# GEOCHEMICAL CHARACTERISATION OF SOILS AND SEDIMENTS FROM ONITSHA METROPOLIS, SOUTHEASTERN NIGERIA

**BY**

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**A THESIS SUBMITTED TO THE FACULTY OF SCIENCE, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY**

**IN**

**APPLIED GEOCHEMISTRY**

**UNIVERSITY OF IBADAN,**

**IBADAN, NIGERIA.**

**April, 2017.**

## ABSTRACT

Studies on the distribution, sources and impacts of Heavy Metals (HMs) and Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments of Urbanised Industrialised Cities (UICs) are integral part of environmental monitoring programme globally. Results from such, have been used to design appropriate mechanisms for the sustainable use of environmental media. However, several Nigerian UICs, such as Onitsha, the most industrialized city Southeastern Nigeria, have not been adequately studied. Therefore, this study was designed to investigate the mineralogical, elemental and PAHs composition of soils and sediments in Onitsha metropolis in order to ascertain their sources, characters and potential mobility.

One hundred and fourteen soils, 42 sediments and 6 rock units (geologic control) were purposively collected for the study. One sample each of galena, coal, soot from vehicle exhaust and used battery cells were also collected for Pb isotopes analysis for pollutant source characterisation. The mineral contents of the soils were determined using X-ray Diffractogram (XRD) technique. All the samples were digested and analysed for total elemental composition using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Samples with the most elevated HMs (Pb, Zn, As, Mn, and Cd) were further subjected to sequential extraction and analysed with ICP-MS. The soils, sediments, galena, coal, soots from vehicle exhaust and used battery cells were analysed for lead isotopes, ($Pb^{204}$, $Pb^{206}$, $Pb^{207}$ and $Pb^{208}$) using ICP-MS. The concentrations of the PAHs were determined using Gas Chromatography/Mass Spectrometry (GC/MS). Data were analysed using descriptive and inferential statistics.

Quartz, kaolinites and hematite were the dominant minerals present in the soils. The selected HMs concentrations (mg/kg) in soils, sediments and rock units revealed that Pb ranged from 7.2-2026.0, 19.7-540.1 and 7.2-28.1; Zn, 3.0-8395.0, 101.1-502.5 and 3.0-35.3; As, 0.5-19.8, 80.6-16.9 and 0.5-27.3; Mn, 7.1-1920; 180-1410 and 10.0-221.0; Cd, 0.1-1.03, 0.21-1.6 and < 0.01, below detection limits, respectively. Soils and sediments showed higher concentrations for Pb, Zn, Cd and Mn than the rock units except for As. The sequential extraction showed that Zn and Cd were more in the carbonate bound fraction, while As was higher in the Organic bound fraction with Mn and Pb more in the hydroxide and residual fractions, respectively. The estimated mobility of HMs was Cd>Zn>As>Mn>Pb. The standard plots of $^{206}$Pb/$^{204}$Pb vs $^{207}$Pb/$^{204}$pb and $^{207}$Pb/$^{204}$Pb vs $^{206}$Pb/$^{204}$Pb in the soils and sediments, respectively exhibited linear relationship suggesting similar origin of Pb in the environmental media. The PAHs mean concentrations (µg/g) were: Fluoranthene, 187.2 ± 146.4, Pyrene, 187.5 ± 133.7, Benzo[a]anthracene, 93.8 ± 72.0, 150.4 ±94.8 and Benzo[a]pyrene, 178.9 ± 112.2, respectively. The standard plots of the ratios of the Anthracene: (Anthracene + Phenanthrene) and Fluranthene: (Fluranthene + Pyrene), indicated that the PAHs were from Pyrogenic (combustion) activities.

The heavy metals and high molecular weight Polycyclic Aromatic Hydrocarbons in the soils and sediments of Onitsha were of anthropogenic sources except for arsenic that had a substantial geogenic input. Mobility of the HMs were also established.

**Keywords**: Lead isotopes, Sequential extractions, Onitsha metropolis, Geochemical characterisation

**Word count**: 487

# CERTIFICATION

I hereby certify that this research work was carried out by Iyobosa Timothy ASOWATA under my supervision in the Department of Geology, Faculty of Science, University of Ibadan, Ibadan, Nigeria.

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**(Supervisor)** **Date**

**Dr. A. S. Olatunji**
**B.Sc. (Ilorin), M.Sc. Ph.D, (Ibadan)**

# DEDICATION

This research work is dedicated to late Prof. A. F. Abimbola whose contributions especially at the beginning of this research is unquantifiable and to my late grandparents, both paternal and maternal. Ogbeide and Ugieomo Asowata, Ogieva and Evbenatuomwen Eghomwanre. May their souls rest in peace.

## ACKNOWLEDGMENTS

I sincerely acknowledge the benevolent grace received from God almighty, throughout this academic programme. May His name alone be glorified forever, Amen. To my mentor and supervisor, Dr. A. S Olatunji, your contributions, not only to the success of this programme, also to every aspect of my life, financial, moral and spiritual support is most sincerely appreciated, may God almighty continue to enrich your strength and wisdom divinely. Special appreciation goes to the Head, Department of Geology, Professor O. A Ehinola, thank you so very much sir, God bless you. Special appreciation goes to the immediate past Head, Department of Geology, Professor M.N Tijani. You signed my recommendation letter for this programme and have been very supportive, God bless you sir

I also appreciate Profs. A. A Elueze, A. I Olayinka, G. O Adeyemi and O. A Okunlola in the Department for their academic impartation during the course of this program.

I am also grateful for the positive influence and support of Drs, I. M Akaegbobi, A. T. Bolarinwa, O. A. Boboye, O. C Adeigbe I. A Oyediran, O. O Osinowo, M. A Oladunjoye, A. M Adeleye and other members of staff of Geology Department, University of Ibadan.

Special thanks goes to Lecturers in the department of Applied Geology, School of Earth and Mineral Sciences, Federal University of Technology, Akure for their supports; Profs. I. B Odeyemi, V. O Olarewaju, Y. A Asiwaju-Bello (Head of Department, AGY, FUTA) and S. Malomo. Your contributions and advice are highly appreciated. Drs. P.S Ola, S. O Olabode, (of blessed memory), S. A Opeloye, O. A. G Jegede, C. T Okonkwo, A. T Bolarinwa, Adetunji and O. A Ademeso. Mr. M. O Adepoju, O. R Egbeyemi, O. A Ogbahon, J. O Owoseni, A. L Adisa, I. O Ajigo, S. O Daramola, E. E Igonor, B. Adeoti , S. Olabode, Mrs O.A Bamisaiye and other members of staff of the department of Applied Geology, FUTA. Your encouragements and friendliness are very much appreciated.

I appreciate specially, E. Faleye, Adegoke, Ojo Frances, Adelakun, Ojo B.T, Ibe A. Adewole A, Akingbesote A., Adepehin, Oke, Olasupo, Mr. and Mrs. Aronmolaran among others, at Wesley University of Science and Technology, Ondo. Your friendliness was lovely, God bless you all.

I also in a special way thank my parents Mr. and Mrs. S. I Asowata who from the beginning thought me to be focussed in anything that I do. My success is yours, your love radiate the beauty and complexity of the cosmos 'thank you Dad and Mum'. Special thanks goes to my other family members who conscientiously contributed in many ways to the successful completion of this programme, the entire Asowata Ogbeide and Egheomwanre Ogieva's families, your good works will never be forgotten.

Special thanks to Mr. S. A. O Asowata, Engr. and Mrs. Fergus Ogeiva, Dr. and Mrs. Ayodele (My parents In-law) Mrs. Orhue, Barr. E. E Ogeiva, Mr. and Mrs. Godfrey Ogieva, Mr. and Mrs Osemwengie, Dr. and Mrs. Enoma, Dr. and Mrs. Izibili, Mr. And Mrs. Martins Ogieva, Mr. and Mrs. Clement Ogieva, Mrs. F. Agho Idumwonyi, Mr. and Mrs. Afuede, Dr. F. I. Akinnibosun, Imafidon, Ehigie and wife, (Mum Iyobosa), Fredrick, Godwin, Osahon, Bukky, Fumi, Ayomiposi (Bose), in-laws, cousins and Nephews, God bless you all.

To all my friends, Mr. Ufiegbe, I, Okoeri Emmanuel, Ewiwile Konyehi, Stanley Ejimeh, Osagie, Felix, Sheba, Afolabi Olubukola, Mr. and Mrs. Samuel Fabunmi, I love you all, thank you and God bless.

I will like to appreciate the efforts of members of the Applied Geochemistry unit, Drs. Ajebade O. M Kolawole , T and Laniyan T. Funmi Ajayi, Afolabi O.O., F. Okunola, Goke, J. O. Mr. Razak, Mrs Rufiat, Olajide-Kayode, Edema, Kola, among others, God bless you greatly.

To my very dependable friends, Aladejana, J, Dr. Frank Akinluyi, Egbo Khalin, Onoriode Esegbue, Sogo, Saheed Oke, Covenant, Amos, Adeniyi (Jose M), Okpoli, Ajedahun Emmanuel. Your lovely contributions to the success of this programme are in no small measure appreciated.

Words will not be enough to express my appreciation to my immediate family which God alone has instituted for me, my dear wife and friend, Mojisola Abiola, thank you for your lovely support. Same goes to my dear son, Osamuyi Olufemi, God bless and keep you for us. To many names I can't remember, God bless you all.

**Asowata Iyobosa T**

**April, 2017**

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# CHAPTER ONE

# INTRODUCTION

## 1.1 General Statement

The world is experiencing rapid increase in human population with consequent increase in the consumption of various products that brings some level of comfort and good life. This quest for comfort and good life have led to the continue increase in human migration from hitherto rural environment, where life seems to be crude and difficult, to the urban area where to a great extent, there are relative opportunities for good comfort of life. This increase in human migration from rural to urban areas, have in turn increased our towns and cities space or area coverage. The huge demand for goods and services dislocates the natural landscape of the urban environment to the extent that the morphology and chemistry of the earth can be altered. Soils and sediments, water of all kinds are altered thereby affecting the fate and distribution of elements and organic compounds in urban areas.

This alteration in the natural form and in general the geochemistry, of soils, sediments and water, amplifies the need for the study. The results of this research will offer significant volume of scientific information about geochemical phenomena that are found uniquely in the urban environment, which include the varying dispersion, distribution and other geochemical characteristics of these elements and organic compounds, which can be toxic or potentially toxic to the entire biota in general and human health to be specific.

It has been established by several authors that activities in large (urban) cities and towns affect greatly the quality of the environment by contributing to increase concentration of harmful elements and polycyclic aromatic hydrocarbon (PAHs) in soil, water (surface and groundwater), sediments and particulate,( Harrison et al.,1981, Thornton, 1991; Tiller, 1992, Appleton and McCall, 1996, Schumacher et al., 1997, Sutherland et al., 2000, Laluraj and Nair, 2006, Lee, 2005, Lu et al. 2011, Zheng et al. 2011,).

Although some of these elements which include Zn, Cu, Mn, Fe, Cr and to a great extent Se, are biologically essential for life processes, (Bache, 1979), they become toxic when certain optimum ranges of concentrations are exceeded. Other elements such as Cd, Pb, As, Hg, and Al are toxic to human (Bache, 1979).

16 PAH on the other hand have been classified to be generally harmful to human health especially when its bio availability exceed acceptable concentration limit, these include; Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Anthracene, and Phenanthrene. Others are; Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[k]fluoranthene, Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Indeno(1,2,3-cd)pyrene and Dibenz[ah]anthracene. Different PAH compounds have different toxicity levels. Of the 16 Environmental Protection Agency (EPA) priorities PAH compounds, seven (7) are designated as probable human carcinogens with varying potency levels (Baumard, 1999), United State Environmental Agency (USEPA, 2002)

Soils and sediments are clastic materials which may also contain clayey, and are derived from rock bodies through the action of weathering. They are very important component of urban environment which can act as both the source and sink for pollutants that can be of health risk to human. (Balls, 1997, Akujieze, 2004; Lee et al. 2005, Banat et al., 2005, Abimbola et al.; Laluraj and Nair, 2006 , Poggio et al. 2009, Olatunji and Abimbola 2010, Lu et al. 2011)

Stream and river channels are very good natural systems that serve as habitats for diverse means, aquatic biota and the surrounding natural vegetation, they become susceptible to sediments and various kind of contaminant retention.

Soils and sediments are veritable media that help in the preservation of record of both past natural and ongoing anthropogenic activities. Therefore, soils and sediments are important media for the assessment and evaluation of the geochemical signatures of the environment because they reflect in a long term, the quality status that may be independent of the current inputs. (Adeyemo et Al., 2008, Abdel-Satar and Geneid, 2009; Fagbote and Olanipekun, 2010)

During the dry season, most especially when the moisture content in top soils and road side sediment is low, activities like vehicular movement release loosed fraction (fine particles) into the atmosphere, resulting in high suspended particulate matter in the breathing zone. Omar; 2007 have established that these suspended fine particles in the air may contribute significantly to respiratory and cardiovascular diseases and in some cases result in mortality when such particulate contain harmful elements.

Because of the increase in demand for metals in industries and rapid urbanization in many parts of the world, contamination by metals in the terrestrial environment has become widespread on a global scale. Heavy metals from vehicular emissions, incinerators, industrial wastes, the atmospheric deposition of dust and aerosols, input from fertilizers and pesticides and other activities (Tables 1.1, 1.2 and 1.3 ) have continuously added to the pool of contaminants in the environment (Harrison et al., 1981; Thornton, 1991; Schuhmacher et al., 1997; Acero et al., 2003; Akujieze, 2004; Lee et al. 2006,Aelion et al., 2009; Olatunji and Abimbola 2010).

Polycyclic aromatic hydrocarbons (PAHs) are group of organic compounds consisting of two or more fused aromatic rings. They occur in the environment either through petrogenic processes such as volcanic eruptions or pyrogenic sources, particularly from incomplete combustion of organic compounds. These sources can occur naturally or cound be human induced (Chung et al., 2007). Vila-Escale et al., 2007, have identified the main natural sources of PAHs to include forest fires and volcanic activities respectively. While the major anthropogenic sources include the burning of fossil fuels, petroleum spills, and industrial discharges (Albers, 2003; Johnsen et al., 2006, Chung et al., 2007). Base on this, PAHs are widespread in ambient environment as well as in identified contaminated hotspots (Simpson et al., 1996; Johnsen et al., 2006; Chung et al., 2007).

On a global scale, it was found that human activities strongly affect PAH concentration in air, as higher concentration often correlated positively with larger human populations (Hafner et al., 2005). Similar patterns were also detected in soils and river sediments where PAH concentration decreases with increasing distances from high dense to low dense areas. (Trapido, 1999; Yunker et al., 2002; Chung et al., 2007; Placha et al., 2009). In addition to contributing different levels of PAHs to the environment, land uses can also introduce different types of PAHs. Different PAH sources (e.g. petrogenic versus pyrogenic) are associated with different PAH compounds (Gschwend and Hites, 1981; Sicre et al., 1987; Budzinski et al., 1997), and consequently affect the composition of PAHs at specific locations. The ratios of particular PAH compounds or isomers, such as phenanthrene/anthracene and fluoranthene/pyrene, have been used as source indicators for PAH contaminated environments (Yunker et al., 2002; Pies et al., 2008).

The effect of trace elements and polycyclic aromatic hydrocarbon in soils and sediment on the environment and health are a function of the mobility and bio-availibility of these elements and organic compound. (Lee, 2005). Certain environmental conditions such as redox, acidity, salinity, organic matter content and temperature are determinant factors that control their deposition in soils and sediments. Hence, it is essential to identify the binding sites and phase association of these elements in assessing environment the quality of theand risk to human health in the urban environment.

Sequential extraction procedures has been accepted as a useful method for the prediction of long term adverse effects of PAH in soil and sediment , (Ahnstrom and Parker, 1999, Lee, 2005) and in assessing differences in mobility, bioavailability and ultimately the toxicity level in an environment situation.

Whereas in the developed world, Alkyl lead, a major source of lead pollution has been removed from their gasoline (Duzgoren-Aydin et al, 2004), previous works on urban environment in Nigeria (Olatunji et al., 2014) has shown that higher concentration of Pb has been found in high traffic roads with such enrichment likely coming from the usage of petroleum product, such as lubricant, gasoline, diesel among others.

Analysis of lead isotopes has been accepted as a method for the identification of the sources of Pb contamination in soils and sediment (Lee, 2005,) because of the differences in Pb-isotopic ratio between natural and man-induced sources. Tables 1.1to 1.3 show some potentially harmful elements, their anthropogenic sources, industrial uses and toxicity level.

Table1.1: Anthropogenic Sources of Heavy metals In Urban Soils and Sediments (After Reimann and De Caritat, 2000)

| INDUSTRY/SOURCE | Cu | Pb | Zn | Sn | Cd | Hg | Ni | V | Cr | As | Sb | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| General urban activity | + | + | + | + | | | | | | | | |
| Mining (coal) | | + | | + | | | + | | | | | |
| Smelting (nonferrous) | + | + | + | + | + | + | + | | | + | + | |
| Iron-and-steel work | + | | | + | | | + | + | + | + | | Ca, $P_2O_5$ |
| Heavy engineering, tool making | + | | + | | | | + | + | + | | | Mn, Mo, W |
| Metal plating and fining | + | | + | | | | + | | + | | | |
| Electronics | + | | | | + | + | + | | | + | + | REEs, rarer elements |
| Ceramics, glass | | + | | + | | | | | | | + | Mn, Co, U, REEs |
| Incinerators | | | | | | + | | | | + | | |
| Domestic coal burning power station (ashes) | | + | | + | + | | | + | | | + | |
| Vehicles, transport | + | + | + | + | | | | + | | | + | Ba, Mn |
| Crematoria | | | | | | + | | | | | | |

**Table 1.2: Industrial uses of some Potentially toxic elements (PTEs)**

| PTE | Industrial Uses |
|---|---|
| As | Pesticides/herbicides, glass and ceramic works, traditional medicines. |
| Cd | Electroplating, storage batteries, stabilizers, solar cells, pigments, alloys for telegraph and telephone wires, photoelectrical and electron optical devices, nuclear reactors |
| Cr | Alloying additives to stainless steel, chrome plating, dyes, pigments, tanning of leather, textiles, cassette tapes, magnetic storage media for computers, matches, pyrotechnics, photography, seed disinfection. |
| Cu | Electrical goods, kitchenware, alloys, algaecides/fungicides, pigments, supplement in deficient pastures, intra-uterine contraceptive devices. |
| Ni | Alloys for corrosion resistant equipment. Cooking utensils, coinage, heating elements, gas turbines, jet engines, electroplating, paints, pigments, batteries. |
| Pb | Storage batteries, antiknock agent in petroleum/gasoline, paints, ammunition, glassware, ceramics, protection from radiation, bearing Alloys, rubber industry, printing press. |
| Zn | Galvanizing of iron and steel for corrosion protection, alloys, vulcanization of rubber, photocopying paper, paints, TV tubes, rayon Glass, enamel and plastic industries, fertilizers, medicine and cosmetics. |

Souces: Alloway (1990, 1995), Okorie, (2010)

**Table 1.3: Effect of major potentially toxic elements (PTEs) in polluted soils and sediments**

| PTE | Toxicity | Human toxicity | Zoo toxicity | Phyto toxicity |
|---|---|---|---|---|
| As | Various skin lesions appear (after several years of low arsenic exposure ): hyperpigmentation, ie dark spots, hypopigmentation, ie white spots and keratoses of the hands and feet. After a dozen or more years skin cancers are expected . Longer exposures may lead to cancers of the lungs, kidneys, liver and bladder. | H | M | L |
| Cd | Nephropathy, pulmonary lesions and lung cancer | M | M | |
| Cr | Allergic contact dermatitis, possibly carcinogenic in some cases of workers being exposed, mostly because of $Cr^{+6}$ | H | M | L |
| Cu | Cu is absorbed primarily from food. The toxicity for human is not very high. | | H | M |
| Ni | The toxicity for humans is not very high, but it can cause respiratory diseases. | | | M |
| Pb | Lead can be very toxic for human health. For children: reduction in intellectual quotient, Hyperactivity, hearing loss. For adults: increased blood pressure; liver, kidney and fertility damage. | H | M | M |
| Zn | Zinc deficiency may also be a problem for human Health. At high doses Zn may interfere with calcium metabolism and impair immune responses. | | | H |

H = high; M = moderate: L = low.
Sources: Davydova, (2005), Merian, et al. (2004), Pierzynsky et al. (2005). Okorie (2010) Poggio et al. (2009)

## 1.2 Landuse Practices

Onitsha is often described as the commercial hub of southeastern Nigeria. The Land-use are unorganized and therefore the impact of both natural and human activities can be recorded in parts of the South South and Middle belt States of Nigeria  with the impact felt beyond the southeast into the larger part of the south south and the middle belt states of Nigeria. The land-use pattern is thus haphazhard.

The dominant activities at the outskirt of the city consist of  of sand mining and quarrying while the core center of the city host residential houses, public schools, hotels, farm lands, automobile workshops, markets, abattoirs, huge waste dumpsite, transport motor parks and industrial layout. The various wastes generated from these areas find their ways into the soil and are drained into the stream channels that drain the city (Figs 1.1-1.10).

Fig. 1.1 Photograph of Fishing in waste laden NdeMilli River E 6$^{o}$ 45' 50.59" N 6$^{o}$ 4' 37.837"

Fig. 1.2: Photograph of an abattoir where meat is being proceesed with bunt tyre very close to NdeMilli River E 6$^o$ 50' 52.732" N 6$^o$ 3' 37.96"

Fig. 1.3: Photograph of some inhabitants washing meat in the waste laden river E 6° 50' 52.832" N 6° 3' 37.49"

Fig 1.4 Photograph of heep of domestic waste along a major (Onitsha – Owerri road) drainage (E $6^0$ $46^1$ $22.976^{11}$ N $6^0$ $7^1$ $53.594^{11}$)

Fig.1.5Photograph of g of laterites and ironstone mining site along  Awka – Onitsha road (E $6^0$ $51^1$ $27.075^{11}$ N$6^0$ $10^1$ $56.492^{11}$)

Fig. 1.6: Photograph of Sand and Standstone mining along Awka – Onitsha road (E $6^0$ $47^1$ $7.134^{11}$ N$6^0$ $9^1$ $43.185^{11}$)

Fig. 1.7: Photograph of Metal scrap yard at Azikiwe round about (E 6$^o$ 48' 38.443"  N6$^o$ 10' 15.485")

Fig. 1.8: Photograph of irrigated cultivation of different crops along River Nkisi (E $6^0$ $50^1$ $29.475^{11}$ N$6^0$ $8^1$ $44.815^{11}$)

Fig. 1.9 Photograph of irrigated land with  water from Nkisi river (N $6^0$ $50^1$ $29.492^{11}$ E$6^0$ $8^1$ $45.715^{11}$)

Fig.1.10: Photograph showing over crowded bus park at Upper Iweka ( E6º 47' 50.928" N6º 6' 24.376")

### 1.3 Aim of Study

The aim of this research is to evaluate the geochemical distribution, dispersion, and characteristics of some potentially harmful elements and persistent organic compounds in Soils and Sediments in Onitsha Metropolis.

### 1.4 Objectives of the Study

The objectives of the study include;

I. Determine the mineralogy of the soil, sediments and lithologic units within Onitsha.
II. determine the elemental concentration of these geologic materials
III. quantify and assess the spatial distribution of Polycyclic Aromatic Hydrocarbon in the soils and sediments
IV. use all the information obtained to evaluate the quality of the environmental media
V. determine and discriminate the various pollutants sources
VI. produce geochemical spatial maps that would be useful for sustainable Planning in the greater Onitsha

### 1.5 Scope of Work

The scope of this work include detail field work to obtain the soils, sediments and lithologic units from the study area. Detailed study of the sedimentary exposures and successions in order to construct a detailed geological map of the area**.** The use of various analytical methods to analyse the samples and in order to achieve the stated objectives.

### 1.6 Location and Accessibility

Onitsha is located in southeastern Nigeria. The city is about 45 km east to Awka. The city is characterized by an extensive flood plain that covers the entire Iyowa-Odokpa community in the southern part of the city and part of the Harbour industrial layout with average elevation of 26 m while in the the northeast around trans-Nkisi, Ogidi and the GRA elevation ranges from 34 m to 159 m above sea level .

Onitsha is located within and latitudes $6.45^0$ to $6.53^0$N and longitudes $6.5^0$ to $6.11^0$E (Fig. 1.). Onitsha can be accessed from the western part of Nigeria through the Benin-Asaba Expresswayroad and from the

Eastern part through the Nnobi-Nnewi Expressway and the Enugu-Awka road. Onisha could also be reached from the Southern part of the Country by Atani, and Obosi-Owerri roads. (Fig.1.14).

The total area coverage of Onitsha is about 72km$^2$. The area as it is presently developed from merging of various indigeneous communities. Onitsha is known for its attendant commercial activities, servicing most States and cities around it.

### 1.7 Climate of the study area

The climate is tropical equatorial, with well defined wet and dry seasons . The wet season runs from March through October with a lull in August usually called August break. This nearly divides the wet season into two. The remaining months constitutes the dry season period. Like a good portion of West Africa, the city experiences the harmattan (dry) season between the months of November and February. The area falls within the tropical rain forest belt and the climate is characterised by seasonal variation and the wind pattern blowing from the Sahara desert (Akanni 1992; Ojo 1977) with mean precipitation of 2100mm.

### 1.8 Drainage pattern

The study area is drained by River Niger a that runs from North to South of the city, and its tributaries Nkisi and NdeMilli Rivers. The NdeMilli river in the southern part drains the city from East to West, while the Nkisi river also drain the city from East to West in the Northern part , figure**. 1.11.** These three rivers play critical role in irrigation of farming during the dry by the flood plains, dredging of sand, fishing among others.

### 1.9 Vegetation

The vegetation is mainly the forest type. However, the original forest has been reduced to secondary forest bush. Evidence of largely grown up trees are found at the outskirt of the city where the trees have not been cut down. The height of the tress ranges between 5-10 meters, and they bear broad evergreen leaves that form a continuous canopy.

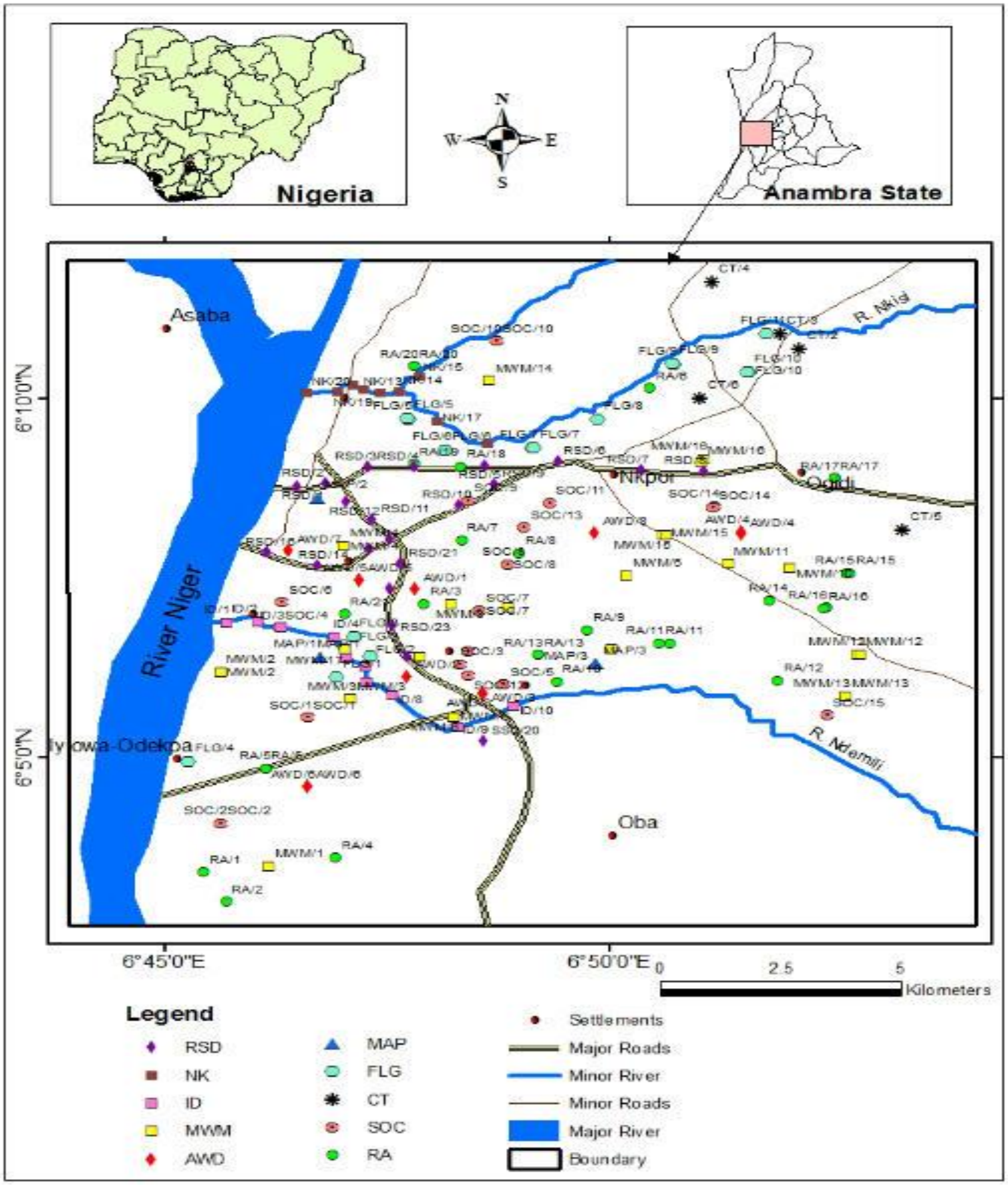

**Figure 1.11:** Location Map of the Study Area **(Modified Sheet 263, Federal Survey Nigeria, 1964)**

## 1.10 Review of previous works

Several studies on the trace elements and Polycyclic Aromatic Hydrocarbon (PAHs), constituents of soils and sediments have been carried out.These works have revealed that there are relatively high concentrations of these elements and organic compounds in the soils that underly most urban and suburban cities and that the presence of these metals and organic compounds are associated with industrialization and urbanization.

