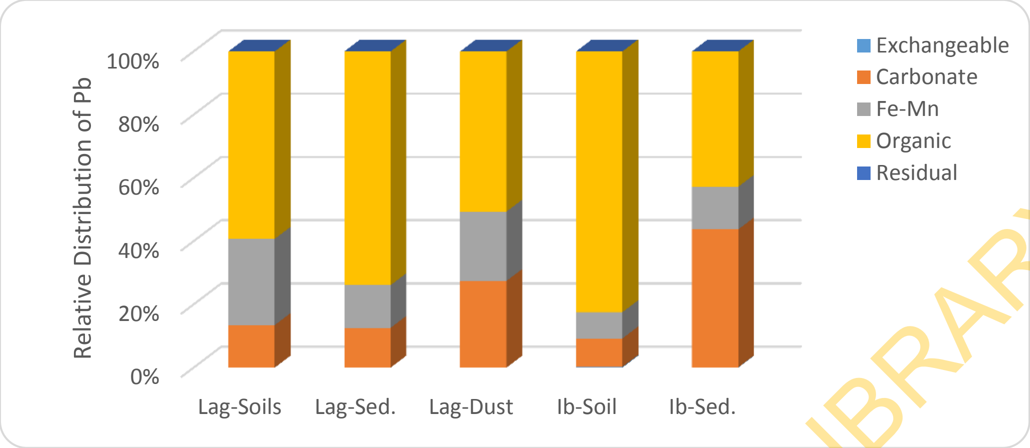
In both Lagos and Ibadan, Manganese is generally associated with the non-residual fractions with most of it found in the organic-sulphide fraction (56.8 –75.8%), followed by the carbonate (13.5 - 23.9%) and Fe–Mn oxides (5.1 - 16.4%). This is an indication that it is strongly affiliated with organic complexes and sulphide (Peng et al., 2004). Physical and geochemical changes of these media, such as removal of organic matter (i.e. reduction of municipal wastewater discharge) and oxidation of anaerobic sediments, soils and dusts could potentially trigger the release of Mn from the sediments, leading to an increase in dissolved Mn concentration most especially in aquatic environments.

Similarly, the chemical distribution of Cu in the Lagos and Ibadan environments differed significantly from the observed chemical distributions of Pb, Zn, Mn and Cd. This chemical distribution pattern was consistent with the distribution of total Cu concentrations recorded in soils, sediments and dusts. In general, Cu in the non-residual fractions in the Lagos and Ibadan sediments ranged from about 87 - 90% of the total Cu, while the remaining 10 – 13% accounted for Cu in residual fraction. The large percentages of Cu in the non-residual fractions could be a thing of concern, as Cu in these fractions could be readily altered into dissolved/soluble forms rendering them mobile and readily bioavailable (Tessier et al., 1979 and Dollar et al., 2001). Furthermore, a decreasing trend was observed for Cu in the Fe–Mn oxides and carbonate fractions from soils – sediments - dusts in both Lagos and Ibadan metropolis with increasing pH. This might also be the effect of pH and possibly a sign of trace metal redistribution in these geochemical environments.

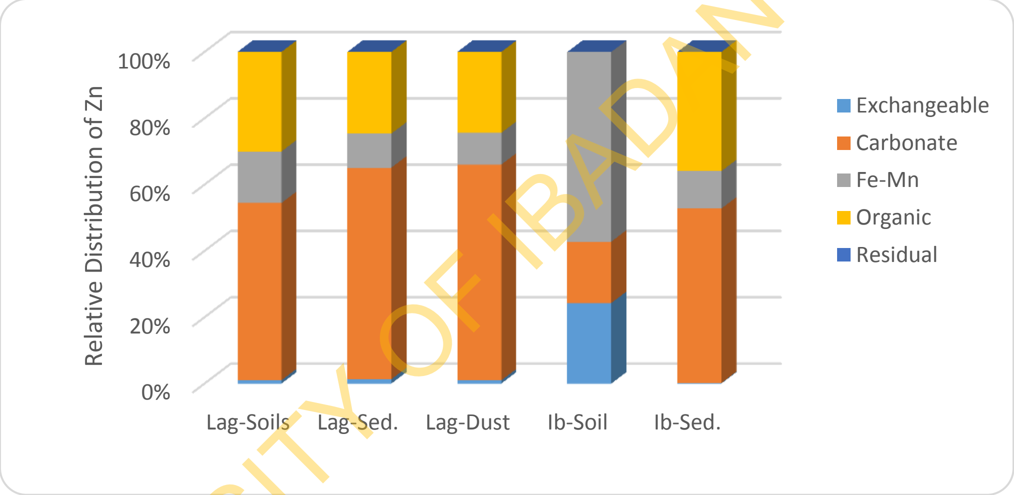
Table 4.30. Relative Percentage of some selected PHMs in Different phases (%)