The impact of land use on the concentration and composition of Polycyclic Aromatic Hydrocarbons (PAHs) on soil and sediments of urban environment have been assessed (Zheng et al., 2011). It was reported that there was considerable elevation of PAHs in the sediments adjacent to industrial and residential areas as against Agricultural area which reported low concentration and composition of PAHs. Similar studies have been carried out on soil (Trapido, 1999) in the city of Talinn, in Parnu and Kohtla-Java and some rural areas. It was found that soil from the city had higher concentration of PAHs than that of the rural areas.

Xing, 2006 carried out a research on soil in valley under different land use patterns in Yangtze Delta region. In the research, it was discovered that high concentration of PAHs were found in areas close to smelting activities and had higher concentration as well as possible deposition of particulates by the southeastern wind effect may have led to the spatial distribution of PAHs in the study area. (Placha, et al., 2009) Also carried out a research on the concentration of PAHs in the soil of Valasske region, Mezirici, Czech Republic, assessing the region, it was discovered that there was a considerable decrease of the concentration of PAHs in soil as one move out of the city. This indicated the influence of urbanization and its associated activities on the concentration of PAHs in soils and sediment.

The distribution of metallic ions in urban soils and their relationship to soil pollution, bedrock composition, mining activities, Industrial and land use have been assessed (Elueze et al., 2001; Li et al., 2001; Aloupi and Angelids, 2001, Zhai et al., 2003; Teng et al., 2004, Ljung et al, 2006, Odewande and Abimbola, 2008, Gbadebo, 2007, Thums, et al., 2008, Anawar, et al., 2011, Zhang, et al., 2011). Their results also indicated that urban soils have elevated concentrations of Cd, Cu, Pb and Zn, high metal concentrations are located in old urban commercial districts and industrial areas. These works concluded that there is the need for instituting a systematic and continuous monitoring of metallic ions and other forms of pollutants and factors that control the quality of the environment

The concentration and distribution of metallic ions and organic compounds (PAHs) in sediments from different urban cities have been studied by many workers with a view to assess their quality and pollution status (Lee, et al., 2005, Xing et al., 2006, Laluraj and Nair, 2006, Olatunji and Abimbola, 2010, Zhang et al., 2011, Li, et al., 2011 ). These authors have reported that sediment serves as sink for metallic ions and PAHs and as pollution source to both plants and animals. Hence they recommended that there is the need for continuous monitoring and stiff regulatory measure to reduce the pollution effects.

Researches have also been carried out to assess the anthropogenic impact of metal concentrations of urban soil and drainage sediments in highly populated city, Seoul, to estimate the potential mobility of selected metals (Zn, Cu, Pb, Cr, Ni, and Cd) using five-step sequencial extraction method. The results that the different metals occur in different in phases. Zinc, Cd and Ni occurr predominantly in the carbonate bound fraction, while Pb was highest in the reducible phase. Cu in the organic fraction, and Cr in the residual fraction. The comparative mobility of these metals decreases in the order of Zn> Ni > Cd >Pb >Cu > Cr. From these findings, it was recommended that careful monitoring of environmental conditions is very important, with respect to ecotoxicity (Lee et al., 2005,) This also corroborate the findings of (Palmer et al., 2006) on the Bioavailability of metals in brownfield soils in Wolverhampton, UK.

The health implication of metallic ions (Pb, Zn, Cd, Cu, Hg, Ni, As, Mn and Cr) and polycyclic aromatic hydrocarbons in soils and sediments have for some years now been worked upon. Published research of work of Andersson et al., 2010 , suggests that diseases like asthma childhood cancer and autistic spectrum disorder (Palmer et al., 2006, Al-khashman and Shawabkeh, 2006) can be contacted through prevalence of these harmful elements in the soils and sediment of the environment hence the need for continues monitoring. Chronic exposure to lead and mercury can contribute to developmental and behavioral disabilities in children (, Al-Shavep and Seaward, 2001, Landrigan, et al 2002, Szpir 2006, Nataf et al 2006) which makes children most vulnerable to Potentially Harmful Elements PHE. The potential hazards posed by

PHEs depend on a number of factors as pointed by Fordyce, et al 2005; these include concentration, chemical form and bioavailability. Human exposure to metals in contaminated land may arise through inhalation, direct ingestion of soil and dust or consumption of food plants (Thornton et al., 2008)

The effect of pH level in the soils and sediments has also be studied, with findings that the mobility of trace elements and PHEs is a function of the pH levels of these media. Baruah and Khare, (2010), working on mobility of Sb, As, Cd, Cr, Co, Cu, Pb, Mn, Ni, V and Zn, and reportedthese elements were greatly influenced by the pH. The more acidic i.e lower pH, thegreater the mobility. This view has also been supported by Thums et al. (2008), Tarchouna et al., (2010) who suggested that the physicochemical form of metals in soils is an important control of metals mobility and their bioavailability

The use of Pb Isotope ratio as an important geochemical tool for the identification of Pb source has been studied. . Lee et al. (2005) have used isotope ratios (206Pb/207Pb) to identify the source of Pb to be mainly industrial activities rather than the leaded gasoline commonly used to power automobile Saether et al. (2011), also Podzolic forest soils using the spatial variation of Pb and the ratio between the isotope 206Pb and 207Pb and discovered that age and type of bedrock rather than anthopogenic sources are the major contributory factors to enrichment of Pb in the studied soils in Oslo area of Norway. However, understanding of the Pb isotope signatures for both soils and sediments within an environment mixed with huge commercial activities have not been accessed to possibly identify the sources of this elemental enrichment in the media, hence a needed geochemical methodology.

Studies have also revealed the use of Geospatial Information System (GIS) a computer package that allows you to record, store, , integrate, manipulate/ analyses your data and display the information in layers geographically are now commonly used to solve metallic ions concentration and distribution in the environment. Lin et al., (2002) used factorial and indicator krigging methods with GIS package to overlay and delineate the variations and pollution sources of soils metallic ions in fields in the northern part of Changhua County, Taiwan. From the result, the short and long-range variations and soil pollution by Cd, Cr, and Cu was attributedlocations and the land use of the investigated area.

Li et al (2004), carried out the study of metal concentration in urban soil, using a GIS- based approach for interpretation of the result in Hong Kong, and produced geochemical maps of spatial distribution of Zn, Pb, Cu, Mn, Ni, Cr, Cd and Co, for the study area. Several spots of metal contamination were identified from the composite metal geochemical map, mainly in the old industrial areas with high human activities. Ohta et al. (2005), applied multi-element statistical analysis for regional geochemical mapping of Central Japan and and highlighted enrichment of Cu, Zn, Cd, Sn, Sb, Hg and Pb in the soils of the study area. Odewande and Abimbola, (2008), carried out the study of metal concentration of topsoil in Ibadan, Nigeria using multi-variate statistical analysis, geochemical contamination indexes, like Metal ratio and geoaccumulation index, enrichment factor as well as GIS-based approach. These author produced geochemical maps of distribution of Cd, Pb, Zn, Cu, Mo, Ni, As Mn Cr and B were produced using the Arc View GIS technology. And a significant spatial relationship was found for Zn, Pb, Cu, and Cd in the soils, which suggest that these metal concentrations in the soils in Ibadan are of common sources. Several spots of metal concentration were identified from the composite metal geochemical map, mainly in industrial areas as well as areas with high population and high human and vehicular activities.

Gbadebo, (2007), also used GIS approach along with multi-variate statistical analysis and other contamination index in delineating degree of concentration on different horizon of the soil and dust of Ewekoro cement factory. Major, minor and trace element concentration of the different media were reported. The results indicated that bedrock composition, soil stratification and cement production contributed to the enrichment of these metals.

# CHAPTER TWO

## REVIEW OF THE GENERAL GEOLOGY OF THE ANAMBRA BASIN

### 2.1 Regional Geology

Anambra Basin is located at the southwestern part of the Benue Trough, which is a structural (synclinal) depression (Figure 2.1) It is one of the intra Cratonic Cretaceous basins whose origin is related to the separation of Africa from South America (Figure 2.2) and the opening of the South Atlantic Ocean (Ofoegbu, 1982). According to Akaegbobi (2005), the sedimentation history in the Lower Benue Trough is related to the evolution of the Anambra basin depression and Abakaliki domain. The evolutionary trend is patterned by an East to West shifting of the depocenters.

The initial area of important sedimentation and subsidence was located in the Abakaliki Trough which was active from Aptian to Santonian. The Anambra Basin became an active depocenter after the Santonian tectonic event. Gravity studies reveal appreciable thickness of the pre-Santonian sediments overlying the basement and reconfirm the subdivision of the basin into two sub-basins by the “Nsukka High”.

The sequence of depositional events demonstrates a progressive deepening of the Anambra Basin, from lower coastal plain and shoreline deltas to shoreline and shallow marine deposits. Coals and other organic rich oolitic materials occur within the Upper Campanian to Lowermost Maastrichtian facies, where they are associated with extensive swamp/flood plain and shoreline deposits. The main feature of the Anambra Basin succession is the lateral facies variations caused either by distance from the shoreline and/or by the rate of subsidence (Akaegbobi, 2005).

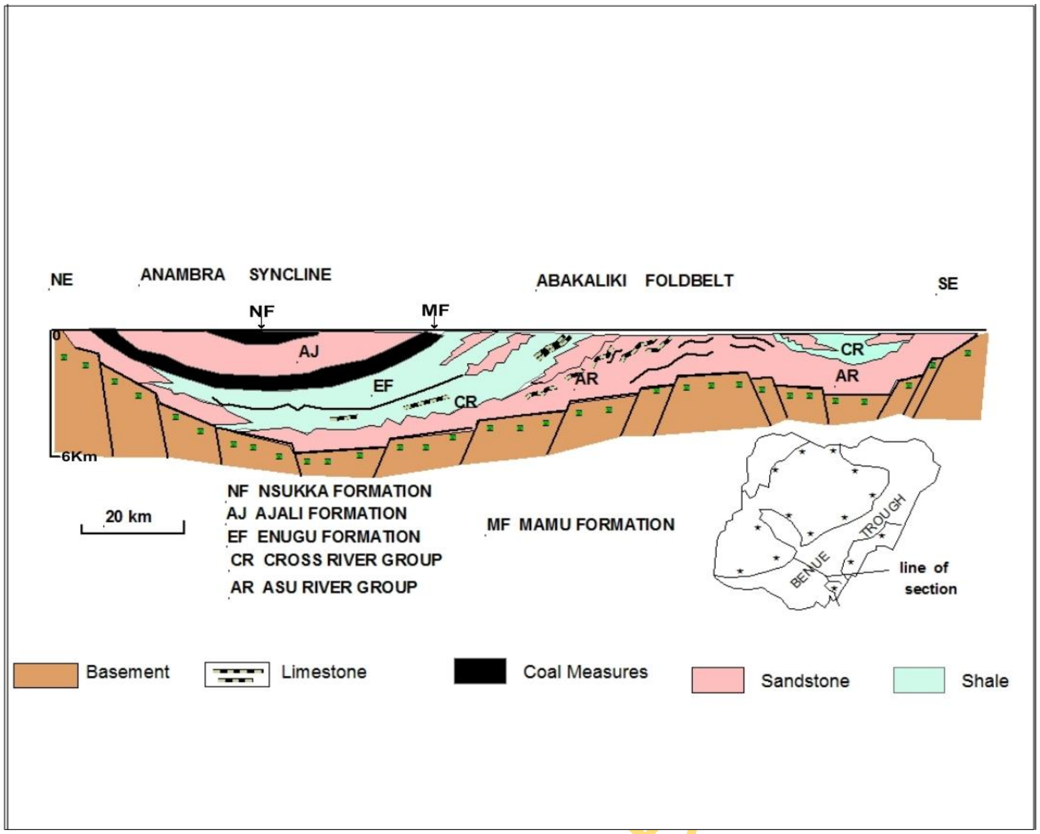

Figure 2.1. Cross section of the Lower Benue Trough showing the synclinal Anambra Basin (Adapted from Petters and Ekweozor, 1982).

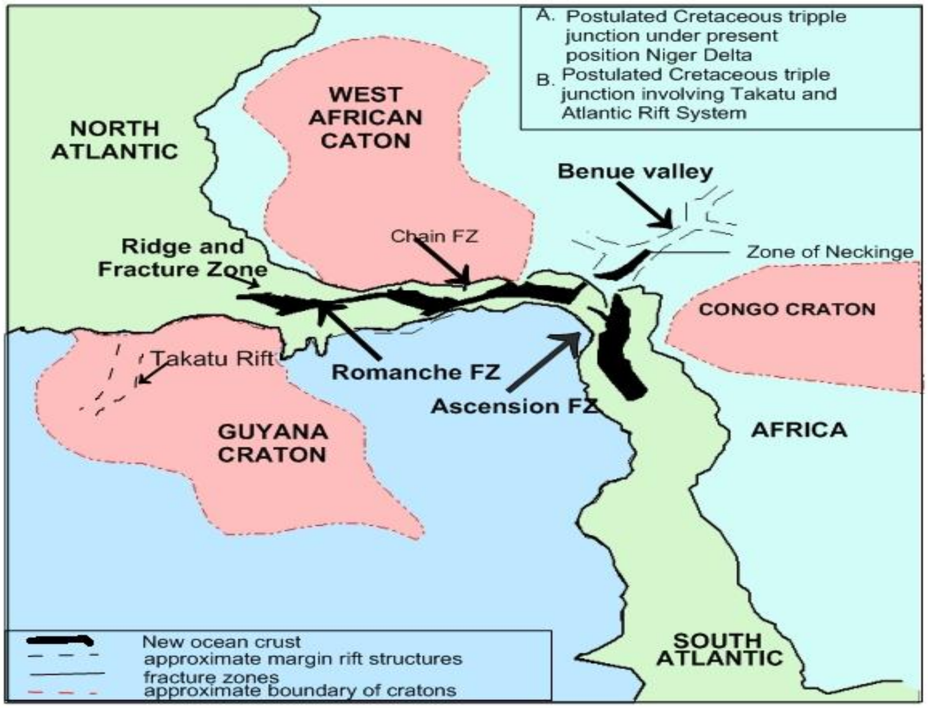

Figure 2.2. Separation of Africa from South America during the Gondwana breakup and the formation of the Atlantic Ocean (After Burke et.al, 1972).

### 2.1.1 General Stratigraphy

According to Whiteman (1982) much is not known about the Lower Cretaceous and pre-Santonian subsurface deposits in the Anambra Basin due to the great thickness of post-Santonian sedimentary fill that occupies much of the basin, and lack of more subsurface information. However, Cretaceous outcrops from the adjoining southern Benue Trough suggest what underlies the post-Santonian deposits in the Anambra Basin. An outline of the stratigraphy and geology has been given by Murat (1972); Akande and Erdtmann (1998) and other workers (Table 2.1)

Sedimentary fill in the southern Benue Trough include three major unconformity bounded depositional sequences namely: Albian-Cenomanian, Turonian-Coniancian, and Campanian-Maastrichtian (Petters, 1978). The pre-Santonian sequences consist of the Asu River Group, Eze-Aku and Awgu Formations while the post-Santonian sedimentary fill consist of the Owelli Formation, Nkporo/Enugu shale, Mamu Formation, Ajali sandstone, Nsukka Formation, Imo shale, and Ameki/Nanka Formation (Whiteman, 1982; Akande & Erdtmann, 1998; and Mode, 2004).

Cretaceous sediments reached a thickness of more than 5000 m. Sediments of the Asu River Group, the Eze-Aku, and Awgu Formations are exposed in the core of the Abakaliki anticlinorium and areas marginal to it, whereas the overlying Nkporo and Mamu Formations occur within the adjacent Anambra Basin (Akande and Erdtmann, 1998). The stratigraphic succession in the southern Benue Trough and its various sub-basins is given in Table 2.1.

### 2.1.2 Asu River Group

The oldest rocks in the southern part of the Benue Trough are the Abakaliki pyroclastics comprising altered amyglaloidal basalts, agglomerates and lithic tuffs which were probably ejected under subaeriel shallow marine conditions during the Aptian to Early Albian times (Uzuakpunwa, 1974).

Overlying the Abakaliki pyroclastics are the Asu River Group (Table 2.1) consisting of about 3000m of micaceous sandstones, mudstones, sandy shales, and shale containing sandstone,

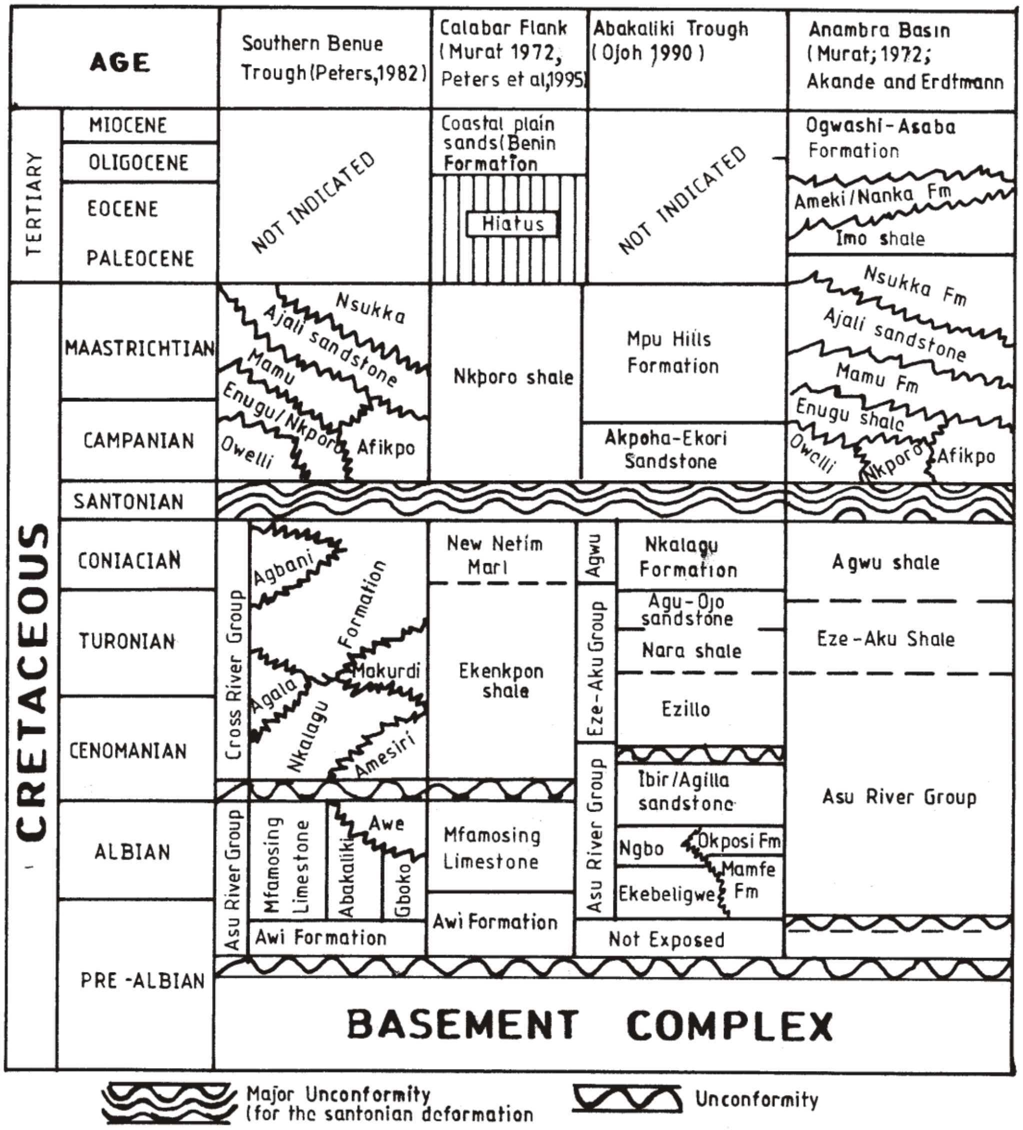

Figure 2.3. Generalized stratigraphic succession in the southern Benue Trough and its various sub-basins (Adapted from Akande and Erdtmann, 1998).

siltstone and limestone lenses. It also contains lava flows, dykes, sills and Cenomanian intrusions.

These sediments are folded around south of Abakaliki along NE – SW, and have been broadly subdivided into the blue-black Abakaliki shale and non-marine coarse grained sandstone, the Mamfe Formation by Petters (1978). The deposition of Abakaliki shales were believed to have taken place in moderately deep marine waters along southeastern Nigeria. The shales contain fossils such as ammonites, radiolarians, echinoids, some pelycepods and gastropods with virtually no foraminifera (Reyment, 1965; Kogbe, 1975; Petters, 1978).

According to Akande and Erdtmann (1998), the Asu River Group represents the first cycle of shallow marine and brackish water sediments rapidly deposited over the gneisses, schists, and migmatites of the Lower Paleozoic Basement Complex and their weathered equivalents. Albian-Turonian age has been assigned by Reyment (1965) and Burke et. al. (1972) to the Odukpani Formation which was interpreted to be deposited under shallow water/near shore conditions. The sediments of the Odukpani Formation were mapped by Murat (1972) as part of the Asu River Group.

### 2.1.3 Eze-Aku Formation

The Eze-Aku Formation belongs to the Turonian deposits. The Turonian period experienced a transgressive stage and three periods of emersion and erosion which resulted in intra-Cretaceous unconformity between the gently dipping Senonian beds overlying the disturbed strata mainly from Albian to Lower Turonian (Petters, 1978). According to Akande and Erdtmann (1998), the Eze-Aku sediments were deposited as a result of renewed transgression during the second depositional cycle.

In most part of the Benue Trough, The Asu River Group is succeeded by the Eze-Aku Formation. This formation comprises dark grey-black shales and siltstones with frequent facies changes to sandstone or sandy shales. The formation represents shallow water or near shore deposit. The fossils consist of vascoceratids, pelycepods, gastropods, echinods, fish teeth, which indicate a basal Turonian age (Kogbe, 1975; Petters, 1978). The thickness of this formation varies; it is very thick in the northern part around Makurdi where over 1000m had been recorded in the subsurface sections by Agagu (1978).

### 2.1.4 Awgu Formation

The Coniancian witnessed a transgressive substage and the sediments have been assigned to the Awgu Formation which conformably overlies the Eze-Aku Formation. Awgu Formation on the surface consists of grey to black well bedded fissile shales, with commonly occurring thin interbeds of shelly limestone, and fine-medium grained/moderately sorted sandstone. The thickness of the Awgu Formation has been estimated to be about 350-1000m (Simpson, 1954; Reyment, 1965; Kogbe, 1975).

The formation was reported by Agagu et.al. (1985), to contain fossils such as planktonic foraminifera and pollens, and thus they assigned a Turonian-Santonian age and a shelf depositional environment for it. On the basis of subsurface data, they subdivided the formation into Awgu shales and Agbani sandstones. Murat (1972) recorded the exposed Agbani sandstone as probable part of a delta developed during Coniacian-Lower Santonian regression, but the lithologic association and sedimentary structure indicate that it is fluvial sandstone. The Agbani sandstone consists of white, medium-coarse grained often pebbly sandstone with occasional interbeds of brown laminated clays and carbonaceous shales with thickness ranging from 9 to 300m.

### 2.1.5 Owelli Formation

After the deposition of the Agbani Sandstone, there was a brief marine shelf incursion that led to the deposition of Ogugu Shale which comprises dark-grey micaceous shale with occasional silty and sandy intercalations. After this brief period of deposition, the Abakaliki Anticlinorium was reactivated again as there was renewed influx of clastic sandstone which led to the deposition of the Owelli Sandstones (Figure 2.4). The Owelli Sandstone varies in thickness from 24 – 750 m, and consists of coarse grained sandstones.

### 2.1.6 Nkporo/Enugu Shale

After the deposition of the Owelli Sandstone, there was a major marine transgression in the Anambra Basin which led to the deposition of the Nkporo/Enugu Shale and its northerly lateral equivalents in the Afikpo Syncline and Calabar Flank respectively (Zaborski, 2000). According to Zaborski (2000), in the Calabar Flank, the Nkporo Shale includes both Upper and Maastrichtian beds but elsewhere it is probably Campanian. The Age of the Enugu Shale has been assigned to Campanian-Maastrichtian. The Nkporo/Enugu Shale (Figures 2.4 & 2.5) have been extensively studied with respect to their fossil content by some workers (e.g. Reyment, 1965; Petters, 1978; Agagu et. al., 1985; Mebradu, 1990; Nwajide and Reijers, 1996). Mebradu (1990) suggested a Maastrichtian age for this formation based on miospores, and Shell BP (in Whiteman, 1982) also suggested Maastrichtian based on Libycoceras angolense. However, Reyment (1965) pointed out that the Enugu Shale is Campanian and extends to the extreme lower part of the Maastrichtian. According to Petters (1978), the Enugu Shale appears to be barren of foraminifera though it has yield Milliamina. Poorly preserved mollusk and plant remains (Whiteman, 1982) as well as dinoflagellates, algal spores, and leaf cuticles (Mebradu, 1990) have been recorded from the Enugu Shale.

The Enugu/Nkporo Shale, according to Nwajide & Reijers (1996) represents the brackish marsh and fosilliferous pro-delta facies of the Late Campanian-Early Maastrichtian depositional Nkporo Cycle. Nyong (1995) inferred the Nkporo Shale to have been deposited in a variety of environments including shallow open marine to paralic and continental settings. As reported by Petters (1978) and Agagu et.al. (1985), arenaceous microfauna observed in the shales were dominated by Milliamina and a marsh environment was thus inferred for it. Nwajide & Reijers (1996) interpreted formations of the Nkporo Cycle to reflect a funnel shaped shallow marine shelf that grade into channeled low-energy marshes.

Outcrop study around Uturu by Agagu et. al. (1985), shows that the Nkporo Formation consists of dark-grey, very fissile and soft shales; mudstones with thin interbeds of sandy shale; fine sandstone; and marl. The Nkporo Shale varies in thickness from 42 to 339m, and grades upwards into the Mamu Formation. This probably happened due to fact that the broad, shallow sea gradually became shallower and the paralic sequence of Mamu Formation was deposited.

### 2.1.7 Mamu Formation

The Mamu Formation (lower coal measures) is overlain by the continental sequence of the Ajali Formation (Figure 2.3), and contains a distinctive assemblage of sandstone, sandy shale, shale, mudstone, and coal seams (Reyment 1965). This formation has been reported to outcrop at several locations by Nwajide & Reijers (1996). It occurs as a narrow strip trending north-south from the Calabar Flank, swinging west from the Ankpa Plateau and terminating at Idah-Auchi near the Niger River. Its best exposures are found in road cuts above the Onyema mine in the Iva Valley at Enugu, and road cut through the escarpment at Leru on the Port Harcourt – Enugu expressway.

Surface sections, reveals that the Mamu Formation comprises mainly white, fine-grained and well sorted sandstones. There are frequent interbeds of carbonaceous shales with sparse arenaceous microfauna, and coal beds (Agagu et. al., 1985). Open strand/coastal plain environments, were inferred for this formation by Agagu et al., (1985), and Nwajide & Reijers (1996) respectively.