Parameter		**Lagos**					**Ibadan**				
	Media	Exchangeable (F1)	Carbonate (F2)	Reducible (F3)	Organic/ Sulphide (F4)	Residual (F5)	Exchangeable (F1)	Carbonate (F2)	Reducible (F3)	Organic/ Sulphide (F4)	Residual (F5)
Zn	Soils	1	54	15.71	30.25	0	24.25	18.52	57.22	0	0
	Sediments	1.3	64	10.3	24.7	0	0.18	53.11	11.38	35.33	0
	RSD	1	68	10	25.52	0	NA	NA	NA	NA	NA
Pb	Soils	0.01	13.4	27.2	59.1	0	0.23	9.00	8.32	82.45	0
	Sediments	0.01	12.57	13.53	74	0	0.11	43.58	13.53	42.78	0
	RSD	0.01	27.6	22.1	51	0	NA	NA	NA	NA	NA
Cu	Soils	4.7	8.08	59.04	14	14.22	4.36	4.46	51.35	29.53	10.3
	Sediments	1.44	18.18	41.56	26.72	12.34	2.90	16.66	48.02	22.43	10
	RSD	6.6	14.25	30.95	25.8	22.38	NA	NA	NA	NA	NA
Cd	Soils	0.16	49.4	12.85	32	5.56	0	55	0	45	0
	Sediments	2.08	46.4	11.15	31.8	8.55	0.2	46.26	7.75	36.6	9.1
	RSD	0.54	52.5	10.73	30.4	5.9	NA	NA	NA	NA	NA
Mn	Soils	0.2	13.5	16.4	69.8	0	0.5	20.3	9.3	70.0	9
	Sediments	0.3	21.1	11.4	67.1	0	8.3	23.9	11	56.8	0
	RSD	0.2	18.9	5.1	75.8	0	NA	NA	NA	NA	NA
As	Soils	1.55	11.91	49.12	19.43	17.99	2.88	26.98	17.99	32	20.15
	Sediments	0.42	5.70	39.5	11.88	42.53	1.23	15.67	36.62	33.28	13.2
	RSD	3.59	23.34	40.58	32.5	0	NA	NA	NA	NA	NA
Th	Soils	-	-	-	-	-	0.51	2.5	96.97	0	0
	Sediments	-	-	-	-	-	0.2	4.18	95.63	0	0

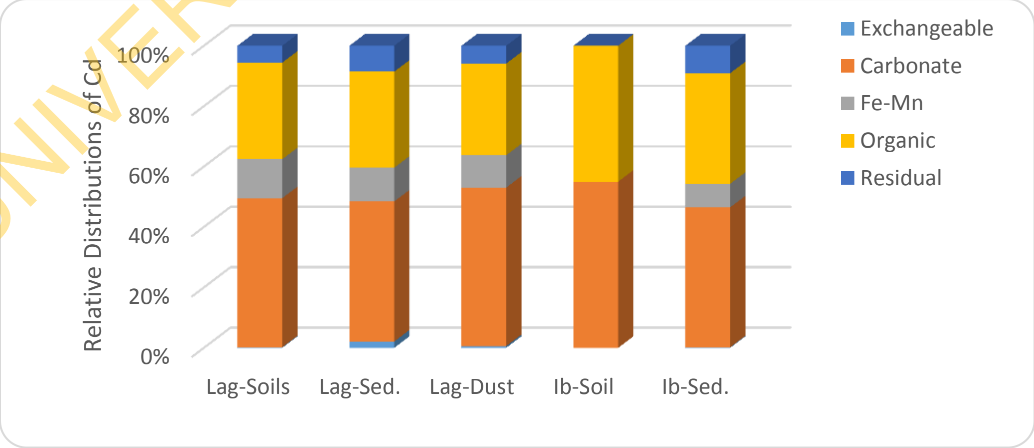
NA=Non-available


Relative Distribution of Pb
100%
80%
60%
40%
20%
0%
Lag-Soils
Lag-Sed.
Lag-Dust
Ib-Soil
Ib-Sed.
Exchangeable
Carbonate
Fe-Mn
Organic
Residual

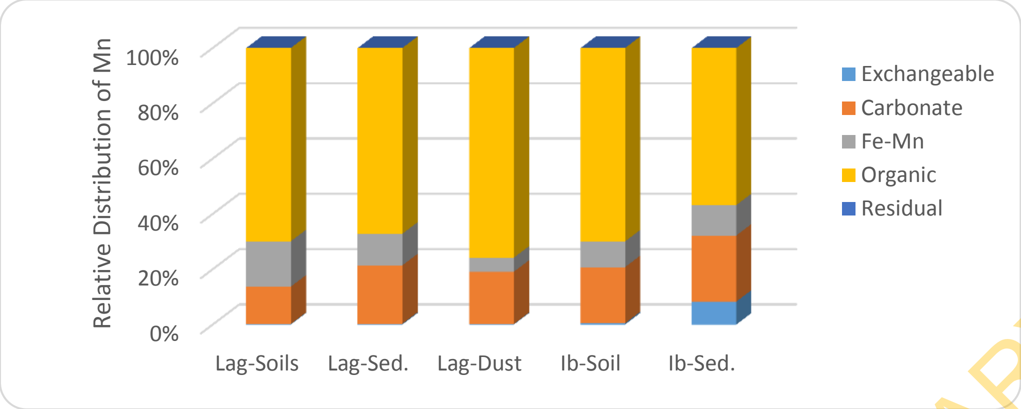
a.


Relative Distribution of Zn
100%
80%
60%
40%
20%
0%
Lag-Soils
Lag-Sed.
Lag-Dust
Ib-Soil
Ib-Sed.
Exchangeable
Carbonate
Fe-Mn
Organic
Residual

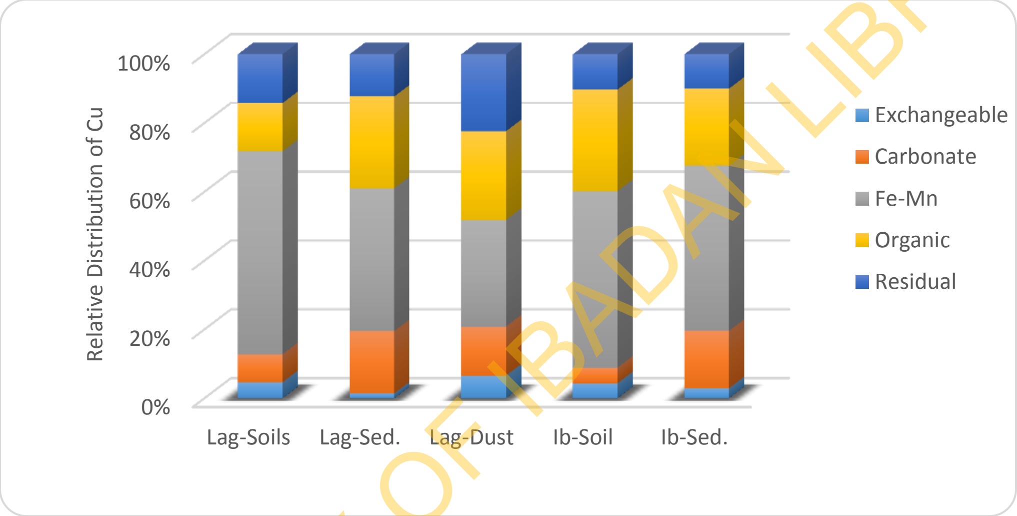
b.


Relative Distributions of Cd
100%
80%
60%
40%
20%
0%
Lag-Soils
Lag-Sed.
Lag-Dust
Ib-Soil
Ib-Sed.
Exchangeable
Carbonate
Fe-Mn
Organic
Residual

c.



d.



e.

Figure 4.84. Relative percentage distributions of Pb and other PHMs into phases in the study areas

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Geochemical mapping of Lagos and Ibadan metropolis have been carried out, using soils, sediments, roadside dusts and rocks

Lagos area fall within the Coastal Plain sands of the Eastern Dahomey Basin, while Ibadan is underlain by the Migmatite Gneiss Quartzite Complex of Southwestern Nigeria. The results of the petrological and mineralogical studies of the Ibadan rocks revealed abundance of quartz, biotite, plagioclase feldspar and microcline with some hornblende over other minerals in all the studied representative rock samples. Soils and sediments of Ibadan metropolis have similar mineralogical compositions including quartz, kaolinite, k-feldspars, illite-muscovite, goethite and plagioclase occur as the dominant minerals while calcite, Anatase, rutile as minor or accessory minerals. These were similar to those obtained from the Ibadan rocks except for the abundance of kaolinite in soils and sediments which had resulted from weathering and leaching.

The results also indicated that the Recent Alluvial/Coastal Plain Sands underlying Lagos metropolis is largely dominated by quartz and kaolinite while calcite and actinolite were identified as minor minerals. Lagos metropolis soils and sediments were largely dominated by quartz while other minerals occurred as either minor or accessory minerals. This was further confirmed by geochemical data derived from analyses of Recent Alluvial/Coastal Plain Sands, Soils, Sediments and Dusts where silica dominates largely. The results of the XRD of both Ibadan MGQC and Lagos Recent Alluvial/Coastal Plain Sands showed no lead (Pb) minerals in the bedrocks underlying Lagos and Ibadan metropolises.

Similarly, the results of the geochemical analyses of soils, sediments and dusts samples revealed heterogeneities in diversity from locations to locations as well as from media to media. High and elevated concentrations of PHMs far above the background values and some regulatory guideline values were recorded in areas with intense human activities such as mechanic and metals scarps workshops, high traffic congestions and motor parks. These areas are hot-spots for PHMs such as Pb, Zn, Mn, Cd, As, Cu, Ni and Hg. The relatively large standard deviations of potentially toxic metal concentrations (Mo, Pb, Cd, As, Zn, Mn, Hg and Cu) of soils, sediments and dusts from Lagos and Ibadan suggested that they were heterogeneous in terms of heavy metal distributions. In general, it was observed that the sediments from Ibadan were significantly enriched with PHEs compared to Lagos, with differences in As, Cd, Cu, Mn, Pb and Zn concentrations between the two cities being the most noticeable. Similarly, soils from Lagos were also significantly enriched with heavy metals compared to Ibadan. The enrichment of these PHMs in soils, dusts and sediments from the two cities ranged from 10 - 300-folds of their respective background values. The distributions of Cu, Hg, Mn, Pb and Zn in the Lagos and Ibadan sediments exhibit similar fluctuations along the rivers and canals, possibly indicating points of anthropogenic discharge and/or locations of preferential heavy metals deposition in the sediments.