### 2.1.8 Ajali Sandstone/Formation

The Ajali Formation which has a thickness range of 210-515m is overlain by the Nsukka Formation (Figures 2.3 and 2.4), and consists of friable moderate to poorly sorted sandstones, typically white in colour but sometimes iron-stained with cross-stratification structures. The formation where exposed, is often overlain by red earth, which consists of red, earthy sands formed by weathering and ferruginization of the formation (Kogbe, 1975). Adeleye (1975) reported the presence of thin interbeds of mudstone with occasional plant impressions, and no vertebrate or invertebrate fossils in the Ajali Formation.

According to Nwajide & Reijers (1996), the coal-bearing Mamu and Ajali formations, accumulated during the epoch of regression of the Nkporo Group with associated progradation. They characterized the Ajali Sandstones as tidal sands.

### 2.1.9 Nsukka Formation

After the deposition of the Ajali Formation, the environment of deposition returned to partially paralic conditions, and these conditions witnessed the deposition of the Nsukka (upper coal measures) Formation during the Paleocene (Figure 2.4). This formation with a thickness range of 200 – 300m, lies conformably on the Ajali Sandstone (Adeleye, 1975) and consists of alternating succession of fine-grained sandstone/siltstones, grey-dark shale, sandy shale with coal seams at various horizons (Simpson, 1954; Reyment, 1965; Agagu et.al., 1985; Mode, 2004). A strand plain/marsh environment with occasional fluvial incursions similar to that of the Mamu Formation was inferred for this formation by Agagu et.al. (1985), who assignned an age of Maastrichtian to Paleocene to the Nsukka Formation.

### 2.1.10 Imo Shale

The Imo Shale which overlies the Nsukka Formation (Figure 2.5), consist of thick, fine textured, dark/bluish grey clayey shale, with occasional admixture of clayey ironstone and sandstone bands. The formation becomes more sandy towards the top where it consists of alternations of sandstone and shale (Anyanwu and Arua, 1990). Nwajide & Reijers (1996) interpreted the Imo Shale to reflect shallow-marine shelf in which foreshore and shore face sands are occasionally preserved. They furthered inferred that in the Niger Delta, the subsurface Paleocene deposits are essentially of (deep) marine origin and are equivalent to the Imo Shale in the Anambra.

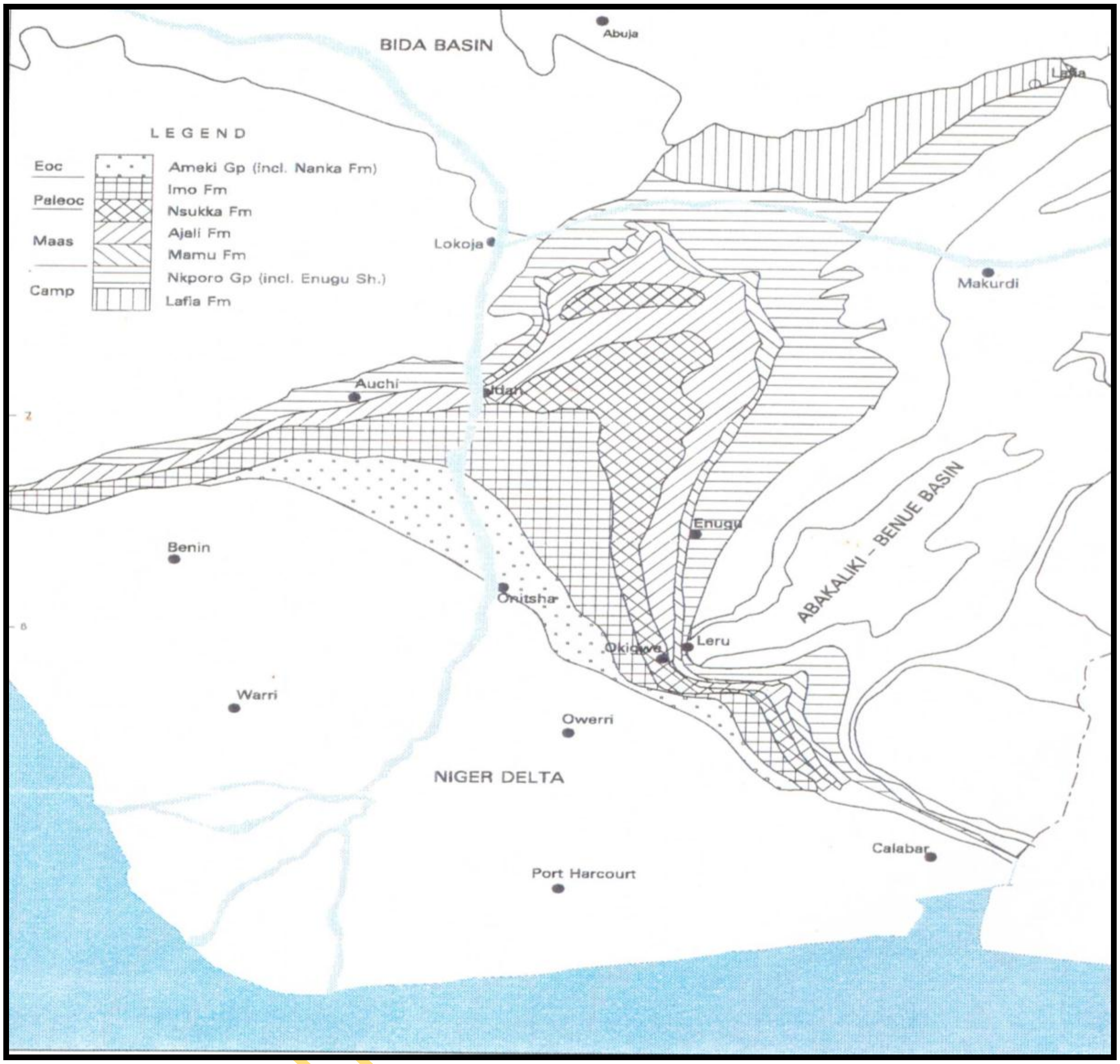

Figure 2.4: Regional Geologic Map of Anambra Basin and Niger Delta showing the Stratigraphy of the Anambra basin (modified after Nwajide and Rejiers,1996).

### 2.1.11 Ameki Group

Accordding to Nwajide (2013), The Ameki Group was given an early recognition by the Geological Survey Of Nigeria, with the name Bende-Ameki Group and Bende-Ameki Series (Wilson and Bain, 1925, 1928; Reyment and Barber, 1956). Nwajide (1979, 1980) noted the Formations to consist of Ameki Formation, Nanka Formation and Nsugbe Formation. The facies constitutes the bulk of Eocene strata overlying the Imo formation. Its type locality consists of a highly fossiliferous, dark grey, argillaceous, weakly consolidated sandy-clay with calcareous concretion and white clayey sandstones. The Ameki group comprises of two lithological divisions: the lower fine to coarse sandstones with intercalations of calcareous shale and thin shelly limestone and upper with coarse cross bedded sandstones, bands of fine grey-green sandstone and sandy clay (Reyment, 1965). Agagu et al.,(1985) and Petters (1978) have interpreted the Ameki Group to be estuarine, lagoonal and open marine setting. There are presence of carbonaceous plants remains and lignite at some horizons. The Ameki group represents the last regressive cycle of deposition within the Anambra Basin.

### 2.1.12 Nanka Formation*:*

According to Nwajide and Reijers (1996) and Allen, 1965, the progradational Nanka Formation marks the return to regressive conditions. The outcropping deposits of the Eocene regression, which marks the beginning of the Niger Delta progradation, constitute the Ameki Group, which includes tidal facies and backshore as well as pro-deltaic facies. The prograding shore face and river deposits are reflected in the subsurface deposits of the Agbada Formation in the Northern depobelts of the Niger Delta (Figure 2.4), while the marine Imo Shale equivalent in the subsurface is termed the 2.1.13 Akata Formation.

The lithology of Nanka Formation is monotonously sand, except for occasional gluconitric shales, mudstones, claystones and ferruginous sandstones horizon, which occurs as interbeds. The sand is clayey and varies widely in size from fine to coarse grained and pebbly. It is texturally immature but compositionally supper matured, being completely feldspar-free.

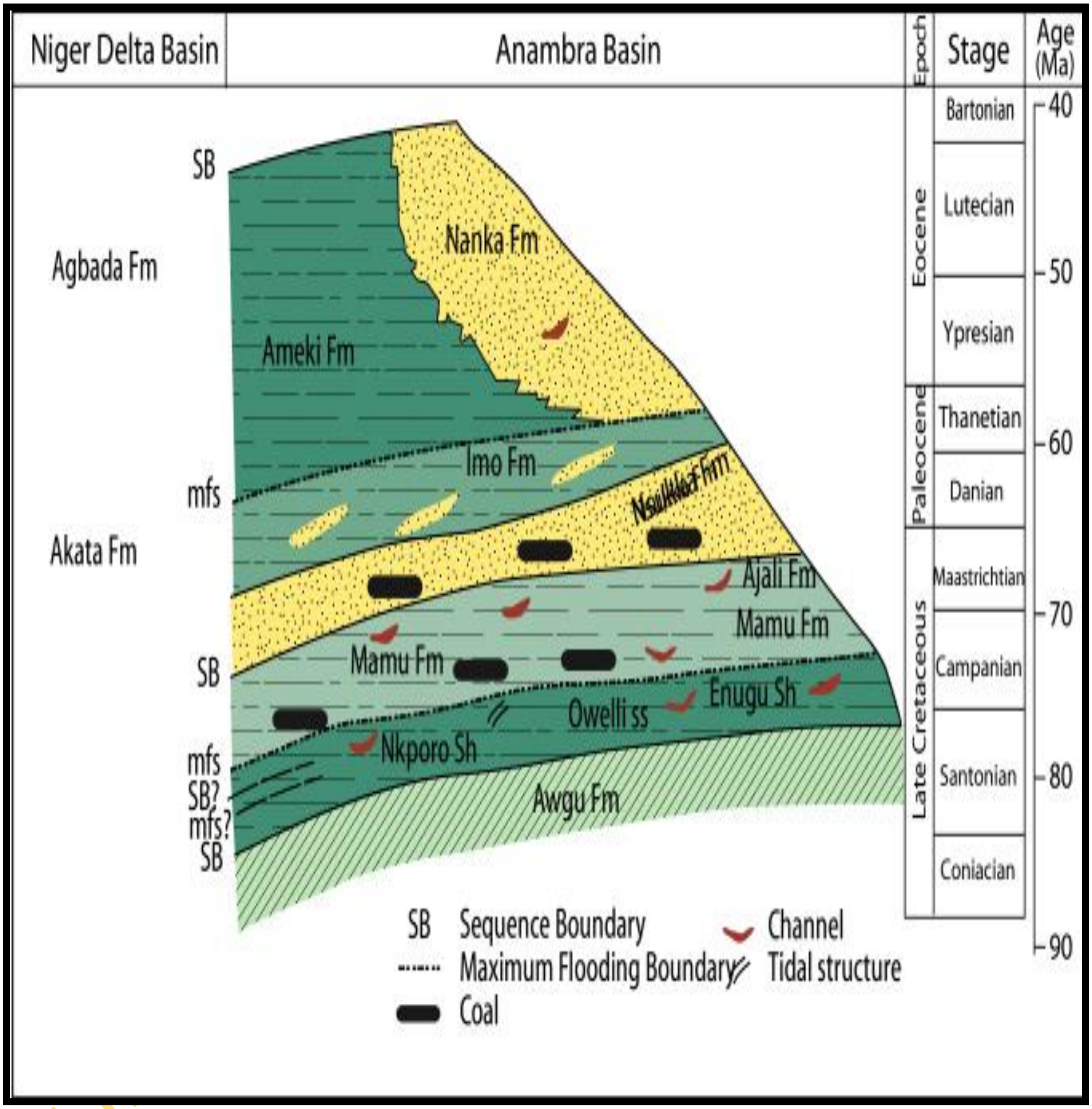

Figure 2.5. Stratigraphic section of the Anambra Basin from Late Eocene and time equivalent formations in the Niger Delta (After Nwajide and Reijers, 1997).

## 2.2: Geology of the study Area

The Onitsha area is underlain by the Ameki Formation and it is bounded at the western part of the area is bounded by the river Niger with edge of the River housing the alluvial deposits (Fig 2.5). The Ameki Formation is Eocene in age and its lateral facies equivalence is the Nanka Formation. The Ameki Formation consists of a series of highly fossiliferous grayish-green sandy clay with calcareous concretions and white clayey sandstone. It comprises two lithological groups. The lower groups is composed of fine to coarse grained sandstone with intercalation of calcareous shale and thin shaly limestone while the upper part consists of coarse grained cross bedded sandstone with bands of fine grey-green sands and sandy clay (Reyment, 1965). Nwajide (2013) refers to the Ameki Formation to have between 1200ft to 1500ft with regressive facies, shallow marine environment as assigned. The formation overlies the Imo Formation. Its lateral equivalente is the Nanka sand. The detailed field investigation of the type localities for the Ameki Formation is discussed in chapter Four (4) of this study.

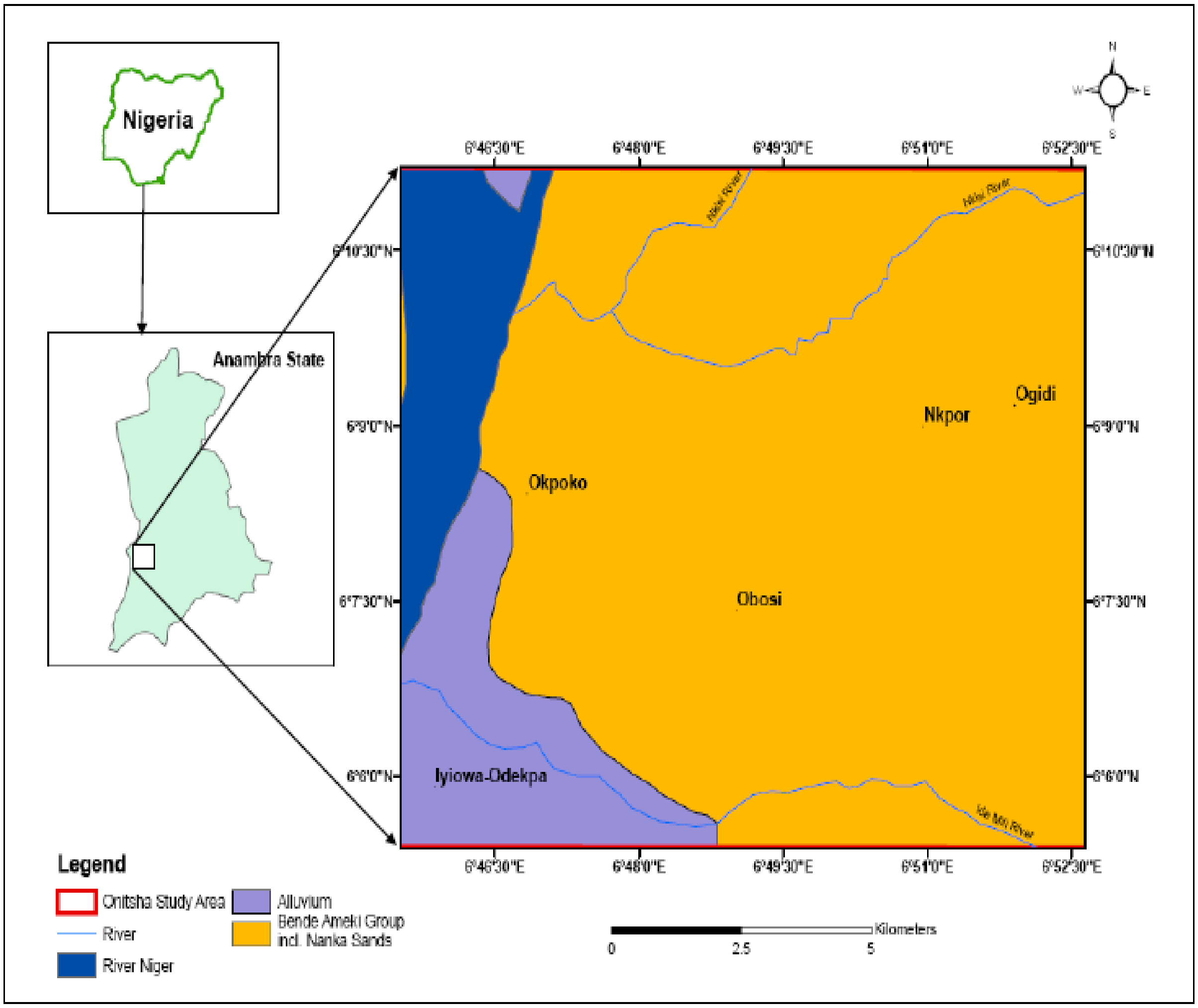

Fig 2.6: Geologic Map of Onitsha Area, part of Sheet 71 (Modified after Geological Survey of Nigeria, 1957)

# CHAPTER THREE

# METHODOLOGY

## 3.1 Field activities

The study area was classified for sampling using Topographic Sheet 300 of Onitsha South East of Federal Surveys Nigeria, 1964 on a scale of 1:50,000.

A total of 162 samples were collected for analyses. 83 top soil (0-30cm depth), 35 subsoil (30 – 100cm depth), 20 stream sediment (11 from NdeMilli River and 9 from Nkisi River) at an interval of 250m to 300m, 21 Roadside drain sediment at an interval of 250m and 3 ferruginised sandstone samples as found from within the soil profile from the various quarry units in the study area. in other to achieve the said objectives, the sample locations were designed to follow landuse parttain and appropriate code were given to the various landuse. Thses include Residential Area (RA), Farmland and Garden (FLG), Active waste dump (AWD), Mechanic and metal workshops (MWM), Market and Abbatoir (MAP), Schools and Office complexs (SOC) and Control samples (CT) from relatively prestine areas. While for the sediement samples, they include Roadside Drian sediment (RSD), Ndemilli River (ID) and Nkisi River (NK)

The soil samples were collected with a stainless steel sampling auger of 1.5meter long this was to enable one get to the required depth of one (1) meter. While the sediment samples were collected with the aid of a clean plastic bowl. Three to four subsamples were collected and composited as one representative sample for every location for the soils and sediment samples. This was adopted in order to reduce point source contamination error. All the soil and Roadside drain sediment samples were stored into polythene bags and labeled at every location sampled.

The stream sediments were first sampled into a plastic bucket with the aid of plastic bowl and wet sieved with < 75µm mesh right inside or by the side of the stream with the aid of the stream water, and the clay fraction was stored inside a 75liter plastic bottle. This sampling procedure was adopted to reduce contamination effect.

All the field sampling was carried out between December and January 2012 and December and January 2013. The choice for this time of the year was for easy accessibility in the study area and to reduce dilution effect that may be caused by rainfall on metals and organic compounds in both the soils and sediments.

The soil and roadside drain sediment samples were subsequently air dried at room temperature for 72 hrs and stored. While the stream sediment collected in plastic bottles were allowed to settle down, the water in the plastic bottle was decanted and the sediment in clay fraction was allowed to dry at room temperature for 5 to 6 days and thereafter stored for further sample preparation.

Four additional samples one each of galena, coal, vehicle exhaust and battery cell were obtained for Pb isotope analyses in order to provide a basis of comparison of Pb contents in the media and to be able to discriminate the sources of the metals in the media.

## 3.2 Laboratory acitivies

### *3.2.1 Sample Preparations*

Nodules and pellets of ferrugenised sand stones were prepared into thin sections for mineralogical analysis.

The soil samples collected were air-dried, sieved with 200µm to remove all large particles. This was then followed by grinding, with the aid of mortar and pestle and subsequently sieved with > 63µm in other to get the clay fraction. The stream sediment were wet sieved with > 75µm, stored in a plastic bottle, allowed to dry at room temperature, and later pulverized and sieved with >63µm. All prepared samples were then analysed for elemental compositions

### 3. 2. 2 Determination of Physical Properties

*Colour determination*

The colors of the sand and sandstone were determined during field sampling on exposed outcrops, using visual inspection.

Determination of Electrical Conductivity, pH, and Total dissolve solid in soil and sediment sample

Fifty (50) gramme of air dried soil and sediment samples were measured and transferred into 200 ml beaker, and 100 ml of distilled water was gradually added and left for 30 minutes to facilitate water movement through the samples. The samples were later stirred occasionally with a glass rod and allowed to stand for 24 hours. The Hach Eco 40 multi, Milwaukee hand held digital meter capable of measuring pH, Electrical conductivity (EC) and Total Dessolved Solid (TDS), was standardized with buffered apropritely after which the electrode was dipped into the samples for measurements of the pH, EC and TDS. These analyses were carried out at the department of Geology, University of Ibadan, Ibadan.

### *Determination of Total cabon and Total Organic Cabon in soil and sediment*

Parts of the samples were grounded to 200 µm and analysed on a LECO CS 230 carbon-sulphur-analyser for Total Organic Carbon content (TOC). The TOC was determined after removing carbonates with 2N HCl at 80 °C.

Soluble organic matter was extracted from the pulverized sample using a Dionex ASE 350 apparatus. The extraction was performed at 80 °C and 1500 psi pressure in three cycles using dichloromethane as the solvent. The extracts were dried under a stream of nitrogen and further separated by column chromatography on activated silica gel using isohexane, isohexane/dichloromethane (2:1, v/v) and dichloromethane/methanol (2:1, v/v) as efluents for the aliphatic fraction, the aromatic fraction and the polar fraction respectively.

The saturated fractions were analysed to determine the Hydrocarbon content in the range between $n$-$C_{10}$ to $n$-$C_{40}$ in principle according to ISO 16703 by gas chromatography using a HP-7890 instrument equipped with a PTV and a DB-1 column (30 m; 0.25 mm i.d.; film thickness 0.25 µm coupled to a flame ionisation detector (FID), Hydrogen was used as carrier gas (26 cm/s). The column were heated from 40 °C to 315 °C, at a rate of 35 °C/min with an additional isothermal step of 2.2 min, then heated to 330 °C, at a rate of 35 °C/min., this temperature was held for additional 5.5 min.

### 3.2.3 Mineralogical Analysis of soils and sediments

150g of samples with particle size of 63 µm (*n* = 3) were analysed for mineral content using X-Ray Diffraction (XRD) Philips X'PERT MPD type, for the determination of the mineralogical composition of the samples. These samples comprise three sand and sandstone samples from lithologic exposures in the study area, at the Mineralogical Laboratory, University of Free State, South Africa. Below are the parameter under which the analyses were carried out.

| | |
|---|---|
| Divergence Slit Type | Fixed |
| Divergence Slit Size [°] | 0.2177 |
| Specimen Length [mm] | 10.00 |
| Measurement Temperature [°C] | 25.00 |
| Anode Material | Cu |
| Generator Settings | 40 mA, 45 kV |

The mineral species in each sample were identified base on their respective crystal lattice spacing as measured.

### 3.2. 4 Determination of Metal content in soils and sediments

Soil and sediment samples of 0.5g were first digested with aqua-regia ($HNO_3$ and HCl). Thereafter, the digests were subjected to elemental (major and trace elements) analysis using Inductively Coupled Plasma-Emission Spectrometry (ICP-MS) at the ACME Laboratories, Vancouver Canada.

As part of quality control for precision and accuracy, analyses of duplicate samples, reference standard materials and blank samples were carried out alongside the unkwnow under the same analytical condition in the course of the analyses of the samples.

Twenty (20g) gramm of soils and sediment samples were also analyzed using X-ray Fluorescence (XRF) method for the determination of both major and trace elements at Federal

Institute of Geosciences and Natural Resources, (BGR) Hannover, Germany. Thirty-two samples were analysed in all using XRF.

### 3.2. 5 Determination of Organic compound (PAH) in soil and sediment samples

Polycyclic aromatic hydrocarbon in 60 soil and sediment samples were analysed by gas chromatography/mass spectrometry (GC/MS), using a HP-7890 instrument equipped with a PTV inlet splitting on two DB-1 columns. (each 50 m; 0.2 mm i.d.; film thickness 0.11 µm), one coupled to a flame ionisation detector (FID) the other one to an Agilent 7000 QQQ mass spectrometer. Helium was used as carrier gas (27 cm/s). The columns were heated from 50 °C to 200 °C, at a rate of 20 °C/min, then heated to 300 °C, at a rate of 10 °C/min, this temperature was held for additional 15 min. Compounds were identified by comparison of mass spectra and retention times with commercial standards. Quantification of 16 PAHs was done via MRM-measurements

### 3.2.6 Determination of Pb (lead) isotopes in soil, sediment, galena ore, coal, battery cell and gasoline exhaust.

About 15g of clay fraction of soils and sediments (*N=30*) as well as a sample each of galena, coal, soot of vehicle exhaust and battery cell were dissolved in a strong acid mixture which include HF: $HCLO_4$:$HNO_3$ in a ratio of 4:1:1 in a beaker. HBr medium along side anion exchange column were subsequently used to separate Lead from the solutionfor analyses. Triplicate digestions of each sample for analyses were prepared so as to improve on the precision of the analysed result.

Lead (Pb) Isotopes ($Pb^{204}$, $Pb^{206}$, $Pb^{207}$ and $Pb^{208}$) were then analysed using ultra trace Inductively Coupled Plasma-emission spectrometry (ICP-MS)

All samples were analyzed and the quality control mechanisms follow the usual procedure of duplicate sample analysis and the use of lead isotope standard reference materials for instrument calibration and mass fractionation correction.

### 3.2. 7 Sequential extraction analysis

Sequential extraction is selective extraction, which is usually carried out to mimic the release of the selective metals into solution under various environmental conditions. The procedure was designed to quantify partitioned metals in different solid phase based on their chemical form. (Jones, 1993, Ahnstrom and Parker, 1999, Lee, et al., 2005, Thums and Farago, 2008, Divvela, 2010, Zimmerman and Weindorf, 2010).

At each step of the process, calculated concentrations of chemicals and buffers were added and the samples were shaken on an end-over-end shaker. The leachate from each step was then digested and analyzed with an inductively coupled plasma mass spectrometer (ICP/MS), This multi-step procedure enssures that all the metals of interest are completely extracted from the sample. The results from all the different steps were calculated and used to determine the absolute concentrations under different conditions. Factors such as pH of the acid used for adjustment, temperature and duration of extraction are the critical factors that control the concentration of metal extracted from the sample. Stated below are the five step sequential extraction methods that were chosen for this research, for ten (10) samples from locations with relatively high concentration of potentially harmful elements.

Demineralized $H_2O$ leach water soluble components (LH1), at pH 7 for 2h;

Carbonate fraction (LH2) 1 M ammonium acetate leach cations adsorbed by clay and elements co precipitated with carbonates; adjusted to pH5.0

Organic and Sulfide fraction (LH3) 0.1 M sodium pyrophosphate leach for elements adsorbed by organic matter (humic and fulvic compounds).

Reducible fraction (LH4) 0.1 M hydroxylamine HCl leaches for elements adsorbed by amorphous Mn hydroxide, often the most reactive soil phase for scavenging mobile elements.

Residual fraction (LH5) 0.25M hydroxyamine HCl for elements adsorbed by amorphous Fe hydroxide and more crystalline Mn hydroxide.

## 3.3 Data management and statistical Analysis

The various analytical results that were obtained from the analyses were subjected t statistically analysed. The tools used included Descriptive statistical analyses (median, mean, range, percentiles, standard deviation, and coefficient of variance), correlation analysis, and Principal Component Analyses (R-Mode and component plot). These statistical inetrpretation were done using Excel 2007, SPSS (Statistical Program for the Social Scientists) version 15.0, Grapher 8, Origin and Surfer 8 respectively.

Geochemical intetpretative tools such as Geoaccumulation (Igeo), Metal Ratio, Contamination Factor and Degree of Contamination were used to assess the degree of contamination this was carried out by the concentration level at present with preindustrial level of concentration in the area. (Muller 1979) designed the computation formula;

$Igeo = Log_2 Cn/1.5Bn$,

Where Cn is the measured concentrations of the element in the sample

Bn is the geochemical background value

While 1.5 is a constant which allows for natural fluctuations in the content of any environmental media and very little anthropogenic influences. Table 3.1 shows the classification order of practically uncontaminated to extremely contaminated

Table 3.2: Geoaccumulation (Igeo) index Values classification, by 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 |

Normal elemental abundance in unmineralized geologic materials is known as background concentration. In geochemistry, there is no one natural background level that can be used on the in evaluating earth materials like soils and sediments . This is because the earth is geochemically non-homogeneous, therefore, in terms of uniform distribution of elements, soil type and horizon, (Eby, 2004, Hamzeh, et al., 2011) so, in environmental geochemistry studies, natural background values must be evaluated on a local scale. It is base on this that samples were taking from relatively pristine locations away from the urban area of study and a below one (1) meter depth.