Further evaluations of the geochemical data of selected PHMs using the geo-accumulation indices proposed by Muller on soils, sediments and roadside dusts from Lagos revealed that these media are extremely to heavily polluted with Cd, Pb, Zn and Hg. High to moderately polluted with Cu, Ni and As while the degree of pollution with respect to Th, U, As, Co, Mo and Ag remained practically uncontaminated. Similarly, the pollution levels of the selected metals in both soils and sediments of Ibadan metropolis as expressed by their geo-accumulation indices indicated that soils and stream sediments are uncontaminated to moderately contaminated with respect to Mo, Ag, Sr, Co, Ni, U, As, Th and Cu but high to extremely polluted with Cd, Pb, Zn and Hg.

The results of Pb isotopes analyses of the Ibadan rocks and Lagos core samples revealed very low concentrations of Pb isotopes and the concentrations of the three radiogenic isotopes were significantly low when compared to their concentrations in the secondary materials. Soils, sediments and road dusts from the two study areas were characterised by abundance of radiogenic Pb isotopes (Pb-206, Pb-207 and Pb-208) relative to the primordial isotope (i.e. Pb-204). There was no Pb mineral in the bedrocks to account for these enrichments in the analysed media. These enrichments were of several folds of the background concentrations, an indication of anthropogenic contributions of Pb. Despite the observed variations, the relative percentage distributions of the four Pb-isotopes in all the studied geochemical reservoirs remained fairly constant irrespective of the geological differences. The distribution of Pb concentrations and ^{206}Pb/^{207}Pb ratios indicated that Pb concentrations of the dusts, sediments and soils increased with decreasing ^{206}Pb/^{207}Pb ratios.

From the results of the Pb isotopes in all the media of both studied locations and the evaluated Pb isotopic ratios (LIRs), it was observed that over 80% of Pb in the environmental media was derived from anthropogenic sources. The LIRs of soils, sediments and dusts from the study areas displayed distinct IRs which were different from that of the rocks samples. These samples were characterised by lower lead isotopic ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) while the underlying materials from both study areas were characterised by higher ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios. This study revealed three generations of Pb in the study areas characterised by low to medium ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb ratios which were source related. The linear relationship between the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of soils, sediments and dusts from Lagos and Ibadan were significantly correlated ("r^2" ranged from 0.501 - 0.817), indicating possible binary mixing of Pb in the geochemical reservoirs.

From the evaluation results of Pb isotope ratios, the Pb contents of the studied environmental media have differentiated between the anthropogenic Pb and the natural Pb. The LIRs of soils and sediments of Lagos and Ibadan showed relatively narrow range of variations while the LIRs of dust samples varied within the same sampling locations. This observed variation in isotopic ratios of dusts can be attributed to significant difference in vehicle types, traffic volumes and different influx of petroleum products characterised the study areas. Also, the narrow variations observed in both soils and sediments are direct reflections of mixture of different industrial operations and domestic activities as well as contributions from automobile emissions. It can be concluded that soils, sediments and dusts from the study areas have received diffuse inputs of Pb from long range sources and for areas with close proximity point sources.

The results of the five steps sequential analysis carried out on soils, sediments and roadside dusts to determine the migration patterns and the chemical forms or species of Pb and some other heavy metals revealed that organic phase is the major sink and efficient scavenger for Pb, and Mn and Cd. Fe-Mn oxide (reducible) phase act as a major sink for Cu, Th and As in Lagos soils, sediments and road dusts as well as Zn in Ibadan soils. Zn and Cd are the major elements in the carbonate phase in virtually all the media sampled with the exceptions of soils from Ibadan. Zn, Pb and Th remained practically zero in residual phase while Cu (10 - 22%) dominate the residual phases in all the sampled media. In this present study, it is obvious that the residual and exchangeable phases are less significant for metals scavenging in the media. The relatively low percentage of heavy metals in the exchangeable fraction is an indication of low bioavailability of metals in the studied media under normal conditions. The chemical partitioning and Pb isotope results showed that most of the anthropogenic Pb may be accumulated by organic and Fe-Mn oxides in the soils, sediments and road dusts.

In conclusions, the extent and sources of Pb and other contaminants in urban soils, sediments and dusts of Lagos and Ibadan metropolises have been investigated.

- In Lagos metropolis, the severity of pollution by anthropogenic activities followed the increasing order of magnitude sediments<dusts<soils while in Ibadan, degree of pollution was more severe in stream sediments than soils. This may be as a result of long accumulations of PHMs and the age long traditional practice of indiscriminate discharge of urban wastes and effluents into drainage channels.

- The results of Pb isotopes clearly demonstrated that both study areas were significantly enriched in radiogenic Pb. Despite the difference in geological setting, locations and sampling media, the Pb present in soils, sediments, dusts and rocks were differentiated into two distinct groups characterised by lower and higher Pb isotopic ratios.
- That soils, sediments and dusts from the study areas consist of non-indigenous radiogenic Pb characterised by lower LIRs while bedrocks materials contained non-radiogenic Pb characterized by higher LIRs.
- That Pb isotope signatures of soils, sediments and dusts of the two study areas indicated that the elevated concentrations of Pb in Lagos and Ibadan were originated from anthropogenic sources characterised by low ^{206}Pb/^{207}Pb ratios which are similar to Chinese, European, Broken Hill and Durango Pb ores.
- It is also observed that Pb present in both Lagos and Ibadan environments were sourced from older generations of Pb ores (older than the MVT).
- The organic phase acted as the operationally defined phase partitioning for Pb in dusts, soils and sediments of the study areas. This suggests that any change in the chemo-thermal dynamic conditions of these media can lead to bioavailability of Pb and other PHMs in the study areas.