### 3.4 Contamination Factor and Degree of Contamination

The level of contamination of the soils and sediment samples were also assessed using both contamination factor (CF) and the degree of contamination ($C_{deg}$.) according to Hakanson (1980). This was done with an equation to compare the concentration in the sample collected to that of a background samples collected from a geologically uncontaminated area. Contamination factor refers to the degree of contamination as a single – metal index, while the degree of contamination refers to overall contamination level of the sediment/soil in relation to all metals found in the geologic media . The formulae for CF and $C_{deg}$ are shown below.

$$CF = Cn / Bn$$

$$C_{deg} = \sum \{ Cn/Bn \}$$ Where:

Cn – is the average concentration of the metal in the sediment category.

Bn – is the background concentration of that metal.

In geochemistry, standards serves as reference materials to which more detailed analyzed survey results can be related. For this work, the standards used are Abundant Element in Average Crustal Rock (AEACR), Average Shale Concentration and control (Background) values.

### 3.5 Detection limit for Trace Elements

The minimum detection limit (MDL) for the trace elements in the study area is included in appendix 3 (a- g) and represented as MDL in the tables.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## 4.1: Field investigation

Onitsha is underlain by chronostratigraphic units of the Anambra basin comprising of the Ameki formation (eighty (80) % of the study area) and alluvian deposit in Iyiowa-Odekpa axis of the study area (Fig. 4.1). The geology of the area was studied at road cuts, erosional surface, artisanal mining surfaces which are presented as both pictural view and section lithological logs, (Fig 4.2 to Fig 4.8).

The Ameki Formation in the area is made up of thick reddish brown lateritic sands (1- 3m thick) as the top followed in sequences by sand, sandstone, silty sand and silt clay units with varying colours that exhibit some heterolith sequence charactristics. The sand, sandstone and silt are loosely bound and friable in most of the exposed profile. Also of ferroginised sandstone within the various strata as exposed, within the relatively thick lawered laterite, there where presence of dark brown noddles of ferrogenous sandstone of different sharps and sizes as seen in Figure 4.7, why in some other locations, they were occurring as larminar horizontal form within the lateritic soil as seen in figure 4.3 and the section. Also in some other locations the feroginous sandstone are found within the strata of the sand and siltstone unit occurring at different thickness of between 4cm to 12cm. This characteristic was very prominent in most of the exposures found in the study area. At an exposure along Onitsha – Enugu express way by Ogidi area, Fig.4.6, and at some locations around the prison yard area, they occur as massive outcrop of different sizes (Fig. 4.5). The soil profile exhibits structural cross bedding within the sand and silt layers dipping west direction.

The alluvian deposit is poorly exposed. This is because the area is almost at the same elevation with the Levee of the River Niger. However, observations from an excarvated pits (1m deep) revealed that the alluvian deposit is characterized by sand and clayey-sand horizons, which are rich in organic materials.

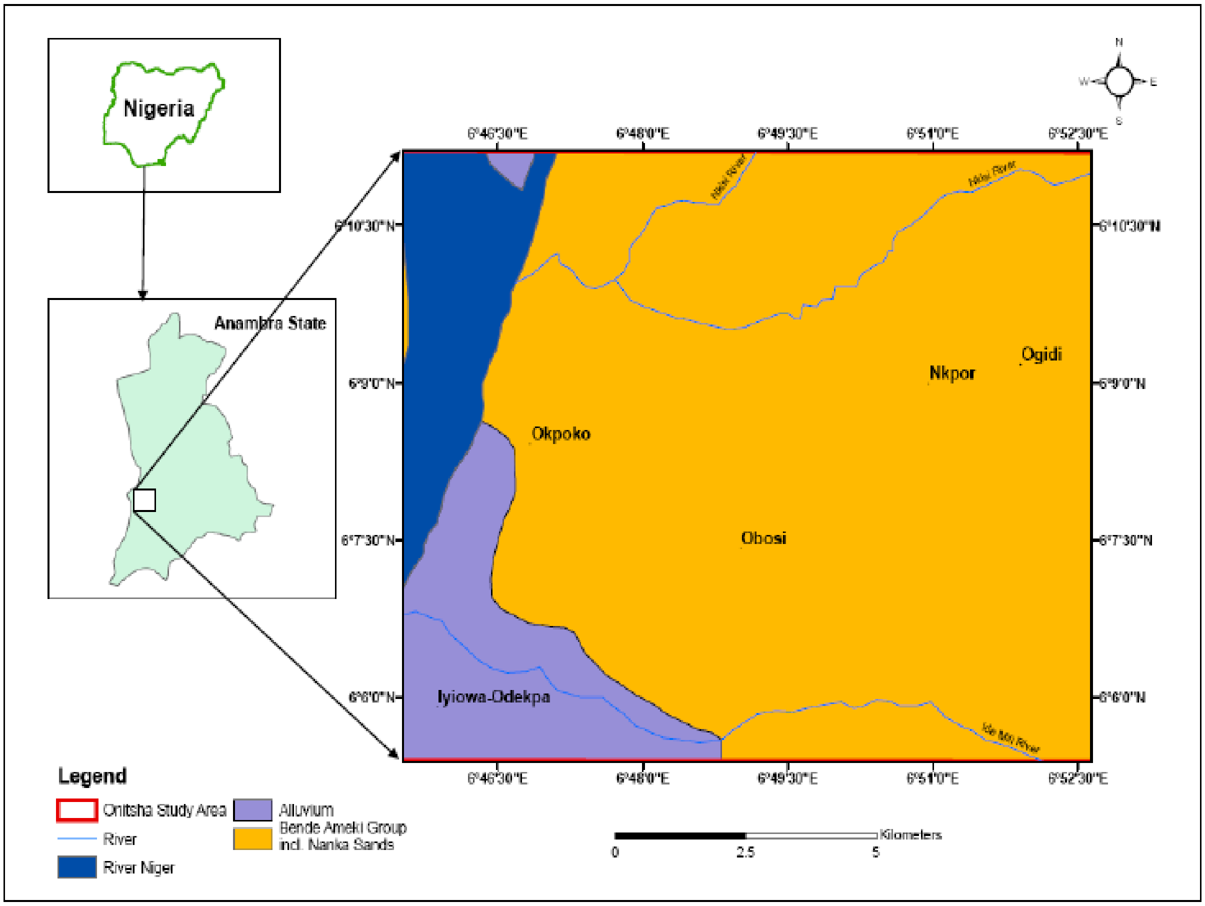

Fig 4.1: Geologic Map of Onitsha Area part ofSheet 71 ( Modified After Geological Survey Agency, 1957)

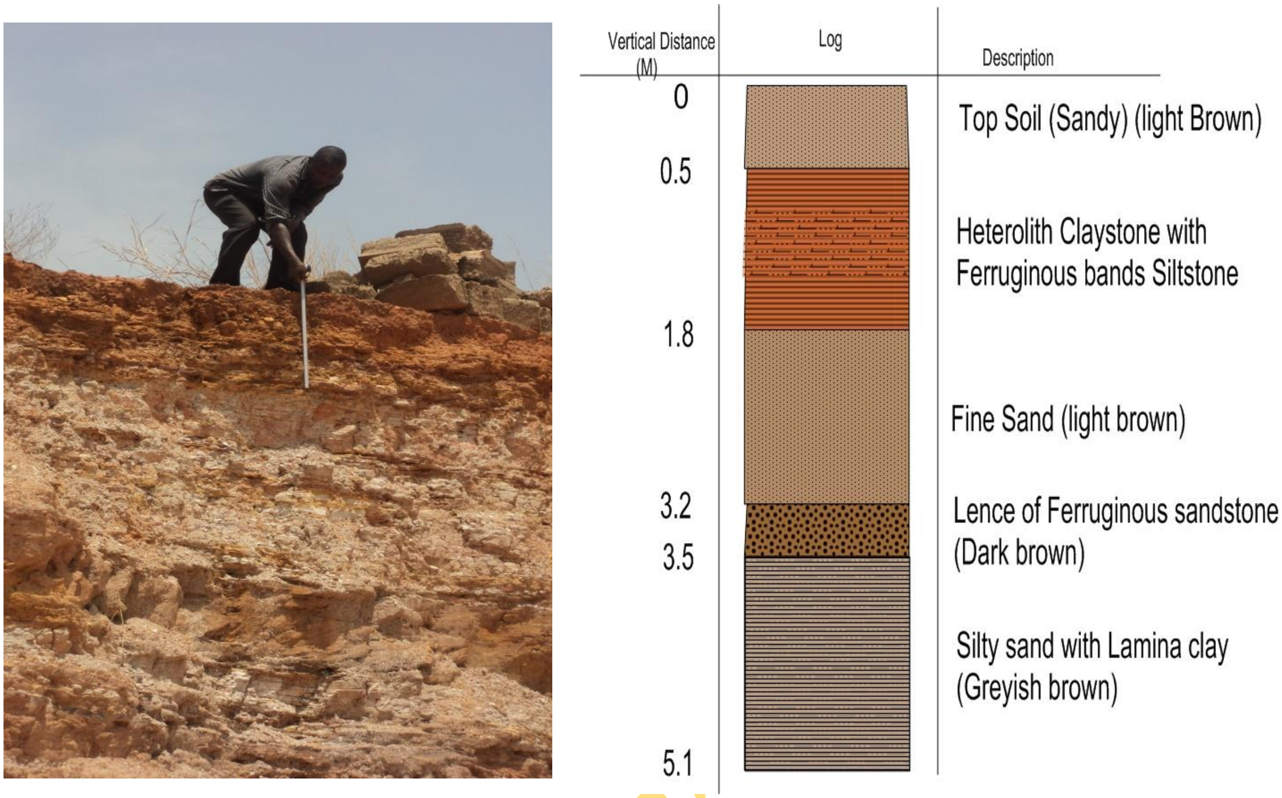

Fig.4.2: Lithostratigraphic Section of Ameki Formation at a mini sand pit along Trans-Nkisi road.

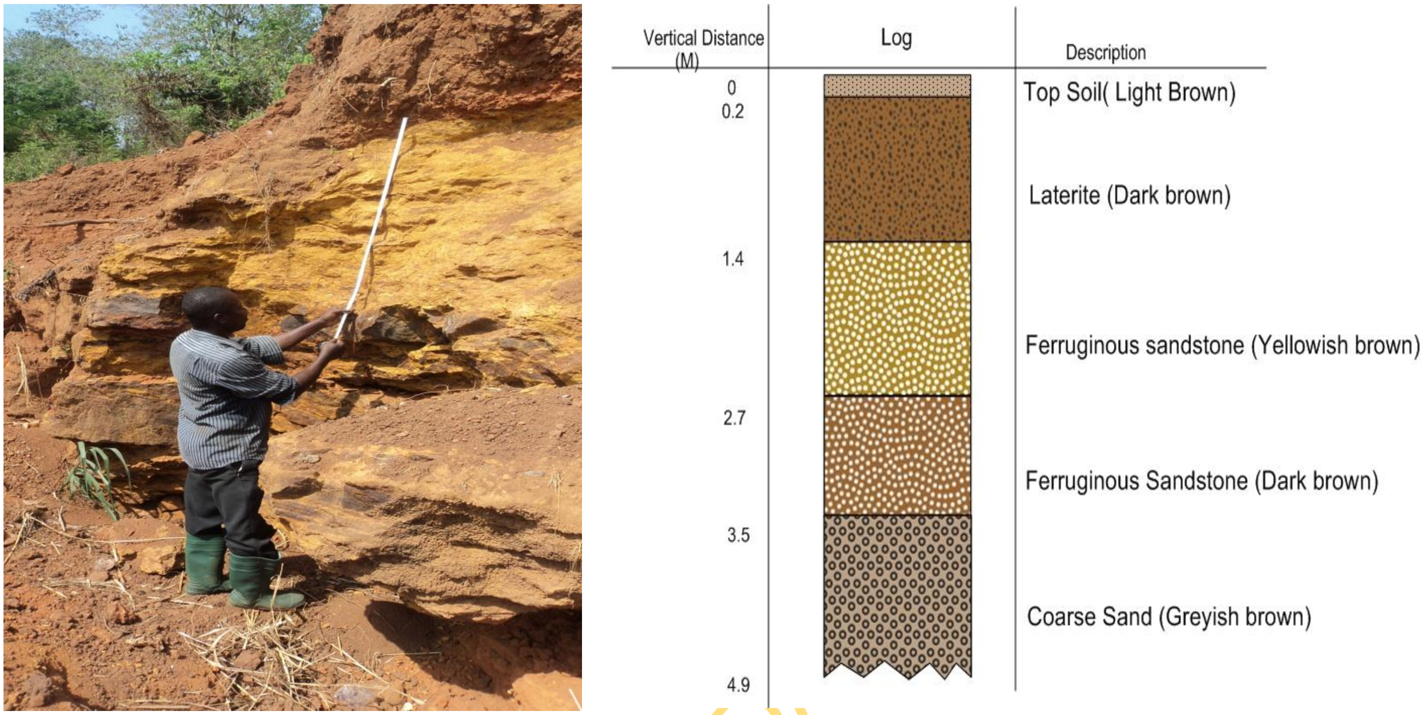

Fig.4.3: Section of ferroginised sandstone with overlain of laterite along Trans-Nkisi road

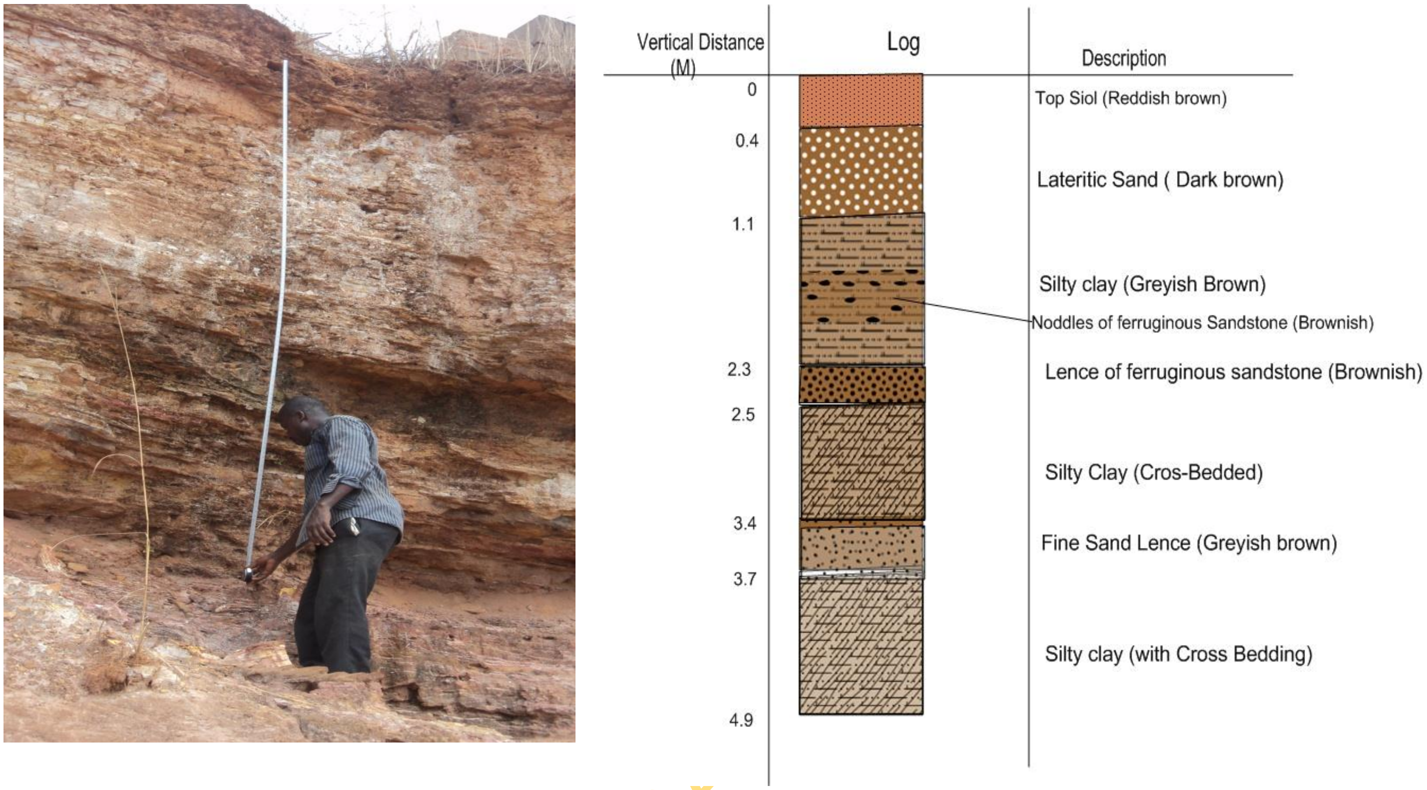

Fig.4.4. Lithologic Section around Trans-Nkisi road showing sand sequence with strata of ironstone.

Fig.4.5: Photograph of massive ferrogenised sandstone at the back of the Onitsha prison

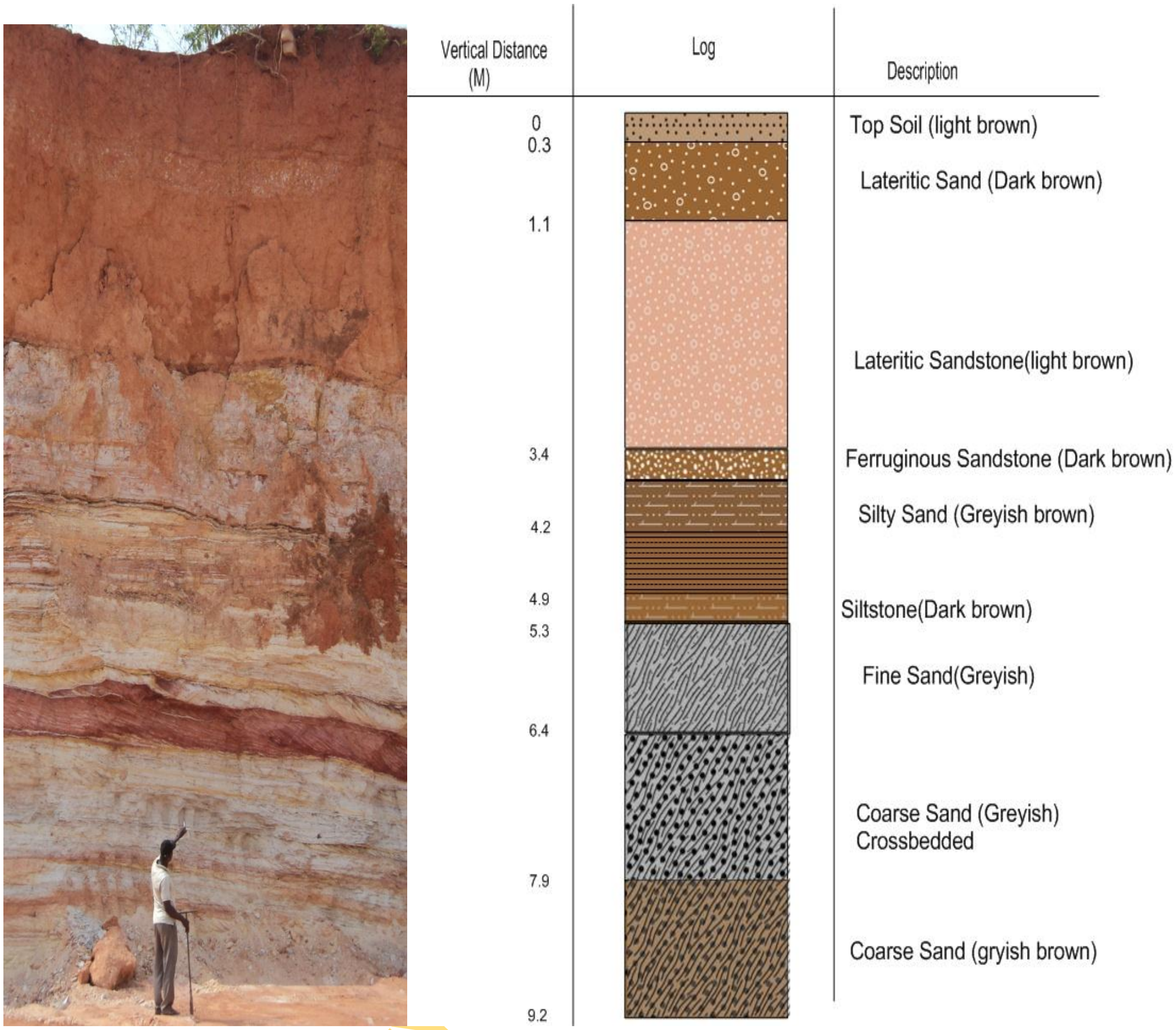

Fig. 4.6. Lithologic Section ofAmeki Formation along Enugu-Onitsha express way, Ogidi.

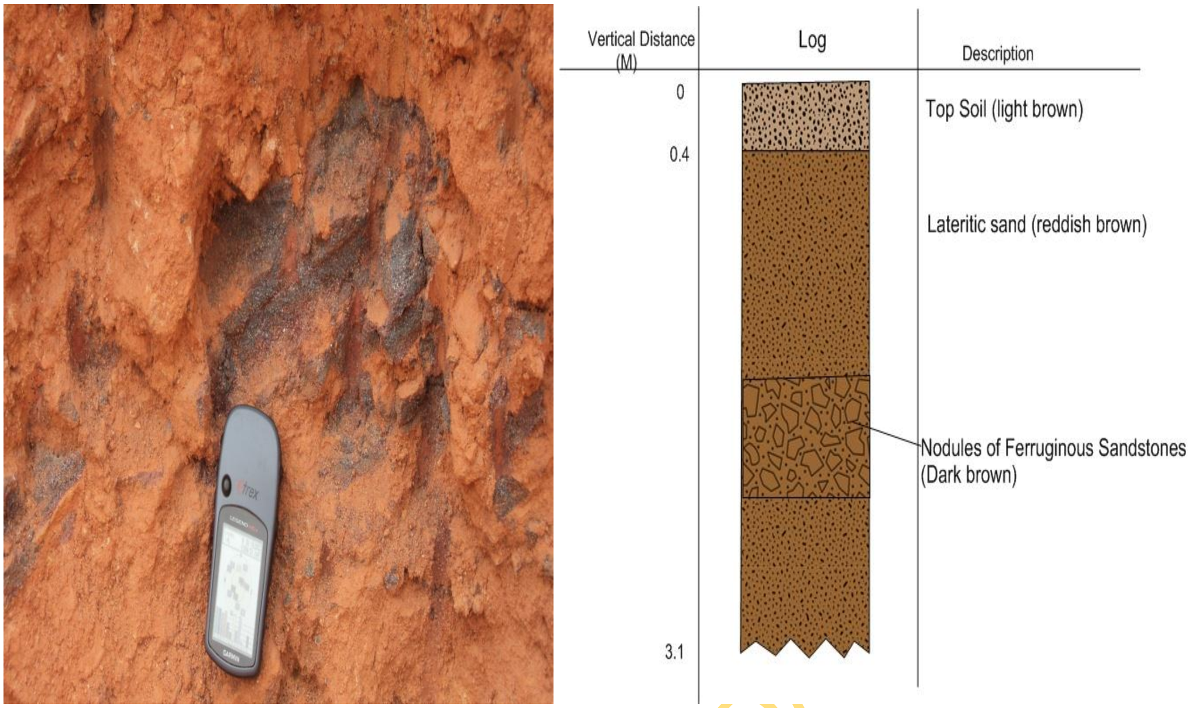

Fig.4.7: Lithologic Section of Ameki Formation showing lateritic pile with nodules of ferruginous sandstone with the laterite at new spare parts market, Tazan, Onitsha

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Fig. 4.8 Lithologic Section  showing cross bedding structure, along Enugu-Onitsha express way, Ogidi.

### 4. 2 Petrography and Mineralogy of Soil samples

The mineral constituents of the soil vary from one sample to the other. Minerals identified include Hematite, Quartz Goethite, Kaolinite and opaque minerals. The ferrugenised (Ironstone) sand stone revealed abundance of quartz and hematite, with little amouth of goethite while the silty clay samples revealed abundance of kaolinite, with quartz and hematite as minor minerals.

Other sandstone samples revealed the presence of abundant quartz, hematite, goethite and kaolinite minor occurrence of opaque minerals as accessory (Fig.4.9 to Fig. 4.13)

The various mineral phases of the lithologic outcrop samples were further studied using XRD. The identified mineral include Quartz, Kaolinite, Hematite, Anatase and Brucite which were present at different proportions ranging from dominant to accessory mineral (Figure 4.14 to Figure 4.16 and Table 4.1). A summary of the mineralogical composition of the lithologic outcrop samples (Amk 1, Amk 2 and Amk 3) is presented in Table 4.1. Amk 1 sample contains abundant Quartz (68%) with relatively high but minor percentage composition of Hematite (20%). This is because of its Iron rich constituent of mineral present in the sample.

Amk 2 analysed has relatively high content of kaolinite (60.4%) and 20% of Quartz. Other accessory minerals found are Anatase (9.9%) and Brucite (9.2%) suggesting that the lithologic sample is of mixed composition. Amk. 3 has similar mineralogical composition with Kaolinite (54.9%) being dominant mineral while Quartz (20.7%), Hematite (6.8%) and Anatase (8.8 %), occur as accessory mineral in the sample. The presence of Hematite and Anatase as accessory mineral suggests that the litho. sample is mixed with some low amont of ferrogenous sandstone which are a product of weathering and remobilization of mineral to different places with in the soil profile.