The Pb present in soils, sediments and dusts from the study areas are radiogenic and characterised by low ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb indicating a significant input from non-indigenous Pb with low ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios. It is believed that the findings of this study will not only provide valuable information on the environmental status of Ibadan and Lagos metropolis, but also present a scientific perspective of the environmental effects of radiogenic Pb isotopes present within the geochemical reservoirs of Lagos and Ibadan mega-cities so that further scientific attention can be drawn to the issue.

5.2 Recommendations

Despite the high anthropogenic and radiogenic Pb concentrations recorded in most Nigerian cities, no single study of blood Pb levels in Nigerian children has been conducted in respective of several millions of them living in urban centers. It is therefore recommended that a study of blood lead levels of Nigerian children (age 0 – 6yrs) living in these cities should be carried out.

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APPENDIX

Appendix 1: The result of the calculated Geo Accumulation Index in Lagos Media

S/N	TYPE	M0	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	U	Th	Sr	Hg
S001	Lag-soil	<1	2	12	10	1	15	2	1	0.1	0.08	0.1	<1	7
S002	Lag-soil	,<1	3	19	8	1	23	4	1	0.1	0.15	0.1	1	22
S005	Lag-soil	<1	2	7	27	0	10	2	0	0.1	0.05	0.0	<1	2
S010	Lag-soil	<1	2	17	8	6	20	3	1	0.1	0.09	0.0	1	19
S011	Lag-soil	<1	1	20	9	0	17	2	<1	0.1	0.07	0.0	1	11
S012	Lag-soil	<1	1	4	9	0	5	2	<1	0.1	0.09	0.1	0	2
S013	Lag-soil	<1	2	34	12	1	34	4	1	0.1	0.08	0.0	1	11
S014	Lag-soil	<1	3	16	79	0	19	3	1	0.1	0.04	0.0	<1	1
S016	Lag-soil	<1	3	26	10	3	26	4	1	0.1	0.09	0.0	<1	21
S018	Lag-soil	<1	2	20	13	1	28	4	1	0.2	0.11	0.1	1	4
S019	Lag-soil	<1	1	14	5	0	14	2	<1	0.1	0.06	0.0	<1	8
S020	Lag-soil	<1	1	14	5	0	14	2	1	0.1	0.05	0.0	<1	9
S021	Lag-soil	<1	2	28	4	1	21	3	1	0.1	0.08	0.0	<1	15
S022	Lag-soil	<1	2	19	18	1	23	3	1	0.1	0.09	0.0	<1	17
S026	Lag-soil	<1	2	12	6	1	15	2	<1	0.1	0.04	0.0	<1	5
S027	Lag-soil	1	8	30	52	1	48	8	1	0.2	0.09	0.0	1	9
S028	Lag-soil	<1	2	13	5	1	12	3	<1	0.5	0.08	0.1	1	4
S030	Lag-soil	<1	2	15	4	1	14	3	<1	0.1	0.08	0.1	<1	11
S033	Lag-soil	1	3	7	5	0	13	4	1	0.1	0.12	0.1	1	2
S046	Lag-soil	<1	2	4	12	0	5	2	1	0.1	0.23	0.2	<1	2

S047	Lag-soil	1	3	24	13	1	63	6	1	0.2	0.06	0.1	<1	11

LAGOS ROAD-SIDE SOIL Igeo

S049	Lag-RD	1	2	12	6	1	14	3	1	0.1	0.10	0.1	<1	2
S050	Lag-RD	<1	2	12	12	1	12	3	1	0.1	0.23	0.1	<1	9
S053	Lag-RD	<1	2	13	6	1	17	3	1	0.1	0.10	0.1	<1	5
S054	Lag-RD	<1	2	7	6	1	14	3	<1	0.1	0.07	0.1	<1	1
S055	Lag-RD	<1	15	32	16	0	44	5	1	0.3	0.09	0.0	1	6
S057	Lag-RD	<1	2	7	7	0	10	3	1	0.1	0.33	0.1	<1	1
S058	Lag-RD	<1	3	5	29	0	8	2	<1	0.1	0.14	0.1	<1	<1
S059	Lag-RD	<1	2	6	12	0	12	3	<1	0.1	0.05	0.1	<1	1
S060	Lag-RD	<1	1	5	10	0	4	2	<1	0.1	0.07	0.1	<1	<1
S061	Lag-RD	<1	1	5	8	0	11	2	<1	0.0	0.06	0.1	<1	1

LAGOS SEDIMENTS Igeo

S062	Lag-Sed	<1	2	14	6	2	20	3	1	0.1	0.07	0.0	1	24
S063	Lag-Sed	1	4	27	6	1	50	8	1	0.3	0.08	0.0	1	8
S064	Lag-Sed	<1	3	17	5	10	14	4	1	0.1	0.09	0.1	1	10
S066	Lag-Sed	<1	3	19	4	1	17	3	1	0.1	0.08	0.0	1	76
S067	Lag-Sed	<1	4	26	6	3	29	4	1	0.1	0.15	0.0	1	72
S068	Lag-Sed	<1	3	21	8	1	27	4	1	0.2	0.09	0.0	1	7
S069	Lag-Sed	<1	2	22	5	4	18	4	1	0.2	0.12	0.0	1	16

S070	Lag-Sed	<1	3	14	4	19	12	4	1	0.1	0.09	0.1	1	6
S072	Lag-Sed	<1	3	17	6	1	32	4	1	0.2	0.10	0.1	1	4
S073	Lag-Sed	<1	2	29	5	1	30	4	1	0.1	0.16	0.1	<1	11
S076	Lag-Sed	<1	2	6	10	0	233	2	1	0.0	0.07	0.0	1	1
S078	Lag-Sed	<1	1	3	5	0	5	2	1	0.1	0.11	0.1	0	3

Appendix 2: The result of the calculated Geo Accumulation Index in Ibadan Media

S/N	Sample Type	Mo	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	U	Th	Sr	Hg
S079	IB-Sed	0.32	0.89	0.7	5	0	9	0.4	0.6	0.5	0.08	0.0	0.1	2.4
S080	IB-Sed	0.27	0.99	1.1	9	1	11	0.4	0.9	0.7	0.08	0.0	0.1	2.4
S081	IB-Sed	0.20	0.76	0.7	5	2	6	0.3	0.5	0.5	0.06	0.0	0.1	1.3
S082	IB-Sed	0.24	1.17	0.5	3	0	5	0.5	0.4	0.3	0.05	0.0	0.0	1.4
S083	IB-Sed	0.34	1.33	0.4	3	0	3	0.3	1.0	0.5	0.05	0.1	0.1	0.6
S085	IB-Sed	0.16	0.69	1.0	4	2	13	0.2	0.4	0.5	0.11	0.1	0.1	11.1
S086	IB-Sed	0.25	0.90	1.0	3	5	11	0.3	0.6	0.6	0.09	0.1	0.1	4.4
S087	IB-Sed	1.06	1.85	1.3	10	5	10	0.7	0.5	1.6	0.09	0.1	0.1	3.4
S088	IB-Sed	0.19	1.26	0.4	2	0	5	0.3	0.3	0.3	0.13	0.1	0.0	1.2
S089	IB-Sed	0.52	1.10	1.5	6	0	24	0.4	0.5	0.9	0.07	0.1	0.1	2.4
S090	IB-Sed	0.09	3.97	0.2	3	0	3	0.1	0.5	0.2	0.19	0.2	0.0	1.4
S091	IB-Sed	1.48	5.24	3.7	18	1	44	0.7	0.4	2.6	0.14	0.2	0.1	4.3
S092	IB-Sed	1.34	4.88	3.6	17	1	43	0.7	0.4	2.5	0.13	0.1	0.1	3.9
S093	IB-Sed	0.68	1.82	2.4	8	0	18	0.4	0.4	1.8	0.12	0.1	0.1	4.7
S094	IB-Sed	0.64	1.78	2.3	8	0	16	0.3	0.4	1.9	0.12	0.1	0.1	4.1
S095	IB-Sed	0.20	0.81	1.8	3	1	21	0.4	0.5	0.6	0.09	0.1	0.1	3.6
S096	IB-Sed	0.49	0.82	0.5	7	0	6	0.3	0.8	0.9	0.12	0.1	0.1	1.0
S097	IB-Sed	0.47	0.79	0.5	5	0	6	0.3	0.8	0.9	0.12	0.1	0.1	1.0
S098	IB-Sed	0.30	0.93	1.5	3	0	13	0.3	0.4	0.8	0.14	0.1	0.1	3.9

S099	IB-Sed	0.34	0.77	0.5	5	0	5	0.2	0.4	0.7	0.09	0.1	0.1	41.8
S100	IB-Sed	3.05	5.29	4.6	40	2	54	1.3	0.6	5.4	0.20	0.2	0.2	8.8
S101	IB-Sed	2.99	5.42	4.4	40	2	52	1.2	0.6	5.4	0.20	0.2	0.2	7.6
S102	IB-Sed	0.92	1.21	1.7	9	1	13	0.4	0.4	2.2	0.17	0.2	0.1	2.4
S103	IB-Sed	0.88	1.14	1.6	9	1	13	0.4	0.4	2.1	0.16	0.2	0.1	2.1
S105	IB-Sed	0.17	0.49	0.6	36	0	4	0.1	0.3	0.4	0.11	0.1	0.1	1.7
S106	IB-Sed	0.26	0.61	0.7	10	0	6	0.2	0.3	0.5	0.13	0.0	0.1	2.8
S107	IB-Sed	0.54	0.88	0.7	8	1	8	0.3	0.4	1.3	0.19	0.1	0.1	1.9
S108	IB-Sed	0.37	1.48	1.0	71	0	10	0.3	0.4	0.8	0.16	0.1	0.1	1.2
S109	IB-Sed	0.41	0.85	0.7	6	0	6	0.2	0.5	0.8	0.18	0.1	0.1	3.5
S110	IB-Sed	0.17	0.39	0.8	6	1	9	0.2	0.4	0.3	0.10	0.1	0.1	4.6
S111	IB-Sed	0.25	1.49	0.5	4	0	5	0.5	1.1	0.6	0.13	0.1	0.1	2.4
S115	IB-Soil	0.36	0.28	0.9	3	0	5	0.1	0.6	0.4	0.11	0.0	0.1	0.9
S122	IB-Soil	0.50	1.41	1.4	10	1	32	0.4	0.3	1.3	0.10	0.1	0.1	3.7
S123	IB-Soil	0.17	0.39	0.7	10	0	19	0.3	0.3	0.4	0.07	0.0	0.2	1.3

Appendix 3. The result of Five steps sequential extractions of soils and sediments from Ibadan.