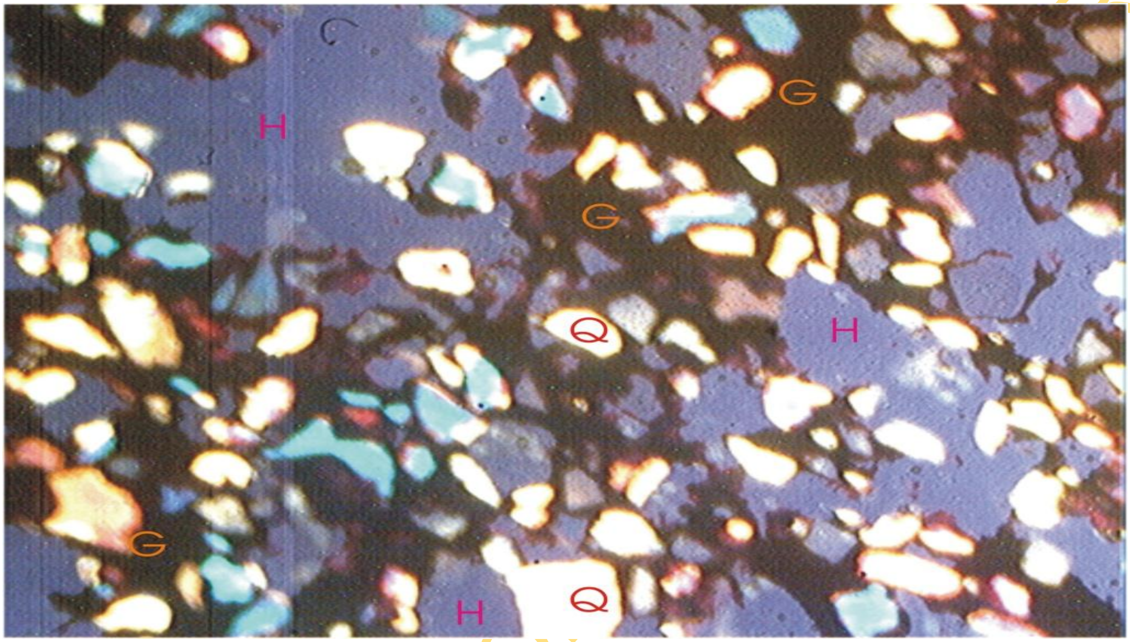


Fig. 4.9: Photomicrograph of Ferrogenized Sand Stone sample (Magnification × 45) under cross nicol. H= Hematite, G= Goethite, Q= Quartz

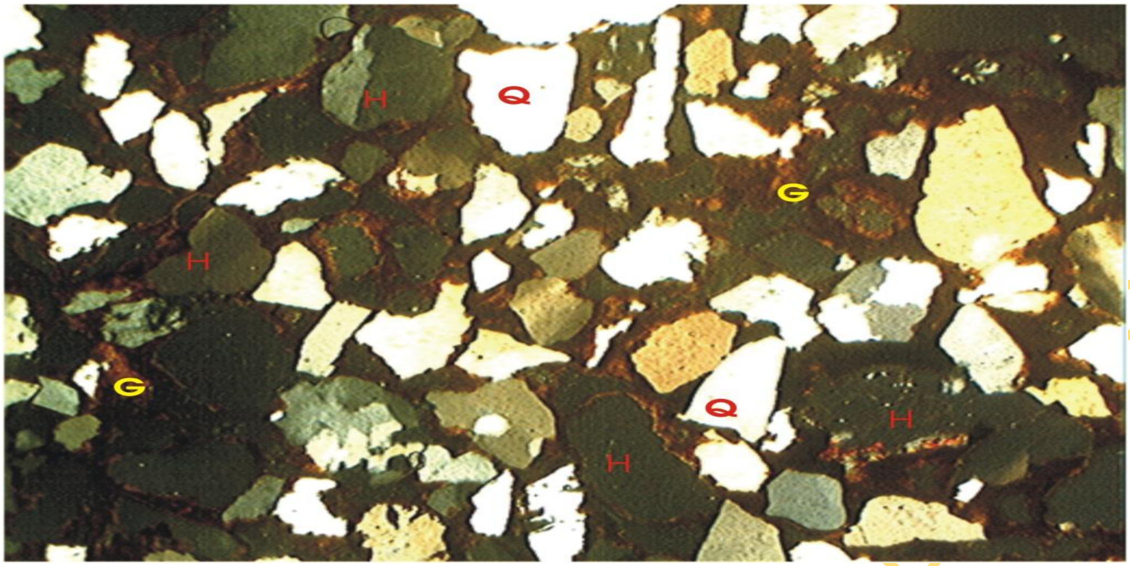


Fig.4.10: Photomicrograph of Ferrogenized Sand Stone sample (Magnification × 45) under cross nicol. H= Hematite, G= Goethite, Q= Quartz

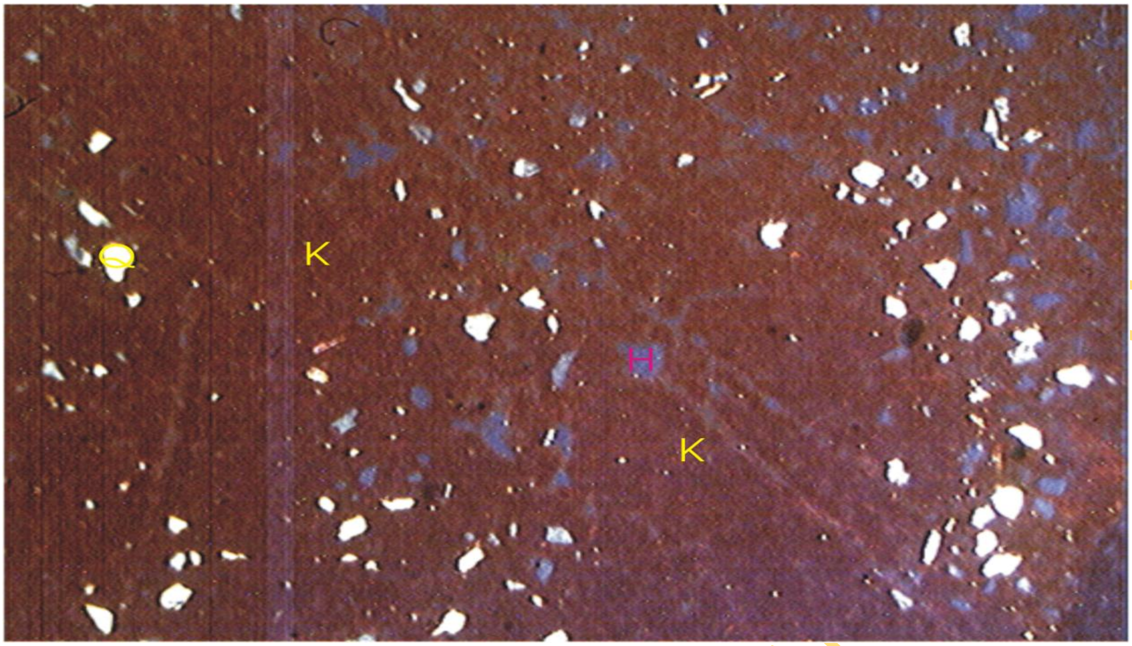


Fig.4.11: Photomicrograph of soil sample (Magnification × 45) under cross nicol. H= Hematite, Q= Quartz, K = Kaolinite

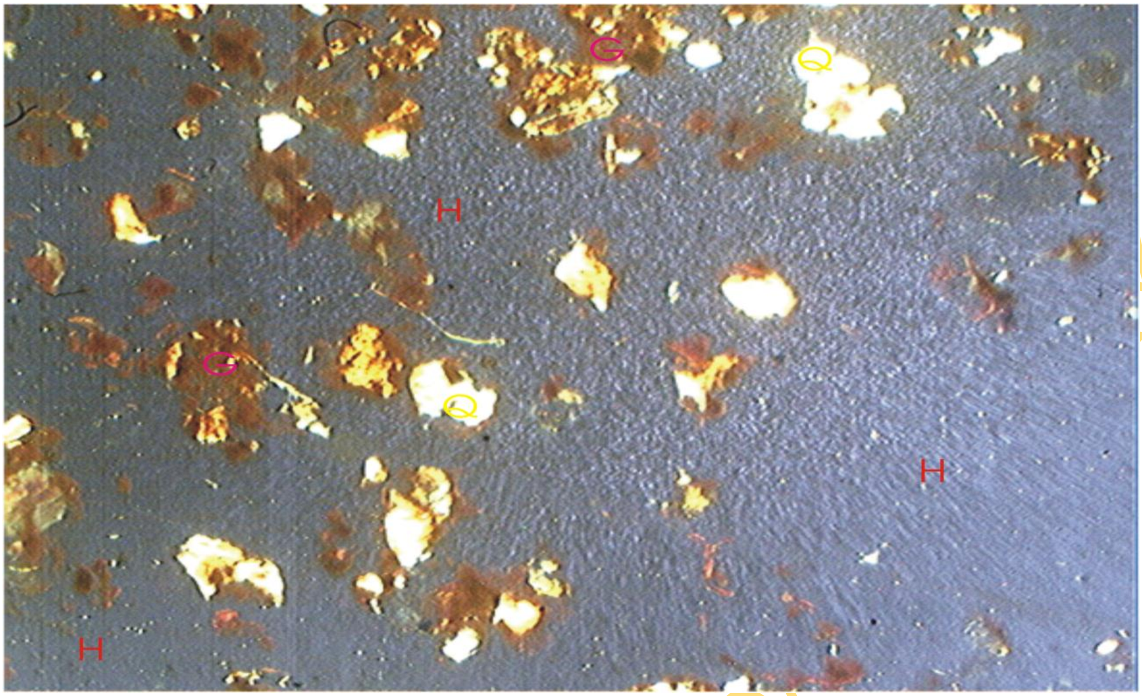


Fig.4.12: Photomicrograph of Ferrogenized Sand Stone sample (Magnification × 45) under cross nicol. H= Hematite, G= Goethite, Q= Quartz

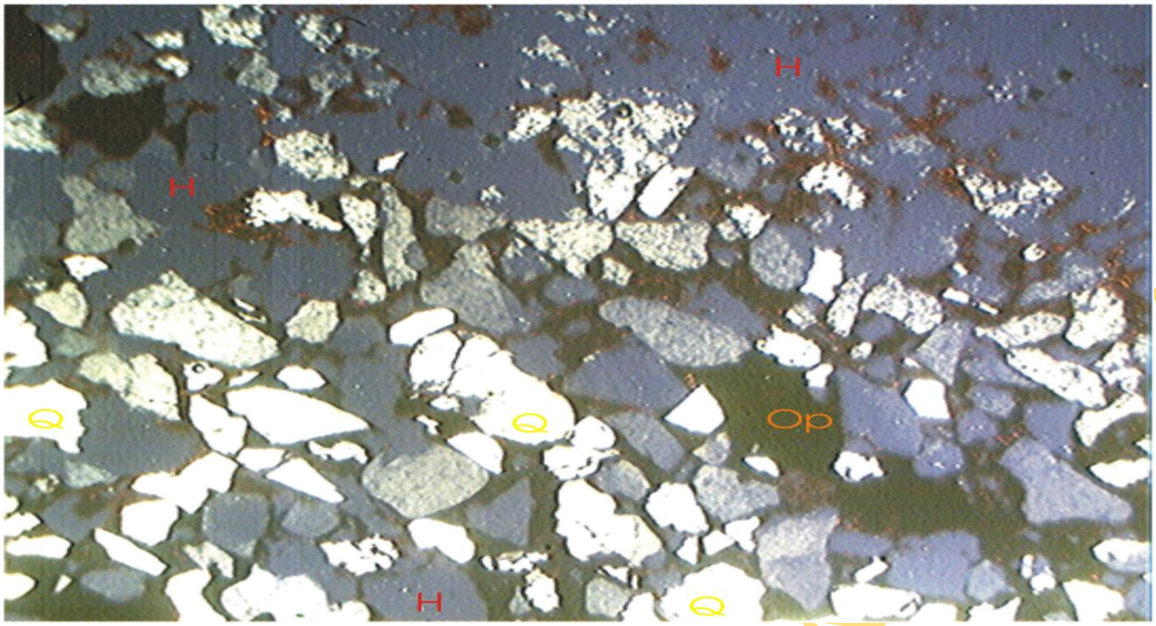


Fig.4.13: Photomicrograph of Sand Stone sample (Magnification × 45) under cross nicol. H= Hematite, G= Goethite, Q= Quartz, Op = Opaque

Table4.1: Quantitative mineralogical composition of selected lithologic outcrop samples

| Sample | Quartz | | Kaolinite | | Hematite | | Anatase | | Brucite | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Wt% | Abd | Wt% | Abd | Wt% | Abd | Wt% | Abd | Wt% | Abd |
| Amk 1 | 68 | Domt | 10.4 | Accs | 20 | Minor | | | | |
| Amk 2 | 20 | Minor | 60.4 | Domt | | | 9.9 | Accs | 9.2 | Accs |
| Amk 3 | 20.7 | Minor | 54.9 | Domt | 6.8 | Accs | 8.8 | Accs | | |

AMK. represent lithologic samples collected from the study area

| | |
|---|---|
| Accs. = | Accessory |
| Abd. = | Aboundance |
| Domt. = | Dominant |

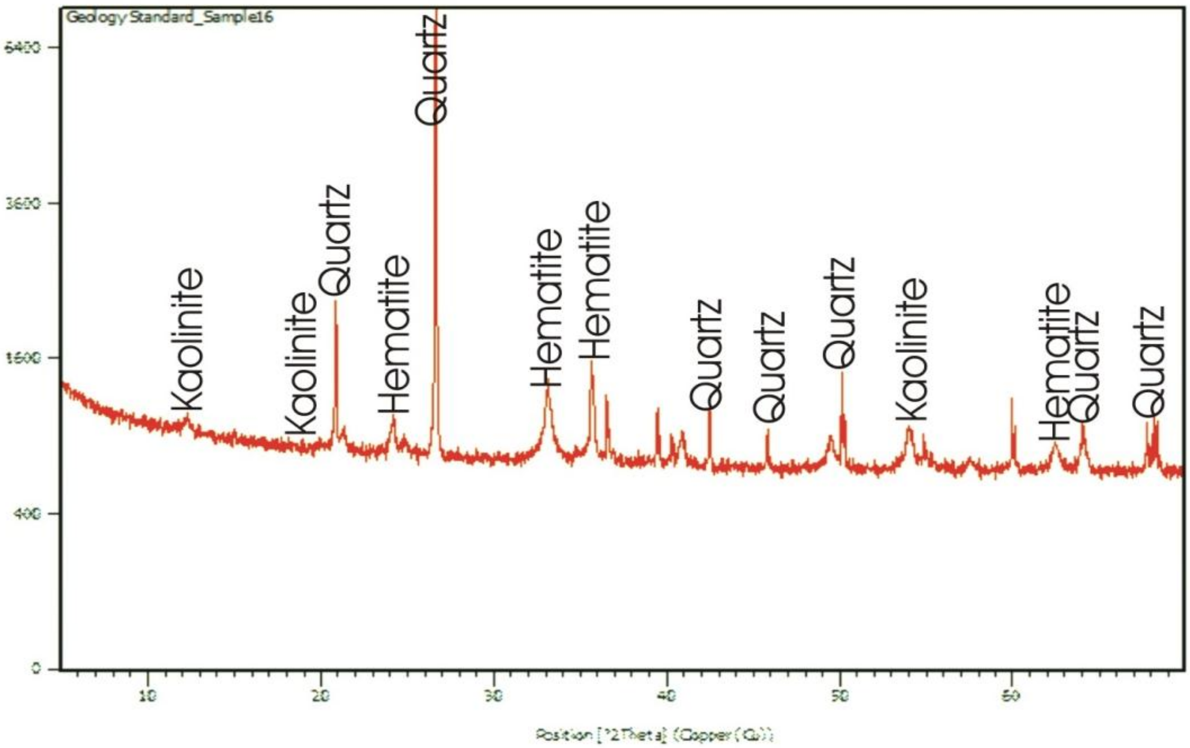


Fig4.14: X-Ray diffractogram of Amk 1of the study area

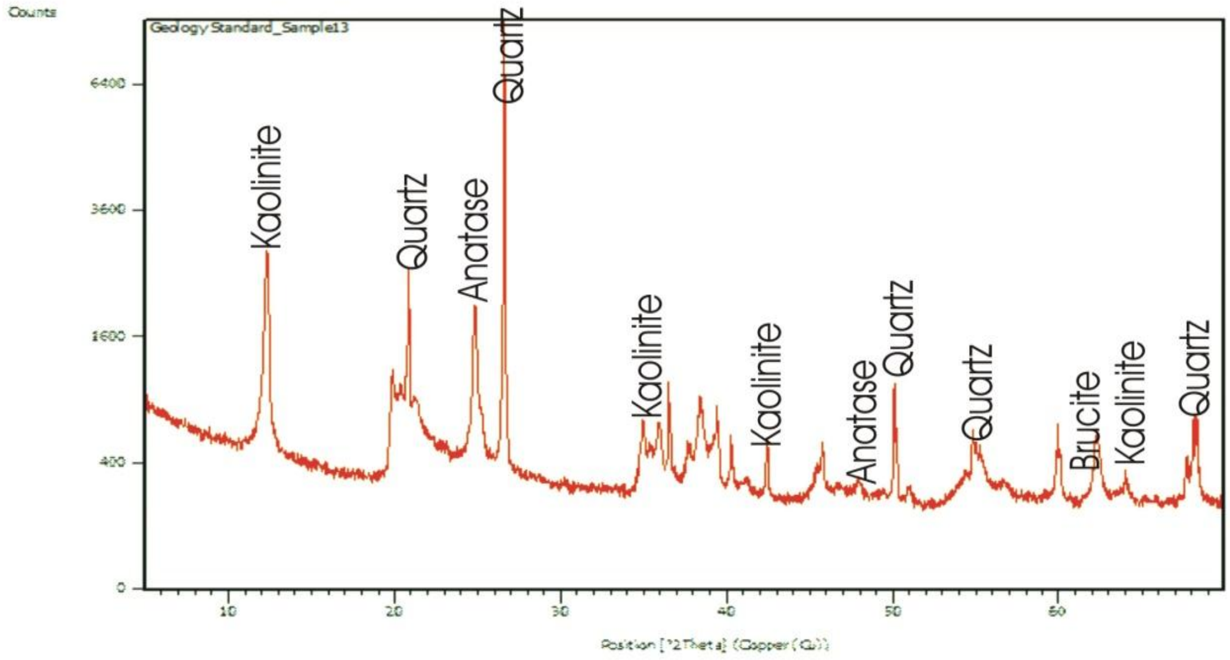


Fig4.15: X-Ray diffractogram of outcrop Amk 2 sample

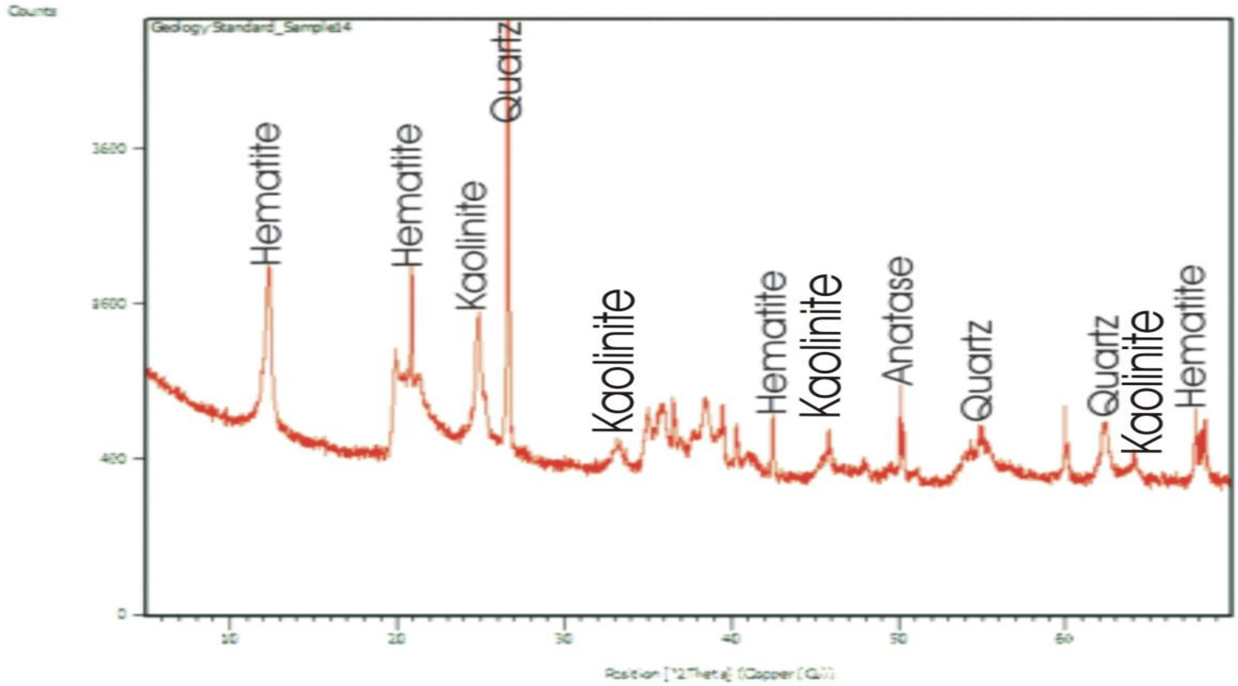


Fig4.16: X-Ray diffractogram of outcrop Amk 3 sample

## 4.3. Physico-Chemical Analyses of Soils and Sediments

The summary of the pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS) and Total Organic Carbon (TOC) is presented in Table 4.2. The pH values of the soils ranges from 4.8 To 7.7 while that of the sediments ranges from 6.1.to 7.3.The EC in (µS/cm) for the soils ranges from 6.41 to 794 whereas in the sediments, it ranges from 31.6 to 1059. TDS for the soils ranges from 4.05 mg/l to 508 mg/l and the TDS value for the sediments ranges from 20.2 mg/l to 668 mg/l while the TOC value ranges from 0.12% to 10.5% and 0.54% to 4.18% for the soils and the sediments respectively, (Table 4.2 and Appendix 1). The pH values for the soils is relatively low in location CT 2 (4.8) which is one of the control samples. The maximum value of pH was recorded in location MWM/3B (7.7). Other locations are slightly acidic to slightly alkaline (Table 4.2). The locations include FLG 7B and FLG 8 with pH of (5.0) at both locations, while location MWM 2 (7.2) and MWM 7 (7.2) respectively. Generally it was observed that the distribution of the pH was influeced to some extent by landuse activities. For example, the soils collected from farmland and gardens recorded relatively slightly acidic pH value in contrast to, the soils collected from the mechanic and metal workshops exhibited slightly alkaline pH, (Appendix 1). The pH of the sediment samples also showsimilar pattern of distribution, with no clear variation of pH based on sediment type except on location some locations (Appendix 1). The few locations with relatively lower pH can be attributed to point source effect which may be due to high decayed organic compounds such as plants remains in the area, The pH of soil and sediment affects the degree of mobility and bioavailability of trace element hence the relevance in determining the acidity or alkalinity of soil and sediment. This is also a function of other physico-chemical characteristics such as Total dissolved solids (TDS), electrical conductivity (EC), Temperature (T) and total organic carbon (TOC) among others. Varying values of electricalconductivity values were observed in the soils and sediments in Onitsha.The electrical conductivity value ranges from 7.67µS/cm in location CT/5 to 694 µS/cm in location AWD/7 for soil (Table 4.2 and Appendix 1). The highest EC value was recorded in location RSD/12 (1059.0 µS/cm). This may have be connected with the fact that roadside drian sediment are major receptor to solute dessolving in the sediment more than the soil, (Table 4.2 and Appendix 1). Similar trend is observed in most of the samples from roadside drian sediment (Appendix 1). The highest value of Total Dissolved Solid (TDS) was found in location AWD/4 (508 .0 mg/L) and the lowest value was found in location CT/2 (4.05 mg/L) for soils while the highest value for TDS in sedments was found in location RSD/12 (668.0mg/L) and the lowers value was found in location RSD/10 (20.2 mg/L), (Table 4.2 and Appendix 1). Locations with relatively higher TDS showed presences of higher dissolved solid, which can be influenced by activities being presently taking place in the area. the concentration of Total Organic Carbon (TOC) content in the soils and sediment in the study area also vary from one location to another, with the minimum mean value recorded in the control samples (CT/4) (0.1 %) to relatively high TOC value in samples collected from the vicinity of Active Waste Dump, AWD/3A (10.5 %) Table 4.2, which also suggest that there is influence of land use as it relate to organic rich materials in the values of TOC in the soils and sediment as seen in Table 4.2. meanwhile the detail result for the total organic cabon in the study area is listed with PAHs result in Appendix 9.

Table 4.2: Summary of the Physico-Chemical Parameters of the soils and sediments from Onitsha Area (N = 162)

| | Sediments (n = 42) | | Soils (n = 120) | |
|---|---|---|---|---|
| Parameters | Minimum | Maximum | Minimum | Maximum |
| pH | 6.1 | 7.3 | 4.8 | 7.7 |
| EC (µS/cm) | 31.6 | 1059 | 6.41 | 694 |
| TDS (mg/l)) | 20.2 | 668 | 4.05 | 508 |
| TOC (%) | 0.54 | 4.18 | 0.12 | 10.5 |

## 4.4 Geochemistry of the Soils and Sediments in the Study Area

### 4.4.1 Major Oxides of soils and sediments

The summary of the major oxides composition of soils and sediments in the study area ispresented in Table 4.3in the soil, $SiO_2$ ranges from 68.36% to 99.59% as calculated, with a mean of 94.2574%, $Fe_2O_3$ ranges from 0.32 to 31.09, mean of 4.108%, CaO, 0 to 3.84%, mean of 0.5897%, $P_2O_5$, 0 to 0.29%, with a mean of 0.042%, among other oxides, Table 4.3, Appendix 2 (a-f). The relatively high abundance of $SiO_2$ compare to the other oxides shows that the soil is sandy and rich in silica. Also the relative enrichment of $Fe_2O_3$ in some of the soil samples is associated with presence of ferruginous sandstone in those locations within the study area, typical of the chemistry of the Ameki Formation. Similarly, for the sediment in the study area, $SiO_2$ content ranges from 83.91% to 96.8%, with a mean value of 93.6465%, $Fe_2O_3$, 1.74% to 13.87%, with a mean of 4.524%, CaO, 0.08% to 2.17%, with a mean of 0.6743%, $P_2O_5$, 0.02% to 0.27%, with a mean of 0.0682% among other oxides, Table 4.3 and Appendix 2 (g and h). The relatively high abundance of $SiO_2$ in the sediment also suggests sandy nature of the environment. The result for both the soil and sediment major oxides as analysed using XRF shows similar trend in the composition of the oxides in both the soil and the sediment, Appendic 2(I) where $SiO_2$ exhibit relatively high concentration more than the other oxides. Also in the result of the ferruginous sandstone the $Fe_2O_3$ is relatively high RK/1 (59.95%) but with $SiO_2$ of 23.68% among other oxides and LOI of 7.24%, Appendix 2 (i). from the results of the oxides from both ICP-MS and XRF, it is observed that the soil and sediment in Onitsha is predominantly rich in $SiO_{2,}$ the relatively low concentration of other oxide such MgO, CaO, Al2O3, Na2O, K2O in almost all the samples analysed showed low presence of clay rich minerals in both the soils and sediments in onitsha.

Table4.3: Summary of major oxides (%) for soils and sediments in the study area

| | Soils ( n= 120) | | | Sediments ( n = 42) | | |
|---|---|---|---|---|---|---|
| Oxides % | Minimum | Maximum | Mean | Minimum | Maximum | Mean |
| $SiO_{2(calculated)}$ | 68.36 | 99.59 | 94.2574 | 83.91 | 96.8 | 93.6465 |
| $Fe_2O_3$ | 0.32 | 31.09 | 4.108 | 1.74 | 13.87 | 4.524 |
| CaO | 0 | 3.84 | 0.5897 | 0.08 | 2.17 | 0.6743 |
| $P_2O_5$ | 0 | 0.29 | 0.042 | 0.02 | 0.27 | 0.0682 |
| MgO | 0 | 0.24 | 0.05 | 0.02 | 0.52 | 0.1365 |
| $TiO_2$ | 0.01 | 0.05 | 0.0179 | 0.01 | 0.03 | 0.0211 |
| $Al_2O_3$ | 0.08 | 1.66 | 0.9172 | 0.32 | 1.13 | 0.8157 |
| $Na_2O$ | 0 | 0.19 | 0.0152 | 0.02 | 0.2 | 0.0505 |
| $K_2O$ | 0 | 0.04 | 0.0018 | 0.01 | 0.45 | 0.064 |

### 4.4.2 Trace Elements distribution for Soil and Sediments

A summary of trace elements concentration in the soils and sediments from the study area is presented in Table 4.4. The trace element distribution pattern in the soils and sediments of Onitsha metropolis reveal varying concentration for observed elements. The soils show significant heterogeneity in the concentration of Mo, Cu, Pb, Zn, Ni, Co, Mn, As, Cd, V, La, Cr, Hg, Sc, and Ga. The element concentration (in ppm) in soil samples for Mo ranges from (0.1 – 46.88), Cu (1.8 – 1123.2), Pb (6.2 – 2026.4), Zn (3.0 – 7563.1), Ni (1.1 – 236.6), Co (0.3 – 136.5), Mn (7.0 – 1920.0), As (0.5 – 27.3), Cd (Nil – 10.3), V (15.0 – 121.0), La (2.0 – 17.6), Cr (7.7 – 443.2), Hg (0.0 – 0.95), Sc (1.4 13.0) and Ga (2.0 – 22.0) (Table 4.5, Appendix 3)

The result of trace element concentration (ppm) in the sediments reveal that Mo ranges from (0.3 – 10.5), Cu (18.4 – 226.4), Pb (19.7 – 540.1), Zn (95.0 – 555.9), Ni (6.7 – 90.8), Co (2.6 – 17.5), Mn (185.0 – 1410.0), As (0.6 – 16.9), Cd (0.1 – 1.6), V (51.0 – 111.8), La (10.0 – 28.7), Cr (33.0 – 123.0), Hg (0.07 – 1.28), Sc (4.8 – 10.1) and Ga (8.0 – 15.0) (Table 4.5, Appendix 3). The heterogeneity of the various trace elements in both soils and sediments were found to be influenced by landuse activities.

Zn exhibits the highest concentration (8395.0 ppm) in the soil sample collected around the vicinity of farmlands and gardens, location (FLG $3^A$).. Other locations with relatively higher concentration of Zn lies within in Mechanic and metal works (MWM) landuse area. These locations include MWM ($17^A$, $4^A$, 5, 9, 10, 11, 16B, $16^A$ and $6^A$) with Zn concentration in ppm of 7568.1, 3477.4, 2079.2, 5218.0, 1228.0, 2208.1, 2026.4, 1730.5 and 1444.3 respectively. Other areas with relatively high concentration were found in locations RA (4, 14, 18) with concentrations in (ppm) of 1221.1, 2557.0 and 1259.5 respectively, MAP (1A, 3A and MAP 3B), 1274.3, 5169.0 and 2899.0 respectively as well as AWD ($5^A$ and 8) 1506.0 and 1337.0 respectively. Comparing the results of these locations with the control samples (CT) (2, 3, 4 and 6) with Zn concentration in ppm of 35.5, 10.0, 9.0 and 3.0 respectively, Table 4.5 and Appendix 2 (a – h). The content of Zn in these locations are 10 to 20 fold higher than the control samples which were sampled from the out skirt of the urban area relatively free from influence of urban activities (pristine locations). Other locations show relatively low to moderately high concentration of Zn in the study area, but all locations are found to have higher Zn concentration compare to the Zn concentration of the control samples. This shows significant enrichment of Zn which may have been affected by anthropogenic sources because of the presence of some out-lier values and relatively wide range in values of the Zn content in soils of the study areas relative to the results of samples collected from the out skirt of the study area which can relatively be regarded as pristine area.