	Zn	**Pb**	**Cu**	**As**	**Cd**	**Co**	**Mo**	**V**	**U**	**Th**	**Ni**	**Ba**	**Sr**	**Zr**	**La**	**Bi**	**Sb**	**Sc**

IBD-SOIL																
	Zn	Pb	Cu	As	Cd	Co	Mo	V	U	Th	Ni	Ba	Sr	Zr	La	Sc
F1	0	65	278	8	bdl	1054	22	169	3.0	3	130	661	1352	19	13	18
F2	7890	2517	284	075	33	686	13	bdl	50	15	207	35536	24201	bdl	926	75
F3	6026	2327	3271	050	Bdl	1164	88	1863	69	576	953	1887	1075	387	2649	1210
F4	18616	23059	1881	089	27	8866	0	6363	14	0	2104	52073	2844	44	2186	152
F5	0	0	656	056	bdl	1777	0	0	0	0	0	6712	0	30	0	0
IBD-SED																
F1	581	2254	2005	7	0.7	124	21	73	3.4	3	233	985	1616	17	08	30
F2	175240	939516	11516	089	173	851	13	2733	329	64	634	57273	13312	28	783	307
F3	37564	291728	33207	208	29	557	355	bdl	299	1466	634	4138	829	1044	3095	1138
F4	116563	922351	15508	189	137	5534	0	8198	25	0	3077	54792	4013	bdl	3463	198
F5	0	0	6910	075	34	1218	0	0	0	0	0	8563	0	54	0	0

LAG-SOILS																		
F1	2123	208	1918	29	1.7	71	39	82	0.8	5	163	627	1286	38	11	0	44	Bdl
F2	547914	28444	3317	223	542	447	20	55	108	bdl	566	38329	14030	38	170	15	244	bdl
F3	159859	57720	24246	920	141	807	226	2219	253	2178	1430	5876	1648	2978	1939	96	559	1390
F4	307903	126210	5750	364	351	3302	bdl	2122	34	0	3773	94488	9432	94	1491	55	93	174
F5	0	0	5839	337	61	826	0	0	0	0	0	31228	0	0	0	0	0	0
LAG-SED																		
F1	21560	3	537	7	25.5	56	89	bdl	0.3	bdl	225	473	9310	2	2		28	<20
F2	1070375	6405	6769	95	570	470	61	82	160	55	2009	26412	10153	48	477	89	147	<100
F3	172425	6898	15471	658	137	253	636	1566	213	1521	1095	3105	1010	2086	1628	98	269	675
F4	414085	37664	9854	198	391	1659	11	4044	18	0	6309	85018	9188	<20	3672	8	64	188
F5	0	0	4593	709	105	507	0	0	0	0	0	17759	0	0	0	64	0	0
LAG-RDS																		
F1	2814	105	1818	20	3.0	84	39	105	3.6	5	337	403	1570	31	19	0	15	bdl
F2	627124	15963	3924	130	293	314	88	70	74	20	1091	24011	32234	33	645	13	216	bdl
F3	58856	13050	8524	226	60	164	222	1177	65	618	565	2727	1467	786	1145	16	386	297
F4	236065	29888	7109	181	170	1659	bdl	2199	27	0	4314	40545	6246	28	1709	bdl	48	168
F5	0	0	6164	bdl	33	609	0	0	0	0	0	9625	0	0	0	12	0	0

Appendix 4. The result of Five steps sequential extractions of soils, sediments and roadside dusts from Lagos.

APPENDIX 5. Summary of the Major Oxides in Lag-Soils

	N	Range	Mean ± Std. Dev.	Variance
CaO	48	0.15 - 4.84	1.84 ± 1.04	1.080
P_2O_5	48	0.03 - 0.99	0.35 ± 0.23	.052
Fe_2O_3	48	0.91- 7.53	3.29 ± 1.29	1.659
MgO	48	0.02 - 0.71	0.23 ± 0.12	.014
AL_2O_3	48	0.50 - 3.37	1.47 ± 0.70	.483
Na_2O	48	0.00 - 0.19	0.06 ± 0.04	.002
K_2O	48	0.04 - 0.29	0.13 ± 0.05	.003
TiO_2	48	0.02 - 0.09	0.04 ± 0.01	.000
SiO_2	48	86.91- 97.21	92.55 ± 2.20	4.850