The concentration of Pb in the soils in the study area was also relatively high is some locations. The highest concentration of Pb(2026.4 ppm) was recorded in location MWM 16b Table 4.5 and Appendix: 3 (a – h). Other locations with relatively high concentration of Pb (ppm) include locations MWM (6A, 9, 14, 16A and 5) with Pb concentration of 1444.3, 1067.5, 1048.1, 1730.5 and 580.5 respectively. Other areas include AWD 8 (448.4ppm), AWD 6A (311.9 ppm) and FLG 6A (366.2ppm). While other locations showed relatively moderate to low concentration of below 250 ppm. But comparing most of these results with results of control samples, CT (2, 3, 4, 5 and 6) with Pb content in ppm of 15.7, 7.2, 22.1, 18.6, and 16.1 respectively, it is observed that most of the locations are 12 to 20 fold higher that most samples collected as control samples. This suggest that Pb content may have been enriched by anthropogenic activities as shown by the presence of some out – lier values and wide spatial values in the Pb content of the soils in the study area.

High concentration of Mn was also recorded in some locations of the study area. Very high concentration of Mn above 1000 ppm were found in locations RA 5A (1069.0 ppm), RA 14 (2127.0 ppm), FLG 11 (1320.0 ppm), AWD 1 (1128.0 ppm), AWD 5A (1073.0 ppm), MWM 9 (1698.0 ppm) and MWM 11 (1920.0 ppm) which was the location with the highest concentration of Mn. Many other location had relatively high concentration below 1000 ppm, such locations include RA $13^{B}$ (969.0 ppm), RA 4 (876.0 ppm), RA 17 (875.0 ppm), FLG $9^{B}$ (879.0 ppm), MAP 1B (860.0 ppm), MAP1B (947.0 ppm), AWD 6A (974.0 ppm), MWM 6A (992.0 ppm), MWM 16B (998 0ppm) and MWM 17B (900.0 ppm) among others that exhibited relatively moderate to low Mn content in the soil (Table 4.4 and Appendix: 3 (a – h)). Comparing the results of Mn content in most of the locations with control samples CT (2, 3, 4, and 6) with Mn content in ppm of 241, 104, 66, and 10 respectively, it shows that most of the locations are significantly enriched by Mn content.

The content of As in the soils of Onitsha were observed to be of varying spatial distribution, with relatively high concentration found in some locations as against some other locations with low concentration. Locations RK 2 and RK 1 had As content of 27.3 ppm and 12.0 ppm respectively while other locations with relatively high concentration of As include MWM 11 (19,8 ppm), MWM 15A (9.3 ppm), MWM 2A (10.8), MWM 15A (9.3 ppm), AWD8 (9.6 pmm), FLG 5B (10.3 ppm), FLG 3A (9.8 ppm), SOC 12B (13.2 ppm), SOC 12A (11.0 ppm), SOC 6 (12.8 ppm) and RA 14 (9.1 ppm), Table 4.4 and Appendix 3 (a – h). Other locations were found to have relatively moderate to low concentrations, while some other areas recorded below detection limit (BDL). One striking observation in the samples analyzed were the relatively high concentration of RK 2 and RK 1. These locations are the ferrogenised sandstone within the sedimentary profile in the study area, the samples recorded high concentration of As content, suggesting secondary geogenic enrichment of As within the ferruginous sandstone. But other locations with relatively high concentrations of As followed the influence of land use activities which is anthropogenic effect.

Cd content in the soils was also found to be of varying concentration from one location to the other. The highest concentration of Cd was found in location MWM 9 (10.30 ppm) closely followed by location MWM 17 (10.19ppm). Other locations with relatively high concentration include location MWM 14 (6.0 ppm), MWM 11 (5.30 ppm), MWM 6 (4.3 ppm), MWM 4A (3.39 ppm) and AWD8 (5.6 ppm), Table 4.4 and Appendix 3 (a – h). Relatively moderate to low concentration of Cd were found in other location, while in some locations below detection limit were observed. Comparing the result of most of the locations with the control samples CT 2 to CT 6 all BDL. One main observation on the enrichment of Cd content in the soils was the influence of anthropogenic effect relating to land use.

The concentrations of Cu, was observed to vary spatially from one location to the other. Locations MWM 11 (1048.88 ppm) and MWM 9 (1123.20 ppm) had the highest concentration of Cu in the soils, Table 4.4 and Appendix 3 (a – h). Other locations with relatively high concentration include location MWM 16 (232.61 ppm), AWD 8 (457.0 ppm) FLG 6A (366.2 ppm), MAP 3A (214.39 ppm), AWD 5A (206.2 ppm), AWD 6A (233.7 ppm) and FLG 3A (259.3 ppm). Other location also recorded moderate to low concentration of Cu in the soils of the study area. Comparing it with the control samples, CT 2, 3, 4, 5 and 6, with Cu concentration of (9.83, 5.6, 5.3, 7.1 and 5.5) ppm respectively, it is certain that most of the locations have been enriched with Cu content, apparently as a result of anthropogenic effect. The other elements investigated which include Ni, Co, Cr, V, Th, Hg, Sc and Ga were found to also follow almost the same pattern of spatial distribution from one location to the other. Considerable enrichment of these metals were observed in some location, comparing the results with the control samples which are relatively uncontaminated, it shows that most of the metals are enriched. for instance for V, locations RA/6, RA/7, RA/20$^B$, FLG /7$^B$, AWD/13$^B$, AWD/6$^B$ MWM/12$^B$, MWM/13$^A$ and MWM/13$^B$ with V content of 102.0, 116.0, 121.0, 115.0, 119.0, 123.0, 121.0, 107 and 102 ppm respectively as compare to the results of the control samples CT/2, 3, 4, 5 and 6 with V contents in ppm of 12.0, 11.0, 24.0, 23.0 and 23.0 respectively, showing that most of the samples have been enriched to between 5 to 7 folds in some locations. Other locations also recorded varying concentrations that may be considered moderate to low concentration of V. detailed geochemical concentrations of the metals investigated in the soils are found in appendix 3 (a – h)

Similarly the concentration of the metals investigated for sediments also exhibited spatial distribution with some locations showing more enrichment of metal content relative to the other. The sediments as earlier explained include the Nde-Milli River (ID), Nkisi River (NK) and Roadside drain sediments (RSD). Lead (Pb) exhibits high concentration in location RSD7 (540.1 ppm), RSD 8 (331.4 ppm). Other locations include RSD 12, RSD 14, ID 5, ID 4 and 6 with Pb concentrations of 320.5, 180.3, 150.0, 147.8 and 140.9 ppm respectively. Comparing the results with the control samples CT 2 (9.83 ppm), CT3 (5.3 ppm) and samples collected far away from built up areas RSD (54.4 ppm) and NK 19 (19.9), it showed that most locations for the sediment samples have been enriched by Pb to between 5 to 10 folds.

Zinc content in the sediment samples also exhibited spatial distribution of metal enrichment, with location RSD 8 (1045.0 ppm), (Table 4.4) as such with the highest concentration of Zn. Other locations with relatively high concentration of Zn include location ID 1 (518.0 ppm), ID 2 (599.0 ppm), ID 3 (596.6 ppm), ID 4 (686.9 ppm), NK 14 (555.9 ppm), NK 20 (357.0 ppm), RSD 7 (439.0 ppm) RSD 24 (410.1 ppm), RSD6 (306.0 ppm), RSD 4 (365.0 ppm) and RSD 12 (320.5 ppm), Table 4.5. Comparing the results with the control samples CT/2, 3 and 4 with Zn content of 35.5, 10.0 and 9.0 ppm respectively it is observed that most of the locations for the sediments have been enriched greatly to between 8 to 15 folds.

The concentration of Pb in the sediments also showed varying concentration from one location to the other. The highest concentration of Pb was found in location RSD (540.1 ppm), with other locations having lesser enrichment of Pb content but relatively high; RSD24 (410.1 ppm), RSD 8 (331.4 ppm) and RSD 12 (320.5 ppm) as against the the results of the Pb content in the control samples location CT 3 (7.2 ppm) and CT 2 (15.7 ppm) and other locations with relatively low concentration of Pb such as location ID 7 (19.7 ppm) and RSD 8 (25.2 ppm), Table 4.4 and Appendix 3 (a – h) This suggest that most of the result of Pb content in the sediment may have been enriched by activities relating to urbanization.

Similar spatial variations where found in the other metals analysed, with most of the locations within the metropolis recording relatively higher concentration of trace metals compare to the results of the control samples, Table 4.4 and Appendix 3 (a – h).

Table 4.4: Summary of Trace Element Composition for Soils and Sediments in the study area

| Land Use | | Mo | Cu | Pb | Zn | Ni | Co | Mn | As |
|---|---|---|---|---|---|---|---|---|---|
| Residential Area (RA) | | | | | | | | | |
| | Min | 0.2 | 8.1 | 12.5 | 15 | 1.1 | 0.3 | 7 | 0.5 |
| | Max | 1.73 | 145.67 | 257.3 | 2557 | 22.7 | 9.9 | 2127 | 9.1 |
| | Mean | 1 | 38.1 | 68.7 | 422.6 | 11.5 | 4.3 | 596.5 | 5.2 |
| | Std. Dev | 0.4 | 30.8 | 66.2 | 591.9 | 5.5 | 2.5 | 431.4 | 1.8 |
| School and Office complex (SOC) | | | | | | | | | |
| | Min | 0.2 | 1.8 | 6.4 | 11 | 1.3 | 0.6 | 98 | 0.5 |
| | Max | 2.5 | 123.2 | 253.1 | 452.3 | 21.3 | 20.1 | 779 | 13.2 |
| | Mean | 0.96 | 25.67 | 61.01 | 173.11 | 9.14 | 3.53 | 402.65 | 5.34 |
| | Std. Dev | 0.48 | 24.05 | 69.08 | 166.42 | 3.9 | 3.83 | 193.27 | 3.48 |
| Control (CT) | | | | | | | | | |
| | Min | 0.3 | 5.3 | 7.2 | 3 | 0.3 | 0.2 | 10 | 0.5 |
| | Max | 0.7 | 11.3 | 28.1 | 35.5 | 5.2 | 1.5 | 241 | 27.3 |
| | Mean | 0.5 | 7.1 | 18.2 | 14.9 | 2.2 | 0.7 | 81.5 | 8.2 |
| | Std. Dev | 0.1 | 2.3 | 6.2 | 10.2 | 1.7 | 0.4 | 72.2 | 8.4 |
| Farmland and gardens (FLG) | | | | | | | | | |
| | Min | 0.2 | 5.3 | 10.9 | 17 | 6 | 1.3 | 109 | 0.8 |
| | Max | 1.9 | 259.3 | 366.2 | 8395 | 20.9 | 136.5 | 1320 | 10.3 |
| | Mean | 0.95 | 33.89 | 51.44 | 654.95 | 9.71 | 12.65 | 423.18 | 4.9 |
| | Std. Dev | 0.4 | 60.24 | 84.71 | 2008.57 | 3.77 | 32.12 | 332.77 | 3.11 |
| Market and Abbatoir (MAP) | | | | | | | | | |
| | Min | 0.5 | 27.3 | 16.3 | 249 | 8.8 | 6.1 | 470 | 0.8 |
| | Max | 1.6 | 214.4 | 270.2 | 5169 | 47.9 | 43.3 | 947 | 7.2 |
| | Mean | 1.3 | 108.6 | 111.9 | 2161.1 | 25.2 | 17 | 679.2 | 4.6 |
| | Std. Dev | 0.4 | 75.1 | 97.1 | 1932.1 | 16.2 | 16.1 | 211.6 | 3.2 |
| Active waste dump (AWD) | | | | | | | | | |
| | Min | 0.6 | 8.9 | 20.4 | 52 | 7 | 1.7 | 181 | 1.1 |
| | Max | 4.7 | 457 | 448.4 | 4298 | 33.1 | 42.1 | 1128 | 9.6 |
| | Mean | 1.8 | 107.5 | 149.1 | 956.2 | 15.3 | 11.6 | 564.7 | 5.1 |
| | Std. Dev | 1.1 | 137.3 | 136.8 | 1211.3 | 8.8 | 13 | 327.8 | 2.3 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Mechanic and metal works (MWM) | | | | | | | | | |
| | Min | 0.4 | 12 | 22.4 | 24 | 4.4 | 1 | 117 | 2 |
| | Max | 46.88 | 1123.2 | 2026.4 | 7568.1 | 236.6 | 24.8 | 1920 | 19.8 |
| | Mean | 3.9 | 150.4 | 379.1 | 1081.6 | 33.3 | 6.9 | 565.6 | 5.8 |
| | Std. Dev. | 8.5 | 268.4 | 545.9 | 1706 | 55.7 | 6 | 417.7 | 3.7 |
| Ndemili river (ND) | | | | | | | | | |
| | Min | 0.3 | 18.4 | 19.7 | 101 | 6.7 | 3.6 | 204 | 0.6 |
| | Max | 2.2 | 104.3 | 180.3 | 776 | 40.2 | 11.3 | 395 | 7.9 |
| | Mean | 1.22 | 64.42 | 106.95 | 482.15 | 18.73 | 7.19 | 282.2 | 5.02 |
| | Std. Dev | 0.5 | 26.2 | 53.66 | 227.93 | 8.54 | 2.43 | 60.28 | 1.97 |
| Nkisi river | | | | | | | | | |
| | Min | 0.82 | 13.7 | 24.1 | 116 | 7.9 | 2.6 | 185 | 8.4 |
| | Max | 1.6 | 77.67 | 83.7 | 555.9 | 16.4 | 6.3 | 1178 | 16.9 |
| | Mean | 1.4 | 37.6 | 50 | 263.5 | 10.7 | 3.9 | 443.6 | 11.4 |
| | Std. Dev | 0.3 | 20.9 | 21.7 | 149 | 3.1 | 1.2 | 337.4 | 2.6 |
| Roadside drain sediment (RSD) | | | | | | | | | |
| | Min | 0.8 | 28.2 | 45.7 | 95 | 11.2 | 3.6 | 250 | 2.6 |
| | Max | 10.5 | 226.4 | 540.1 | 1173 | 90.8 | 17.5 | 1410 | 8.6 |
| | Mean | 2.34 | 86.44 | 151.37 | 502.49 | 23.65 | 6.73 | 451.38 | 5.29 |
| | Std. Dev | 2.19 | 49.09 | 134.07 | 304.48 | 18.04 | 3.4 | 248.52 | 1.73 |

Table 4.4: Summary of Trace Element Composition for Soils and Sediments in the study area

| Landuse | | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|
| Residential Area (RA) | | | | | | | | |
| | Min | 0.1 | 36 | 8 | 24 | 0 | 2.2 | 5 |
| | Max | 2.2 | 121 | 34 | 125 | 0.14 | 14.8 | 23 |
| | Mean | 0.5 | 79.6 | 16.1 | 58.5 | 55 | 8 | 13 |
| | Std. Dev | 0.6 | 21.7 | 6.5 | 18.8 | 0.246 | 2.64 | 4.25 |
| School and Office complex (SOC) | | | | | | | | |
| | Min | 0.08 | 15 | 2 | 15 | 0.03 | 1.4 | 2 |
| | Max | 0.9 | 122 | 26 | 78 | 0.87 | 11 | 21 |
| | Mean | 0.35 | 77.3 | 13.08 | 50.31 | 0.18 | 7.01 | 12.17 |
| | Std. Dev | 0.24 | 29.39 | 6.45 | 16.21 | 0.18 | 2.78 | 5.09 |
| Control (CT) | | | | | | | | |
| | Min | Nil | 44 | 5.4 | 24 | 0.03 | 1.8 | 3 |
| | Max | Nil | 95 | 26 | 44.5 | 0.07 | 10.2 | 14 |
| | Mean | Nil | 73.9 | 17.9 | 33.1 | 0.04 | 6.5 | 8.8 |
| | Std. Dev | Nil | 16.8 | 7.6 | 7.7 | 0.02 | 3.47 | 4.1 |
| Farmland and gardens (FLG) | | | | | | | | |
| | Min | 0.09 | 38 | 9 | 28 | 0.02 | 4.7 | 6 |
| | Max | 1 | 115 | 38.3 | 64 | 0.5 | 11.4 | 21 |
| | Mean | 0.35 | 84.12 | 16.36 | 47.44 | 0.14 | 8.02 | 13.76 |
| | Std. Dev | 0.33 | 19.51 | 7.61 | 10.5 | 0.11 | 1.97 | 3.87 |
| Market and Abbatoir (MAP) | | | | | | | | |
| | Min | 0.5 | 31 | 9.2 | 37 | 0.05 | 3.8 | 6 |
| | Max | 2 | 82 | 28 | 75 | 0.55 | 7.7 | 14 |
| | Mean | 1.1 | 54.6 | 16.7 | 51.5 | 0.396 | 5.38 | 9.4 |
| | Std. Dev | 0.6 | 18.6 | 7.4 | 15.8 | 0.2 | 1.72 | 3.44 |
| Active waste dump (AWD) | | | | | | | | |
| | Min | 0.2 | 60 | 9.6 | 39 | 0.04 | 5.4 | 9 |
| | Max | 5.6 | 123 | 32 | 118 | 0.95 | 9.8 | 22 |
| | Mean | 2.1 | 90.3 | 17.6 | 70.8 | 0.32 | 7.78 | 15.58 |
| | Std. Dev | 2.1 | 19.8 | 7.4 | 21.7 | 0.28 | 1.37 | 3.63 |
| Mechanic and metal works (MWM) | | | | | | | | |
| | Min | 0.1 | 24 | 5 | 29 | 0.05 | 2.3 | 3 |
| | Max | 10.3 | 121 | 35 | 443.2 | 0.91 | 13 | 20 |
| | Mean | 2 | 67.9 | 15 | 78.3 | 0.24 | 6.16 | 10.03 |
| | Std.Dev. | 2.9 | 27.4 | 6.4 | 75.3 | 0.23 | 2.83 | 4.98 |
| Ndemili river (ND) | | | | | | | | |
| | Min | 0.1 | 51 | 11 | 33 | 0.07 | 4.8 | 8 |
| | Max | 0.9 | 117 | 39 | 60.6 | 0.49 | 9.6 | 17 |
| | Mean | 0.57 | 84.6 | 24.55 | 54.62 | 0.31 | 6.93 | 12 |
| | Std. Dev | 0.25 | 20.2 | 7.84 | 8.25 | 0.18 | 1.4 | 2.67 |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Nkisi river |  |  |  |  |  |  |  |  |
|  | Min | 0.1 | 93 | 12 | 46 | 0.09 | 8.2 | 12 |
|  | Max | 0.75 | 121 | 20 | 62 | 0.55 | 10.1 | 15 |
|  | Mean | 0.3 | 111.8 | 14.7 | 53.6 | 0.2 | 9.49 | 13.56 |
|  | Std. Dev | 0.2 | 8.6 | 3.2 | 6.1 | 0.15 | 0.73 | 0.88 |
| Roadside drain sediment (RSD) |  |  |  |  |  |  |  |  |
|  | Min | 0.1 | 30 | 10 | 33 | 0.02 | 2.1 | 4 |
|  | Max | 1.6 | 101 | 28.7 | 123 | 1.28 | 9.7 | 14 |
|  | Mean | 0.65 | 58.33 | 13.89 | 61.38 | 0.25 | 4.6 | 7.67 |
|  | Std. Dev | 0.44 | 18.89 | 4.18 | 18.44 | 0.32 | 2.02 | 3.2 |

### 4.4.3 Spatial distribution of elements in soils

Geochemical maps using Arcview GIS software were created to visualize the spatial distribution of trace elements in soils in the study area (Figure 4.17 – Figure 4. 32). The concentrations were plotted as graduated points to reduce over generalization errors.

Nickel (Fig. 4.22)Most of the areas with relatively high concentration of Ni, are located in the central part of the city, with huge human activities, like in Upper Iweka, Obosi, Nkpor areas. By contrast, the areas with relatively low concentration of Ni are at the out-skirt of the town, suggesting the influence of urbanization on the enrichment of Ni in the study area. Again, some locations where top and sub soils were collected shown higher concentration of Ni at the top soils relative to the subsoils.

The spatial distribution of Cadmium in Onitsha soils is presented in (Fig. 4.23). Just like Ni, are areas with relatively high human activities, in particular Okpoko, Umuaja-Obosi, Atani road area recorded elevated concentration of Cd. Relatively moderate to low concentration of Cd isassociated with residential areas as well as out-skirt of the town with relatively low human influence.

Similarly, geochemical maps of the spatial distribution of Cu, Co, Mo, Pb, Cr, Zn, As, Mn, La, Hg, Ga, Th, V and Sc (Fig. 4.33 – Fig. 4.46), show that the areas with relatively high concentration of these element are within the core of the town, Upper Iweka, Nkpor, New Tazan, old Port High court, Okpoko, Umuaja- Obosi areas of the metropolis, relative to the soils collected at the out skirt of the town as seen in the control samples. Virtually the whole element exhibited the same pattern of enrichment distribution, showing the influence of urbanization and industrialization on the enrichment of the metals in the study areas. Following the landuse pattain , elements such as Pb, Zn, Mn, V and Cr, were found to be elevated in mechanic and metal workshop locations (MWM), active waste dump (AWD) site as well as farm land and garden (FLG) areas respectively. Since this type of land use are common within the city center and in some location a little at the out skirt of the town, such activities are never the less major contributors to the enrichment of these metals to soils in urban environment. Hg concentration though low, also exhibited relatively higher elevation in distribution within the city center and around areas of high vehicular and by implication, high human activities, (Fig. 4.33). It is also of note that most of the elements investigated did not absolutely follow the same pattern of elevations because of a variety of sources of point discharge of human related activities. As concentration distribution though had some locations with higher elevation at the core of higher human activites (Fig. 4.46), some of the locations with relatively high elevation were the ferrogenised sandstone within the sedimentary lothology at Trans Nkisi road, at the back of the Nigeria prison and near formal toll gate at Ogidi area, which were used as part of the control samples. Hence the observation of such in the distribution map.

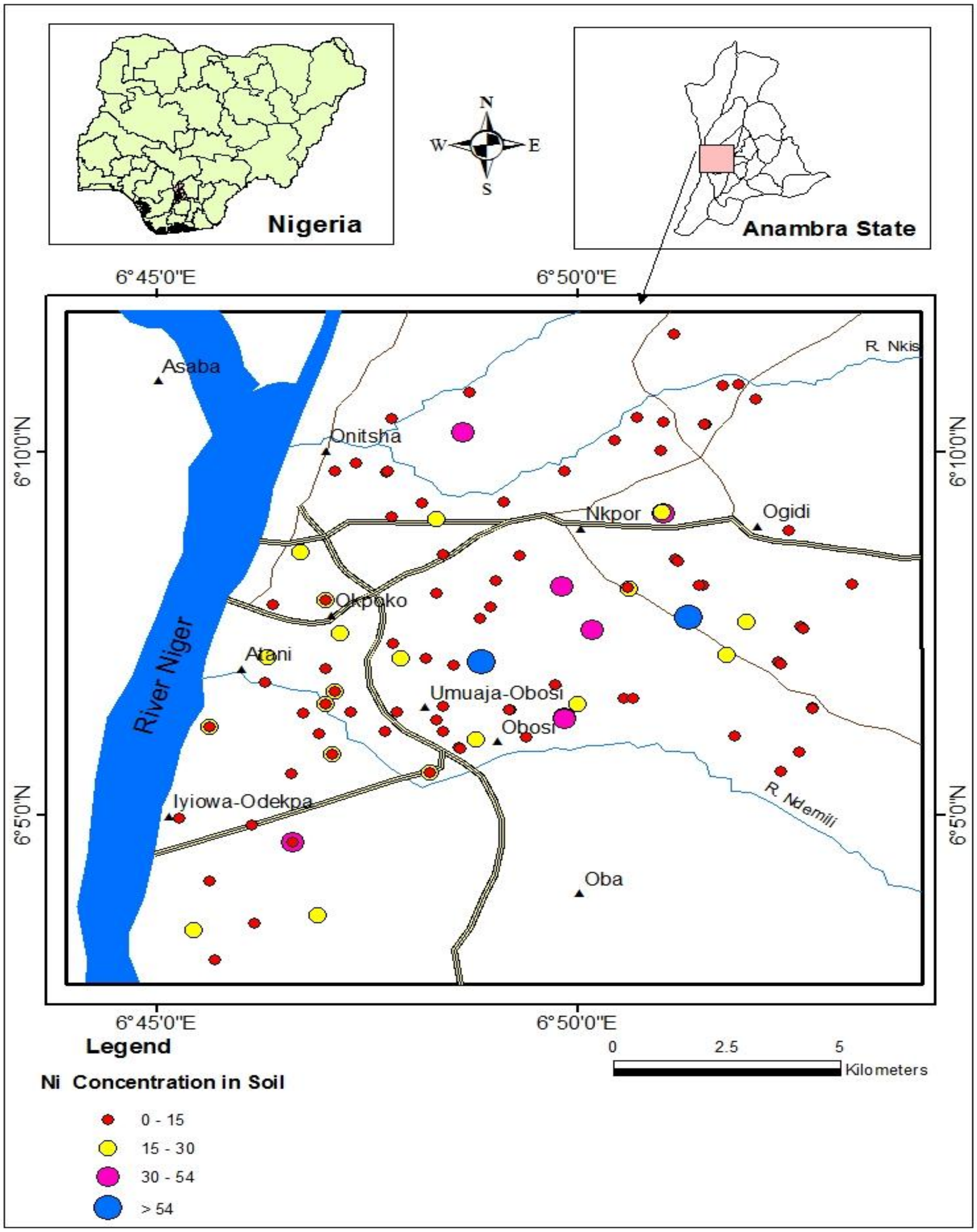


Fig4.17: Spatial distribution of Ni in soils (Concentration in ppm)

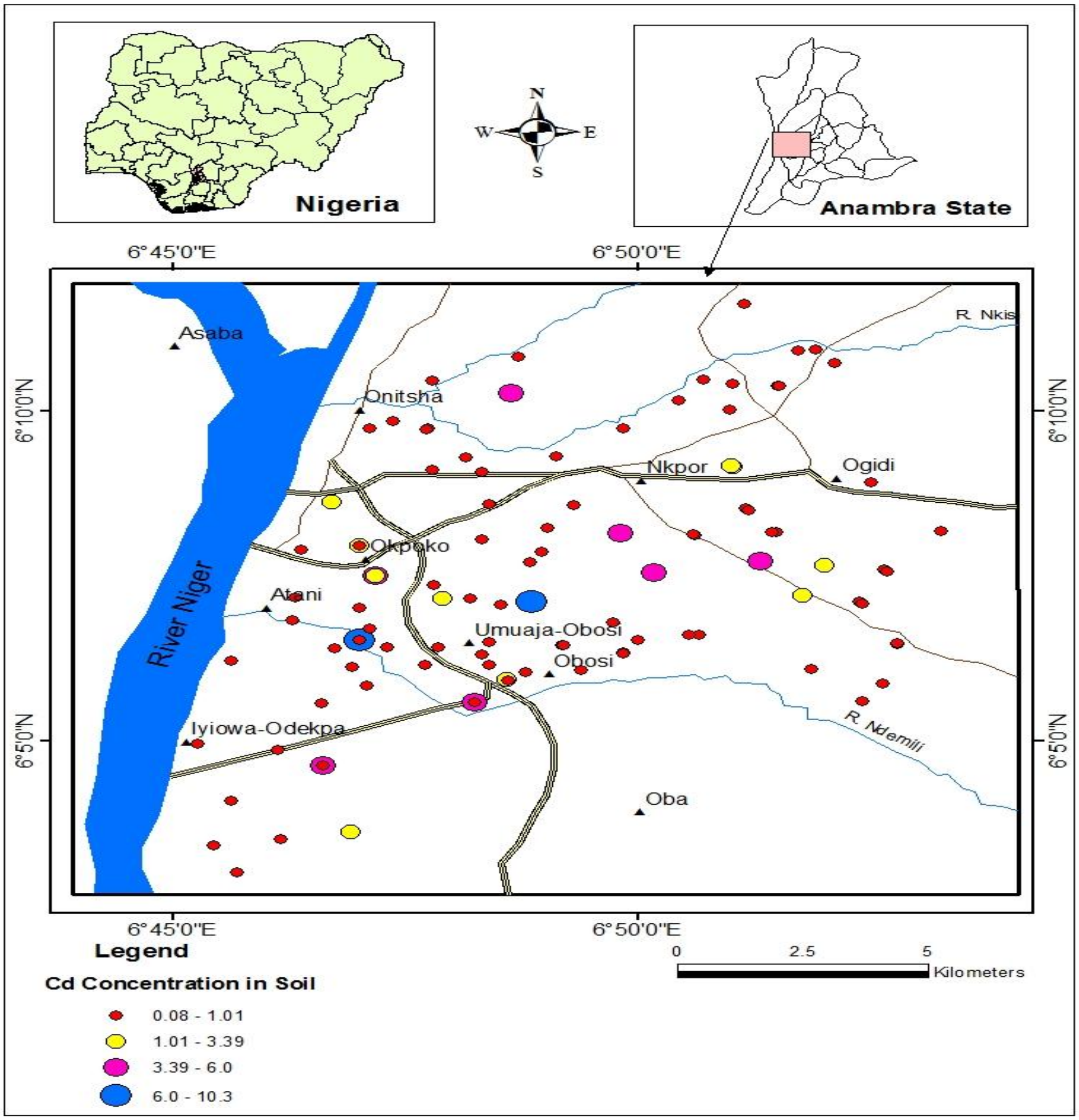


Fig4.18. Spatial distribution of Cd in soils. (Concentration in ppm)

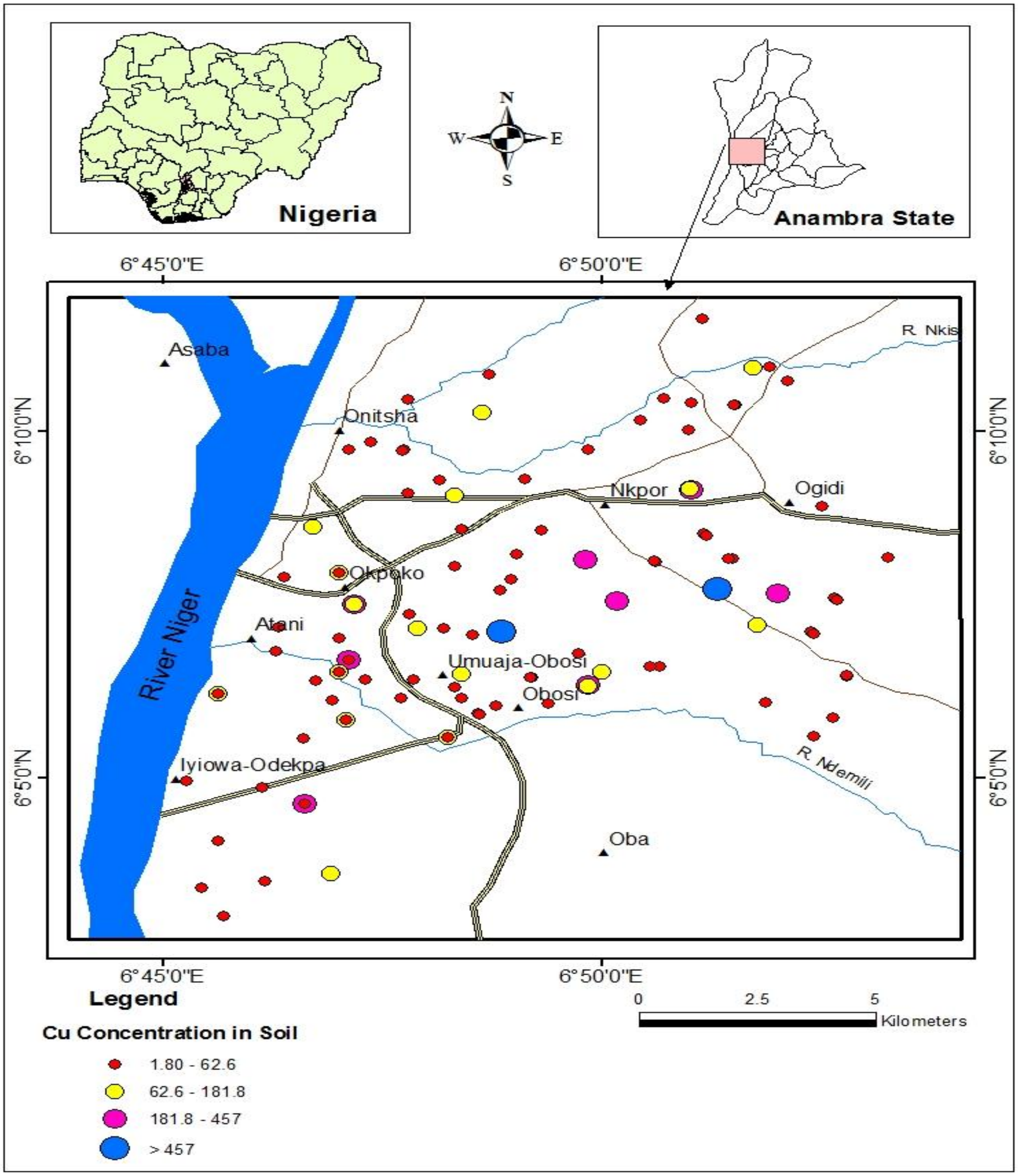


Fig4.19. Spatial distribution of Cu in soils. (Concentration in ppm)

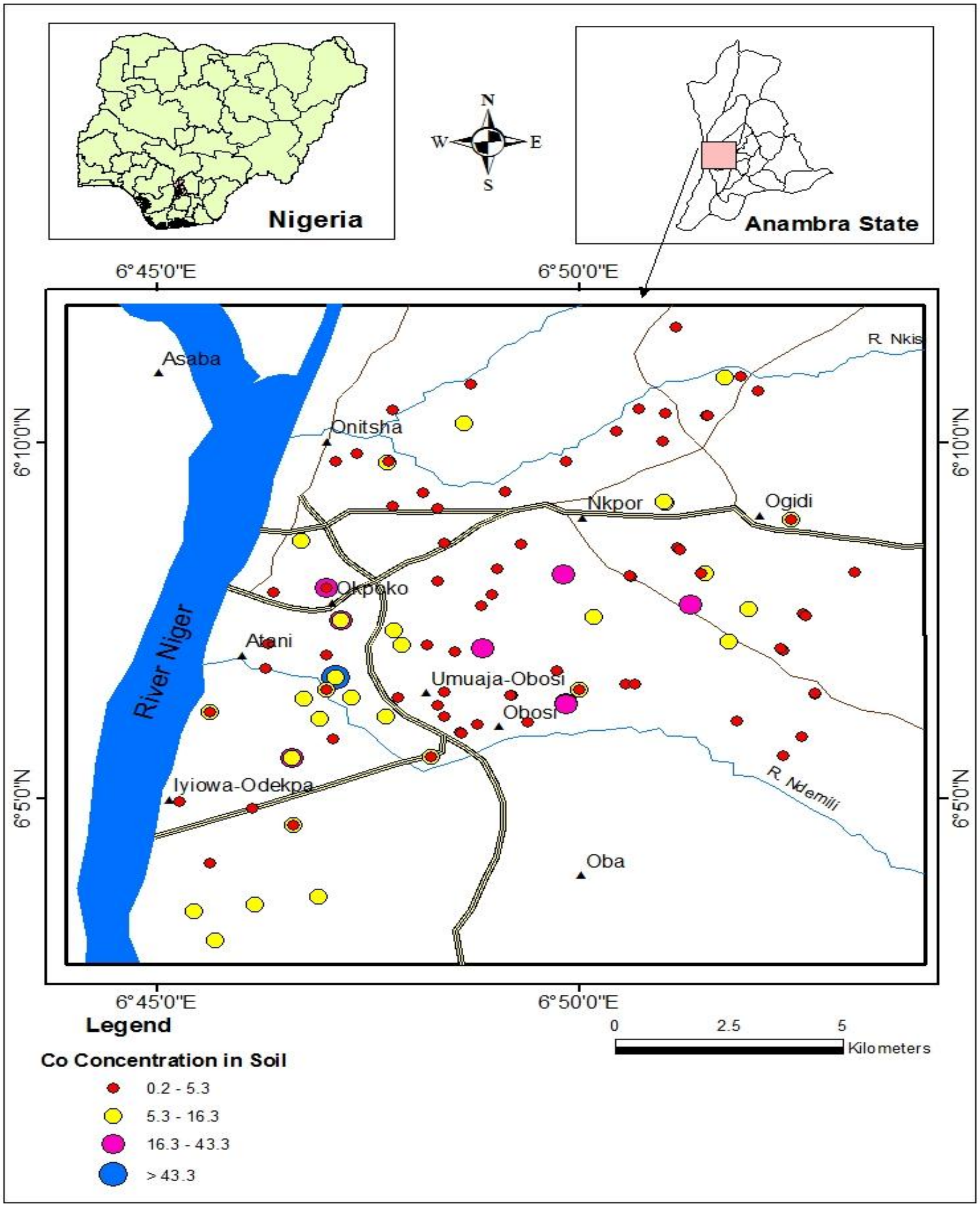


Fig4.20: Spatial distribution of Co in soils (Concentration in ppm)

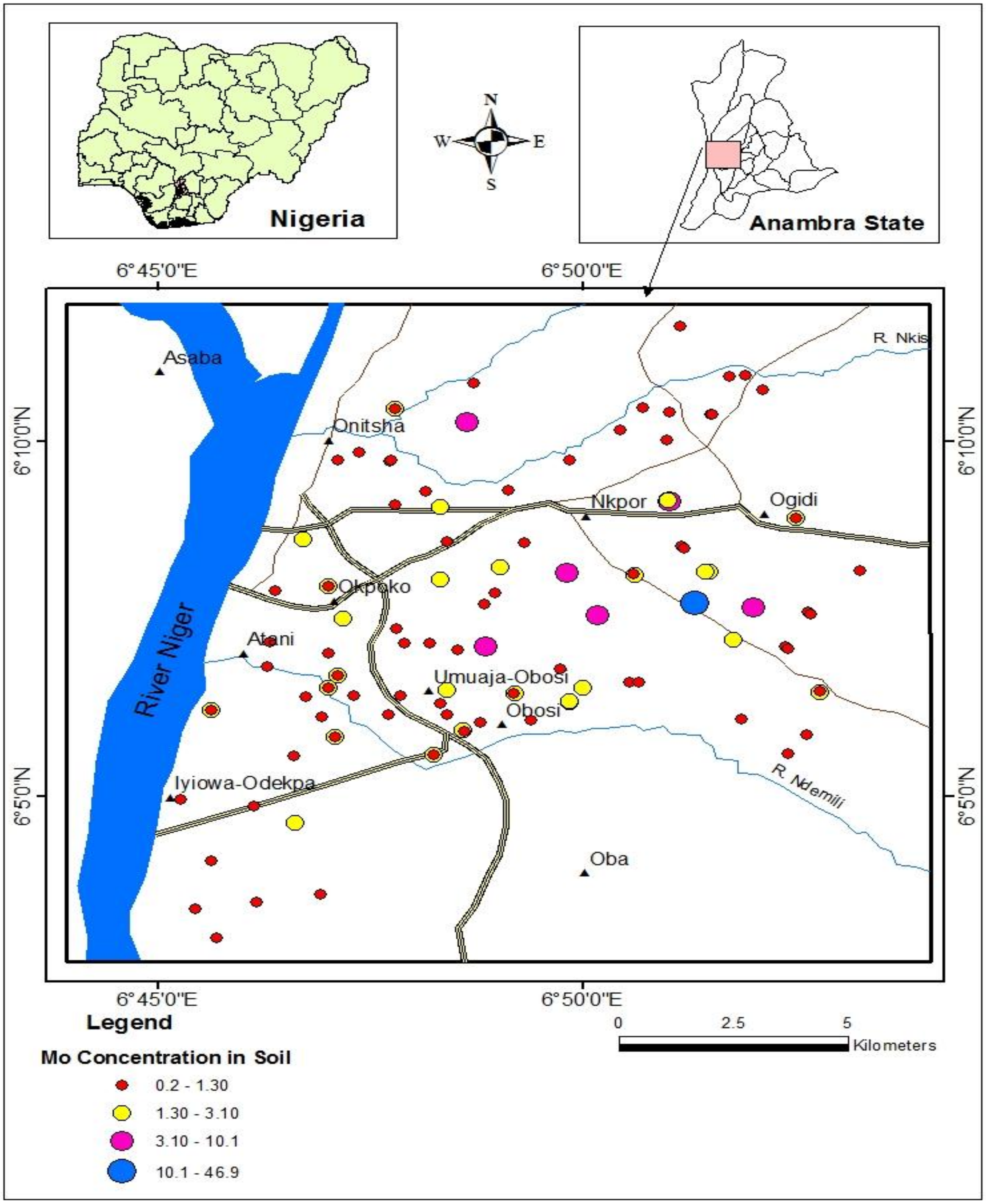


Fig.4.21: Spatial distribution of Mo in soils. (Concentration in ppm)

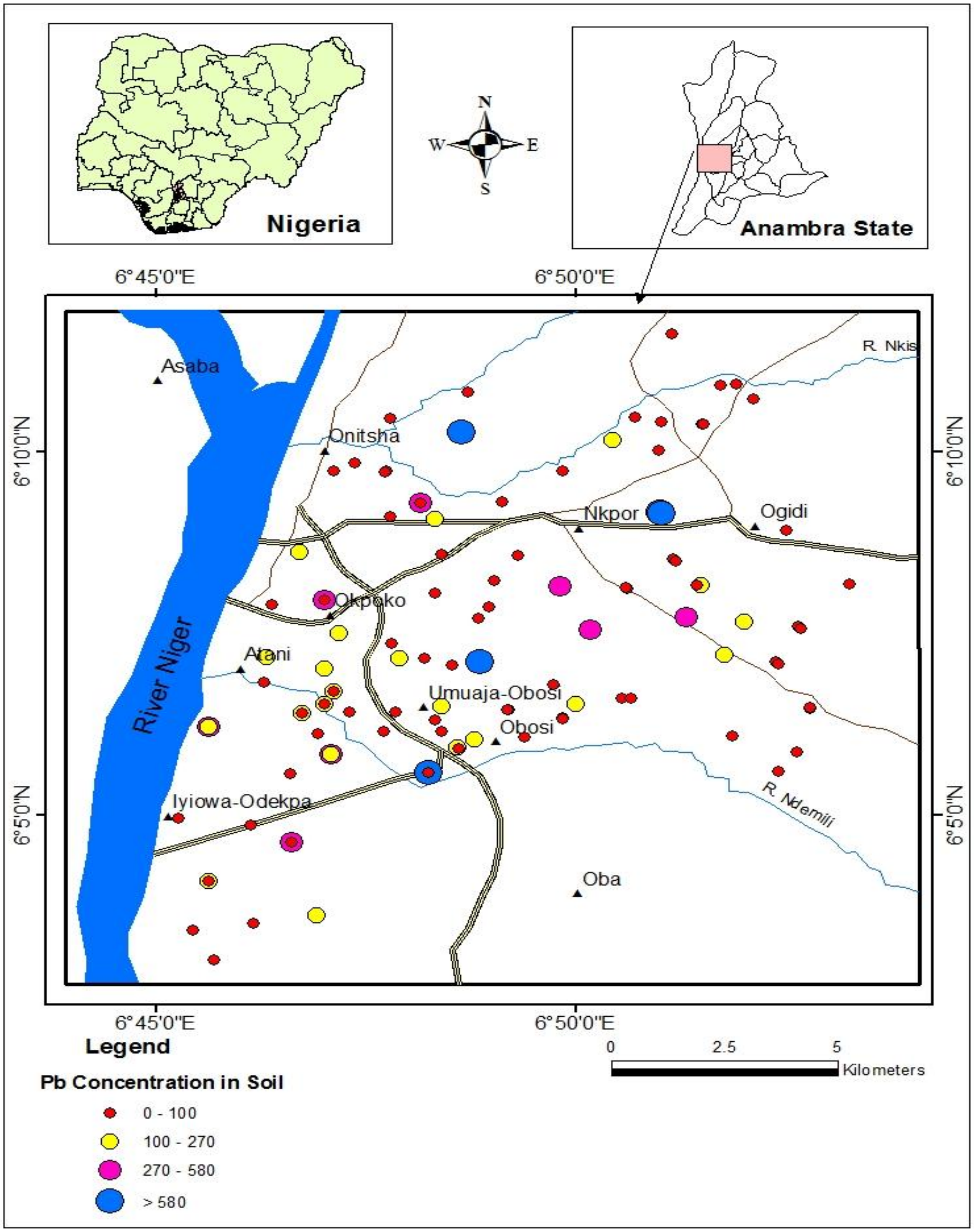


Fig.4.22: Spatial distribution of Pb in soils. (Concentration in ppm)

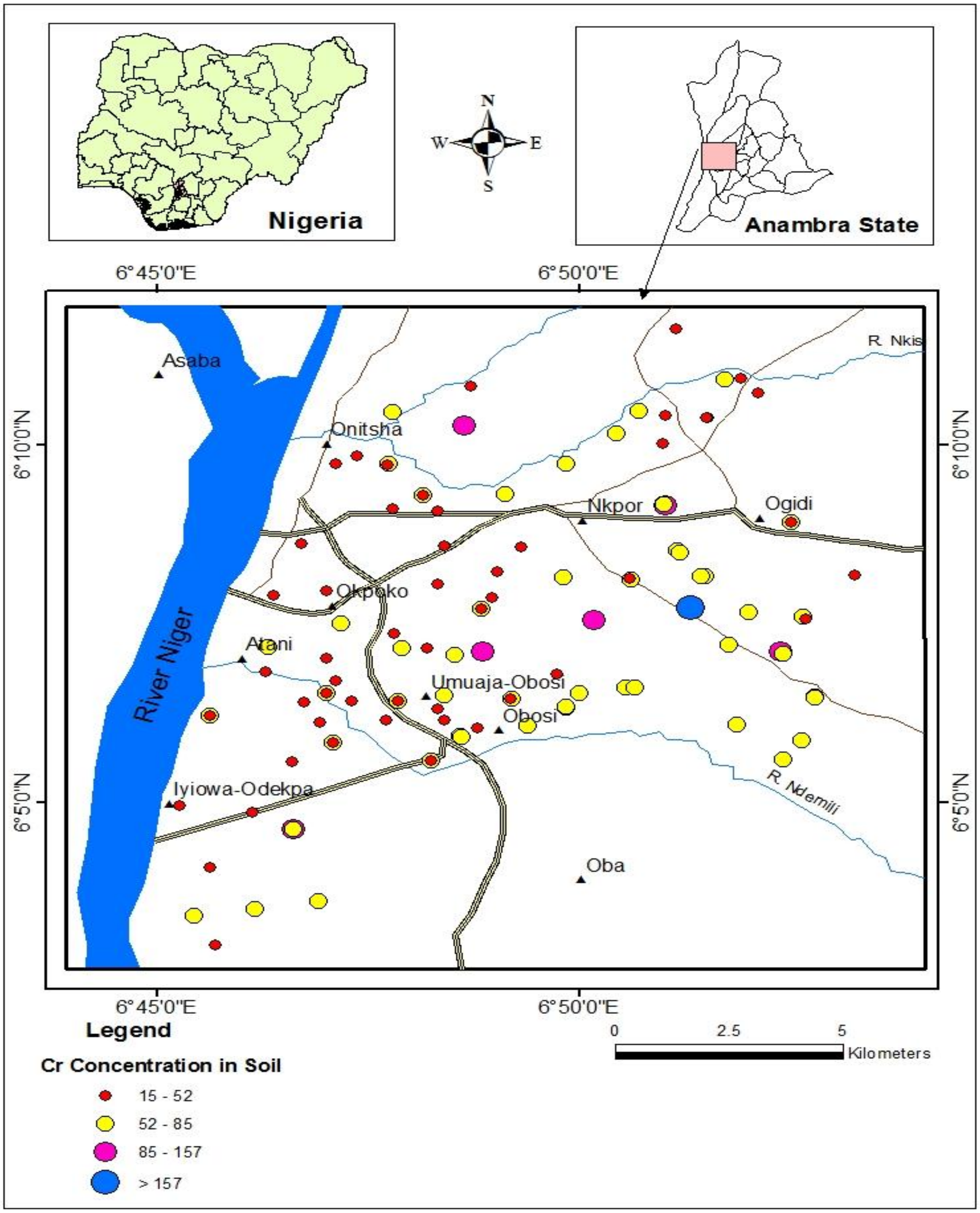


Fig.4.23: Spatial distribution of Cr in soils. (Concentration in ppm)

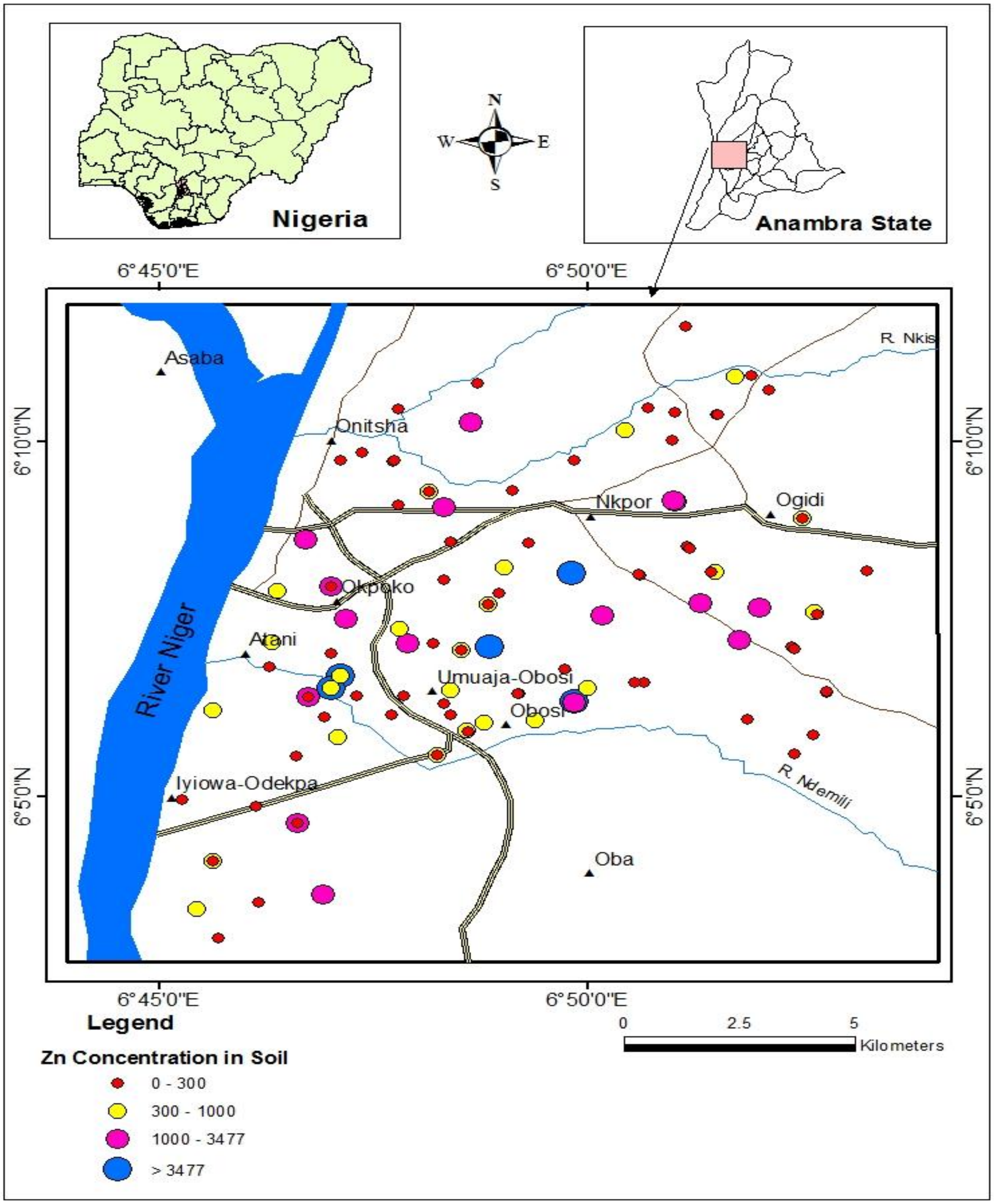


Fig.4.24: Spatial distribution of Zn in soils. (Concentration in ppm)

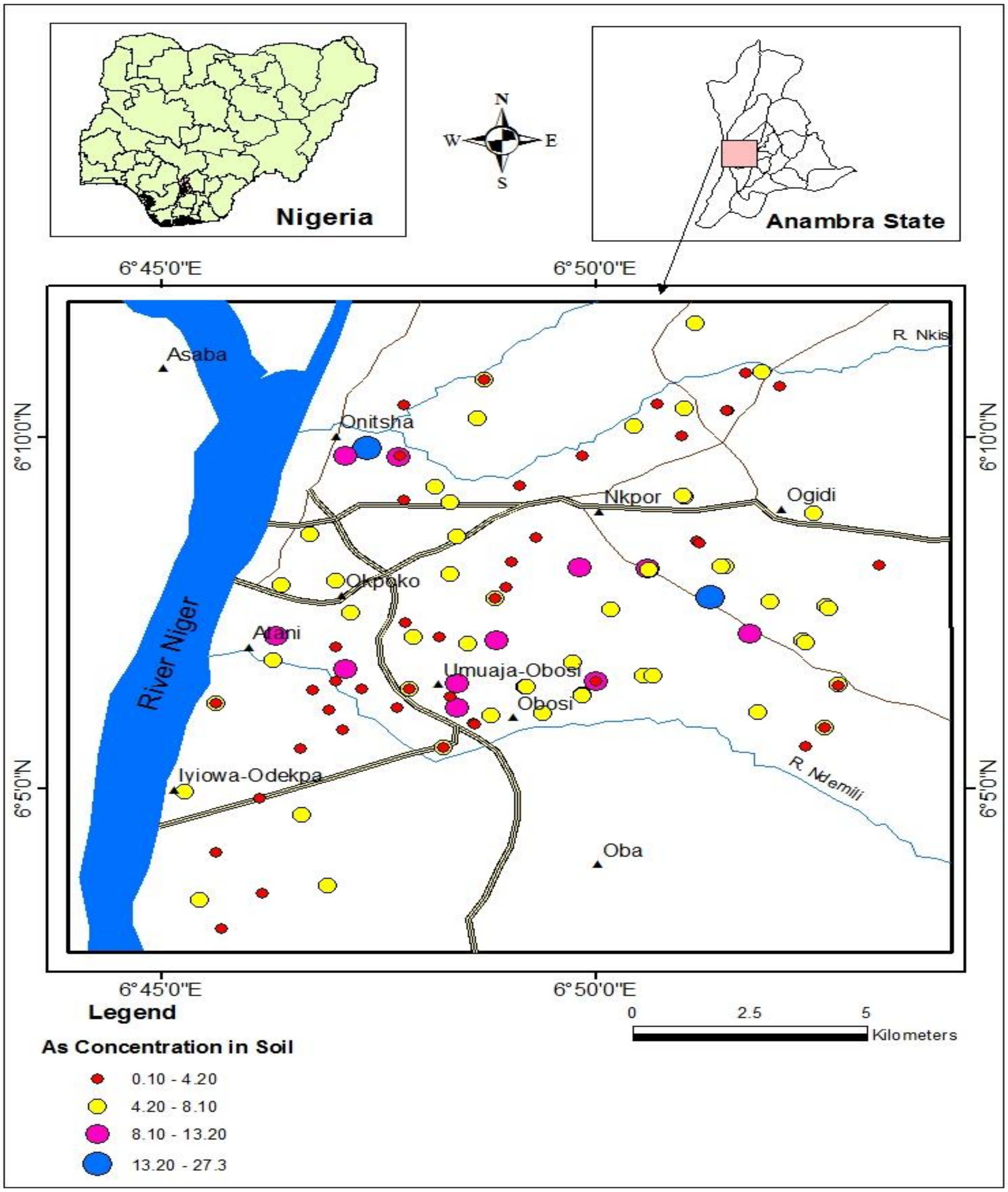


Fig.4.25: Spatial distribution of As in soils. (Concentration in ppm)