APPENDIX 6. Summary of the Major Oxides in Lag-Stream Sediments

	N	Range	Mean ± Std. Deviation	Variance
CaO	17	0.50 - 11.50	4.03 ± 2.76	7.595
P_2O_5	17	0.11 - 1.41	0.56 ±0.36	0.129
Fe_2O_3	17	1.45 - 10.51	4.11 ± 2.36	5.589
MgO	17	0.07 - 2.45	0.49 ± 0.54	0.291
Al_2O_3	17	0.42 - 2.93	1.68 ± 0.67	0.452
Na_2O	17	0.00 - 0.20	0.10 ± 0.07	0.005
K_2O	17	0.05 - 0.44	0.20 ± 0.11	0.011
TiO_2	17	0.02 - 0.10	0.05 ± 0.03	0.001
SiO_2	17	78.32 - 97.12	88.78 ± 4.77	22.727

APPENDIX 7. Summary of the Major Oxides in Ibadan-Soils

	Range	Mean ± Std. Dev.	Variance
CaO	0.18- 3.29	.81 ± 0.82	.673
P_2O_5	.05 - 0.45	.17 ± 0.13	.017
Fe_2O_3	1.88 - 8.19	4.40 ± 1.65	2.707
MgO	.08 - 0.50	.20 ± 0.10	.011
Al_2O_3	1.23 - 3.05	1.89 ± 0.48	.226
K_2O	.08 0.44	0.19 ± 0.10	.009
TiO_2	.03 - 0.16	.06 ± 0.03	.001
SiO_2	86.16 - 95.13	92.29 ± 2.59	6.705

APPENDIX 8. Summary of the Major Oxides in Ibadan-Sediments

	N	Range	Mean ± Std. Dev.	Variance
CaO	33	0.11 - 2.11	1.03 ± 0.56	0.309
P_2O_5	33	0.05 - 0.52	.29 ± 0.13	0.016
Fe_2O_3	33	1.33 - 27.98	10.70 ± 6.70	44.807
MgO	33	0.10 - 0.48	.19 ± 0.09	0.007
Al_2O_3	33	0.69 - 3.27	2.23 ± 0.59	0.351
Na_2O	33	0.00 - 0.04	.02 ± 0.02	0.000
K_2O	33	0.07 -0.29	.13 ± 0.06	0.004
TiO_2	33	0.03 - 0.10	.07 ± 0.02	0.000
SiO_2	33	66.88 - 97.60	85.33 ± 7.49	56.031

APPENDIX 9. Summary of the Major Oxides in Lagos Dusts

	N	Range	Mean ± Std. Dev.	Variance
CaO	13	0.60 -2.87	1.61 ± 0.74	0.550
P_2O_5	13	0.09 - 0.52	0.21 ± 0.15	0.022
Fe_2O_3	13	1.64 - 7.20	3.67 ± 1.65	2.730
MgO	13	0.10 - 0.36	0.23 ± 0.07	0.005
Al_2O_3	13	0.79 - 1.54	1.23 ± 0.22	0.049
Na_2O	13	0.03 - 0.13	0.05 ± 0.03	0.001
K_2O	13	0.08 - 0.35	0.16 ± 0.07	0.005
TiO_2	13	0.02 - 0.08	0.05 ± 0.02	0.000
SiO_2	13	88.87 - 95.49	92.80 ±1.97	3.885

APPENDIX 10. Isotopic Ratios of Some Anthropogenic and Geogenic Sources

	^{206}Pb/^{204}Pb	**^{207}Pb/^{204}Pb**	**208/204**	**206/207**	**207/206**	**208/206**	**208/207**
A source (Coal)	17.64	14.41	34.83	1.22	0.82	1.98	2.42
A source (Aerosol)	18.9	15.21	36.3	1.24	0.85	1.92	2.39
A source (Battery Cell)	17.23	14.43	34.15	1.19	0.84	1.98	2.37
G source (Ibadan MGC)	24.97	15.92	47.69	1.57	0.64	1.91	2.996
G source (Lag-RBS)	19.42	16.25	41.75	1.20	0.84	2.15	2.57
G source (Pb ore T)	18.35	15.75	38.57	1.16	0.86	2.10	2.45
G source (Pb ore B)	18.35	15.75	35.77	1.16	0.86	1.95	2.27

Appendix 11. Concentrations of PHMs in some Cities in South western Nigeria

CITY	**Pb**	**Zn**	**Cu**	**Cd**	**As**	**REFERENCES**
Lagos Soil	200.6	627.64	61.88	1.07	4.07	Odunmbaku, 2012
Lagos Dust	151	465.3	80.2	1.01	3.19	Odunmbaku, 2012
Lagos soils	66.6	159.8	32.7	0.6	1.24	Utomaliki, 2012
Lagos Sediments	20.3	72.3	36.04	0.274	2.99	Olatunji, 2006
Osogbo Soils	498.7	1252.4	416.9	3	5.1	Okunola, 2014
Ibadan Soil	95.1	228.6	46.8	8.4	3.9	Odewande and Abimbola, 2008
Ibadan Sediment	2054	5140	715	10	12	Ajibade, 2013
Ibadan soil	1871	2428	346.9	2	4	Onianwa, 2006
Akure Soils	158	552	71	1.3	0.5	Afolabi, 2010
Ibadan Sediments	72.1	534	134.2	0.3	0.66	Tijani et al, 2004
Benin Soils	232.3	533.1	119.7	5	10	Asowata, 2010