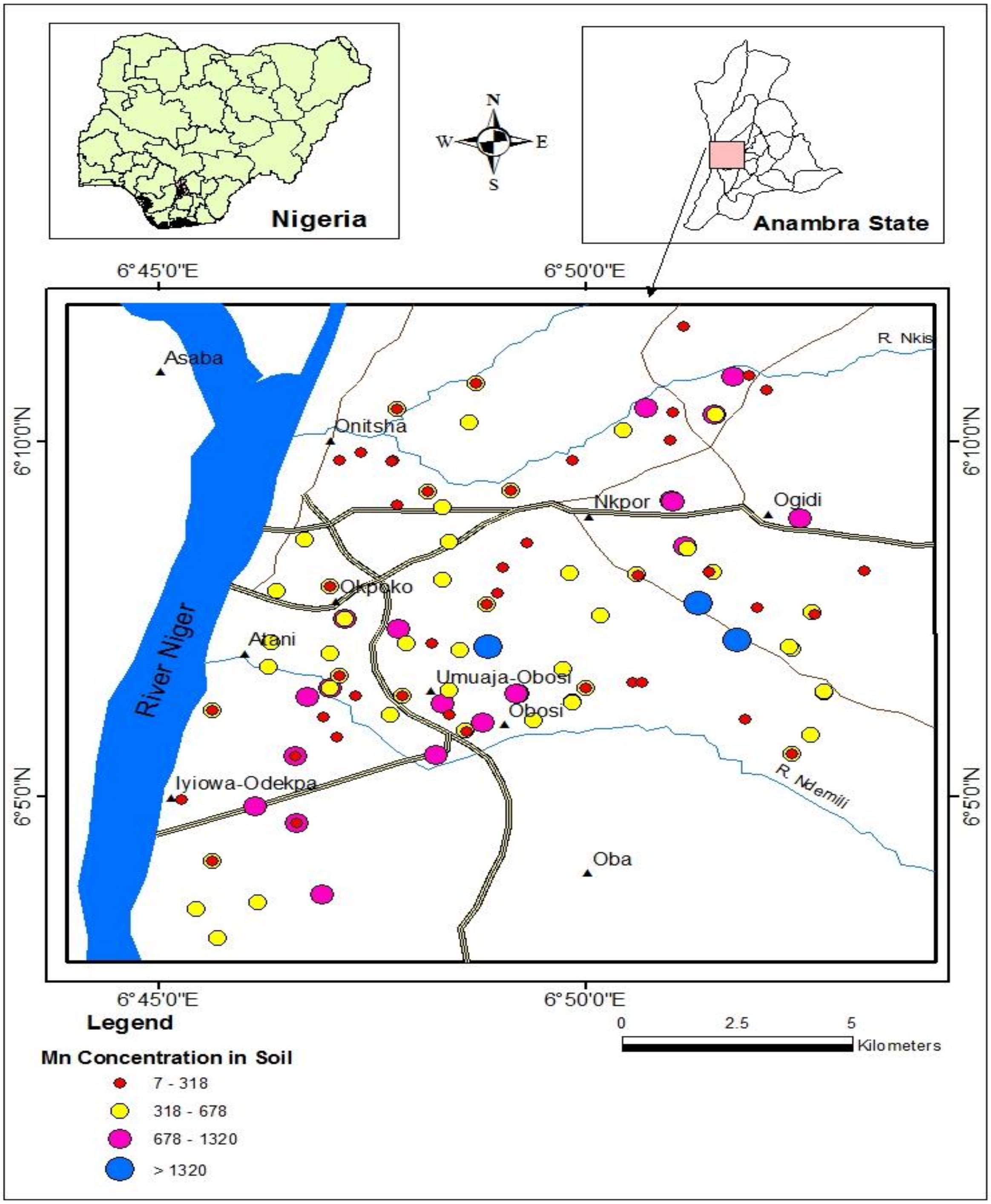


Fig.4.26: Spatial distribution of Mn in soils. (Concentration in ppm)

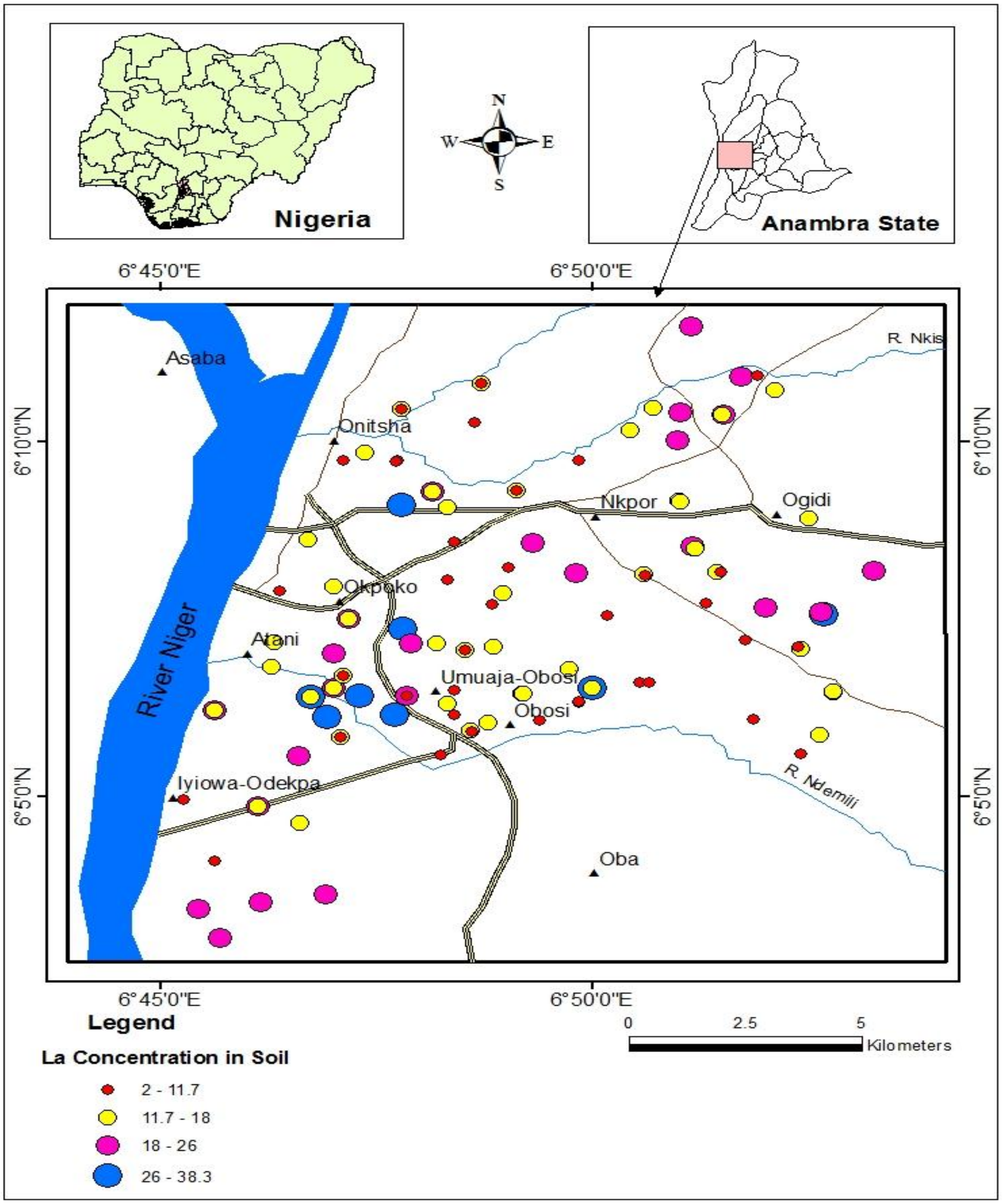


Fig.4.27: Spatial distribution of La in soils. (Concentration in ppm)

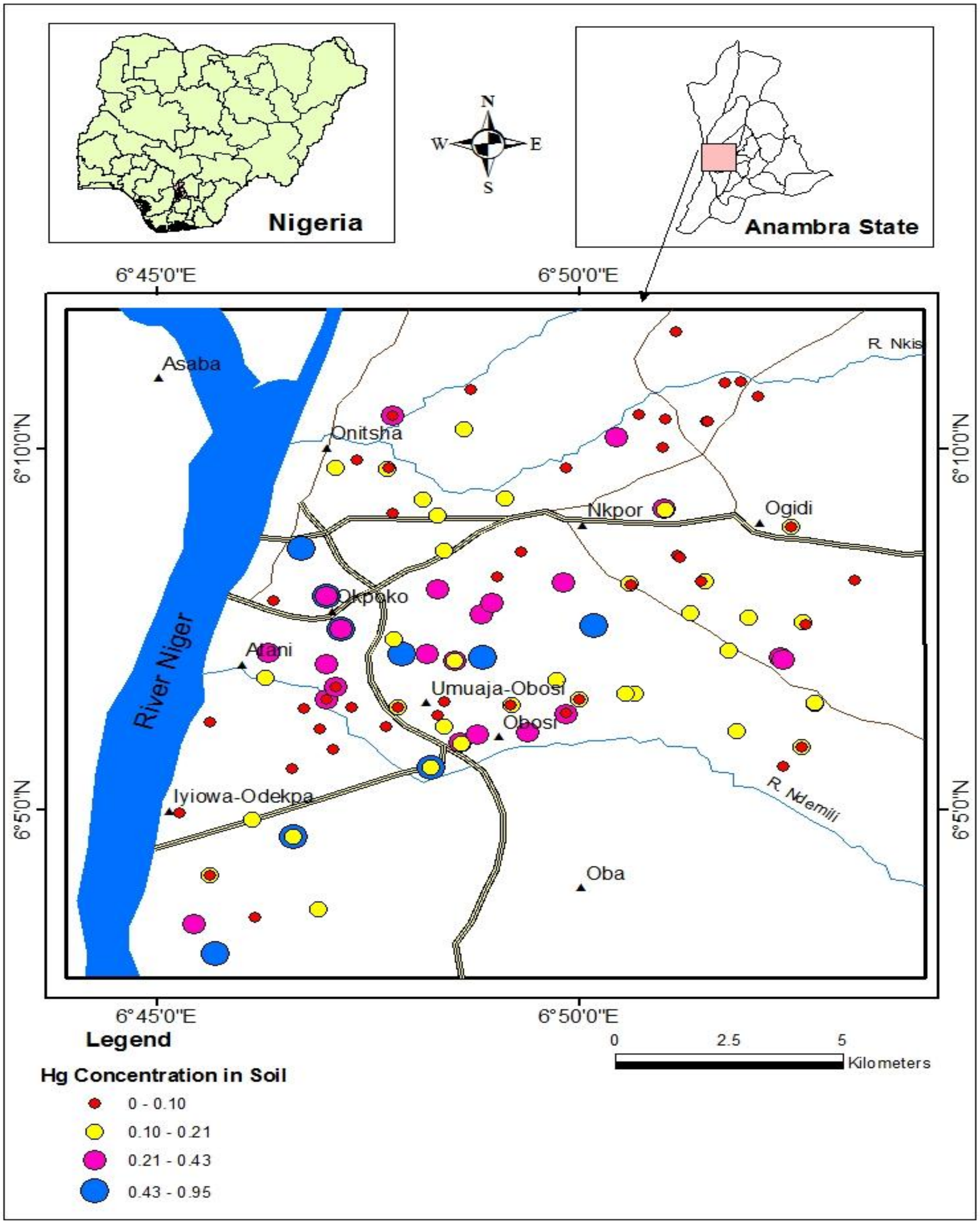


Fig.4.28: Spatial distribution of Hg in soils. (Concentration in ppm)

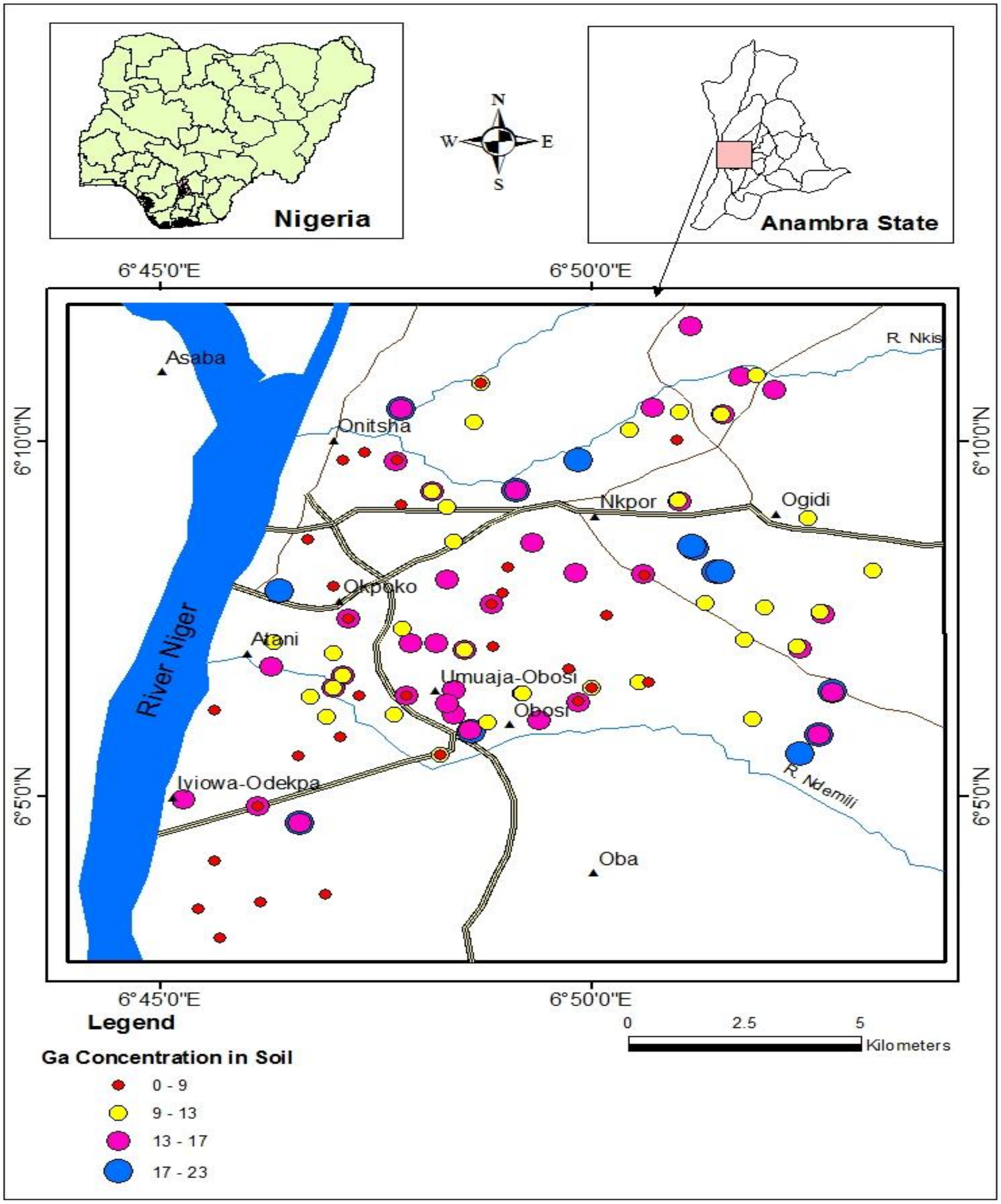


Fig.4.29: Spatial distribution of Ga. in soils. (Concentration in ppm)

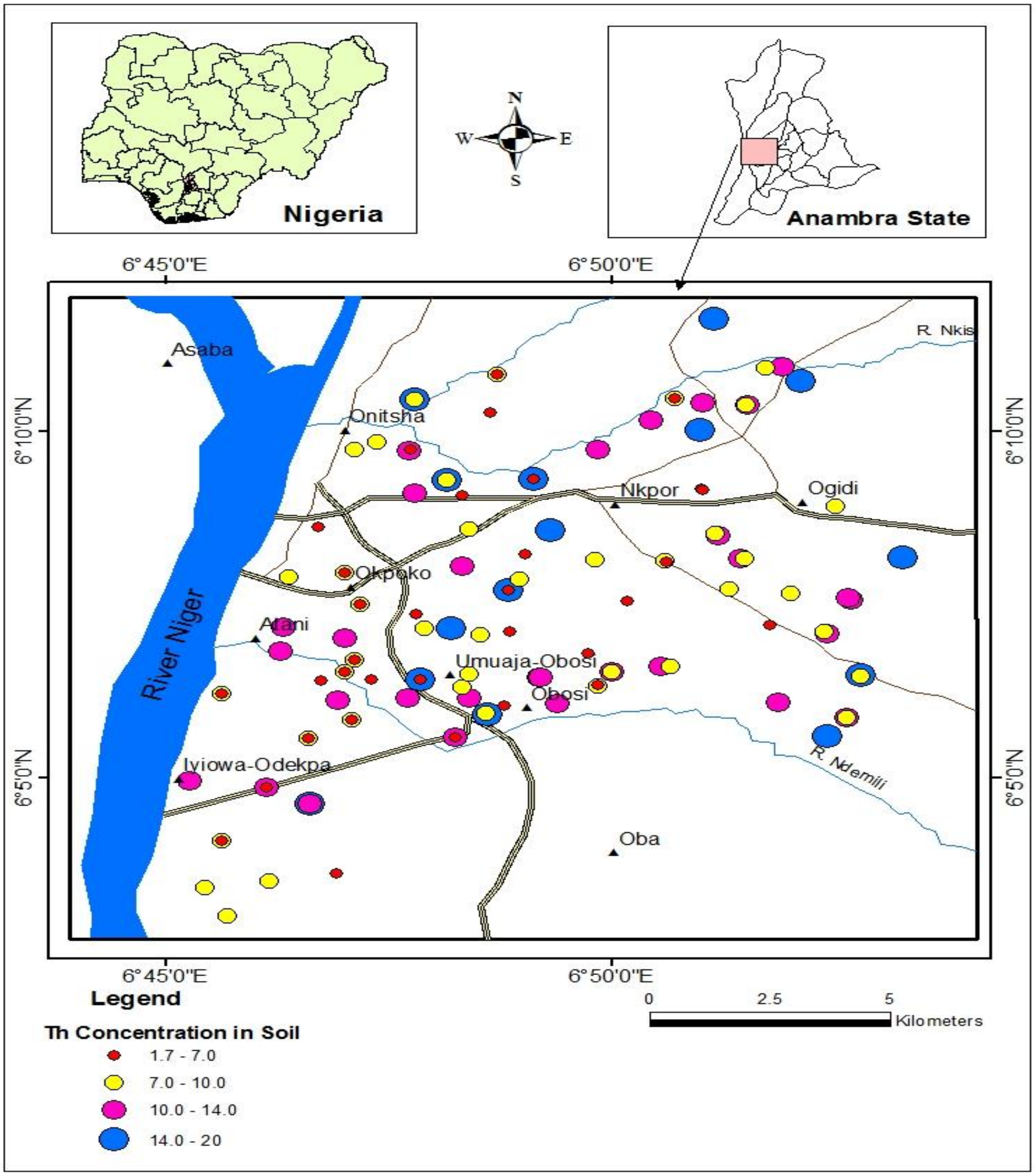


Fig.4.30: Spatial distribution of Th in soils. (Concentration in ppm)

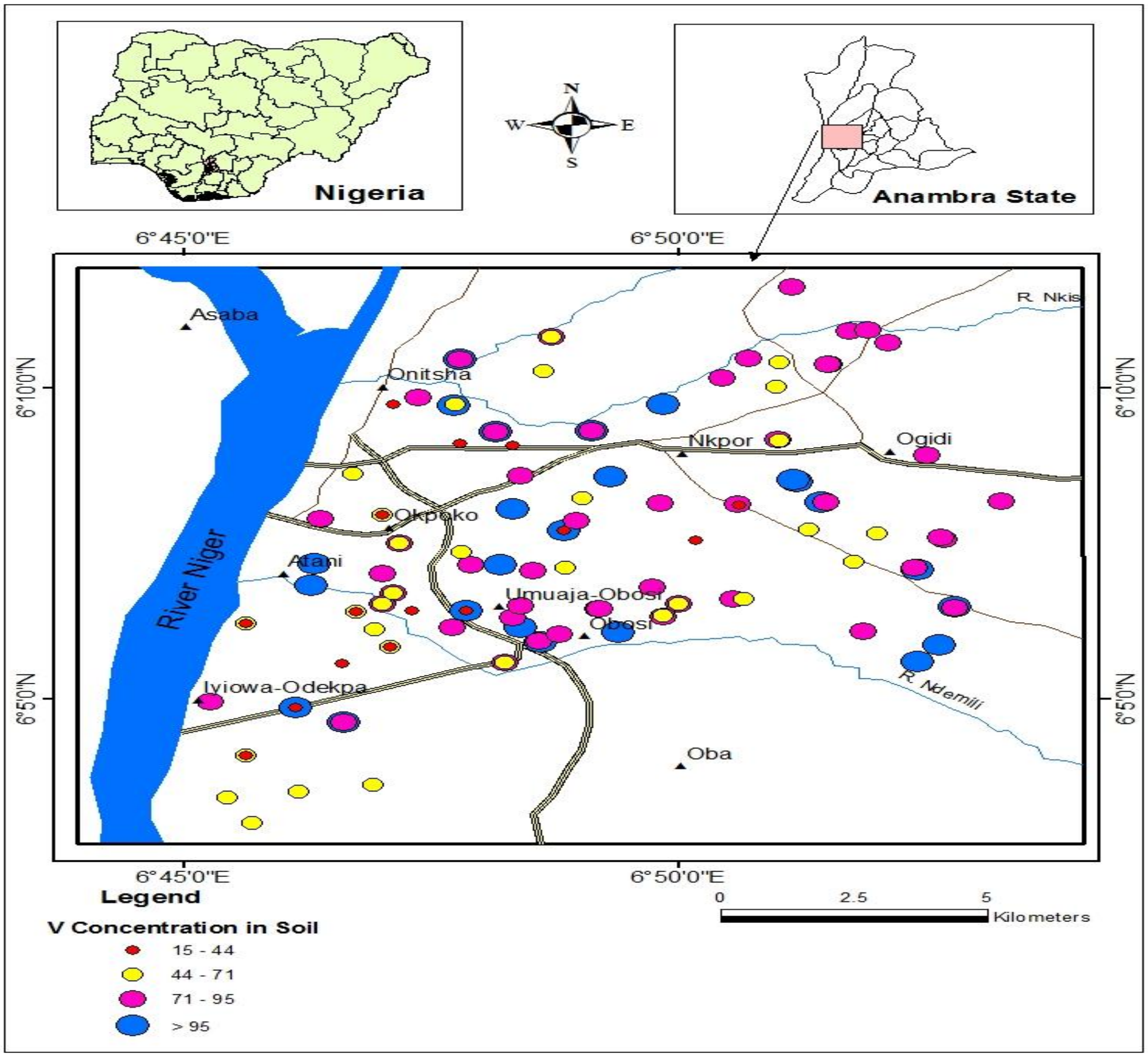


Fig.4.31: Spatial distribution of V in soils. (Concentration in ppm)

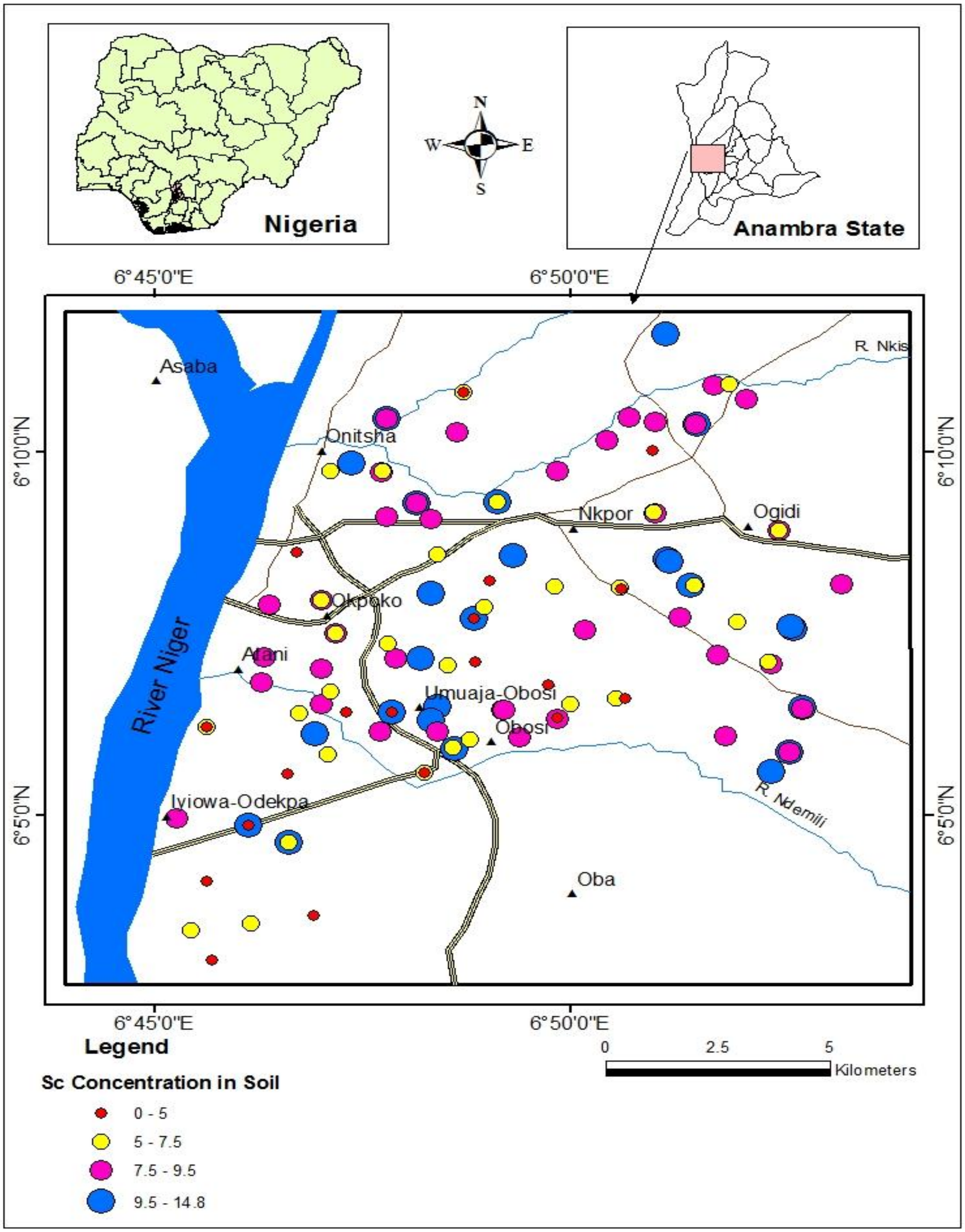


Fig. 4.32: Spatial distribution of Sc in soils. (Concentration in ppm)

### 4.4.4 Spatial distribution map of sediments in Onitsha metropolis

Geochemical maps were also produced of the trace element in sediments specifically, these maps are two dimensional spatial distribution of the trace elements in Roadside drain sediments (RSD), NdeMilli river (ID) sediments and Nkisi river (NK) sediments from the study area (Figure 4.39 – Figure 4.52). A point source type was also used for the same reason stated above in the case of soils geospatial map. Base on the spatial distribution of all the elements; La, Mn, Ga, Ni, V, Mo, As, Sc, Cd, Zn, Cr, Pb, As, and Cu concentration in the study area, (Fig. 4.33 – Fig. 4.46) it is observed that most of the element with elevated concentrations found on the roadside drian sediment (RSD), are on the highway road drains, the drains on the Onitsha – Enugu express way, the Onitsha – Owerri express way and the old PH road relative to the concentration of those elements assessed on less vehicular traffic way like the old Onisha – Enugu road and Nnamdi Azikiwe road. Again, it was observed that the Ndemilli river recorded relatively high elevation for most of the trace element except for La, Ga, V, As and Sc (Fig. 4.33, Fig. 4.35, Fig. 4.37, Fig. 4.39, Fig. 4.40), respectively. The relatively higher concentration of these elements on most of the samples collected from the Ndemilli river may have been influenced by the fact that the Ndemilli river drains over 60% of of the total developed area of Onitsha metropolis relative to the Nkisi river which drain smaller portion of the metropolis and the areas that the Ndemilli drains are more of industrial layout, commercial areas as well as places with huge human and its related activities there by generating different kinds of liquid and solid waste that eventually find its way into the river, on like the Nkisi river with relatively lesser human activities. But for the fact that elements such as La, Ga, V, As and Sc are found to be higher in elevation, it could be said that these elements may have been enriched by similar source, which include direct wash out from vehicle related materials.

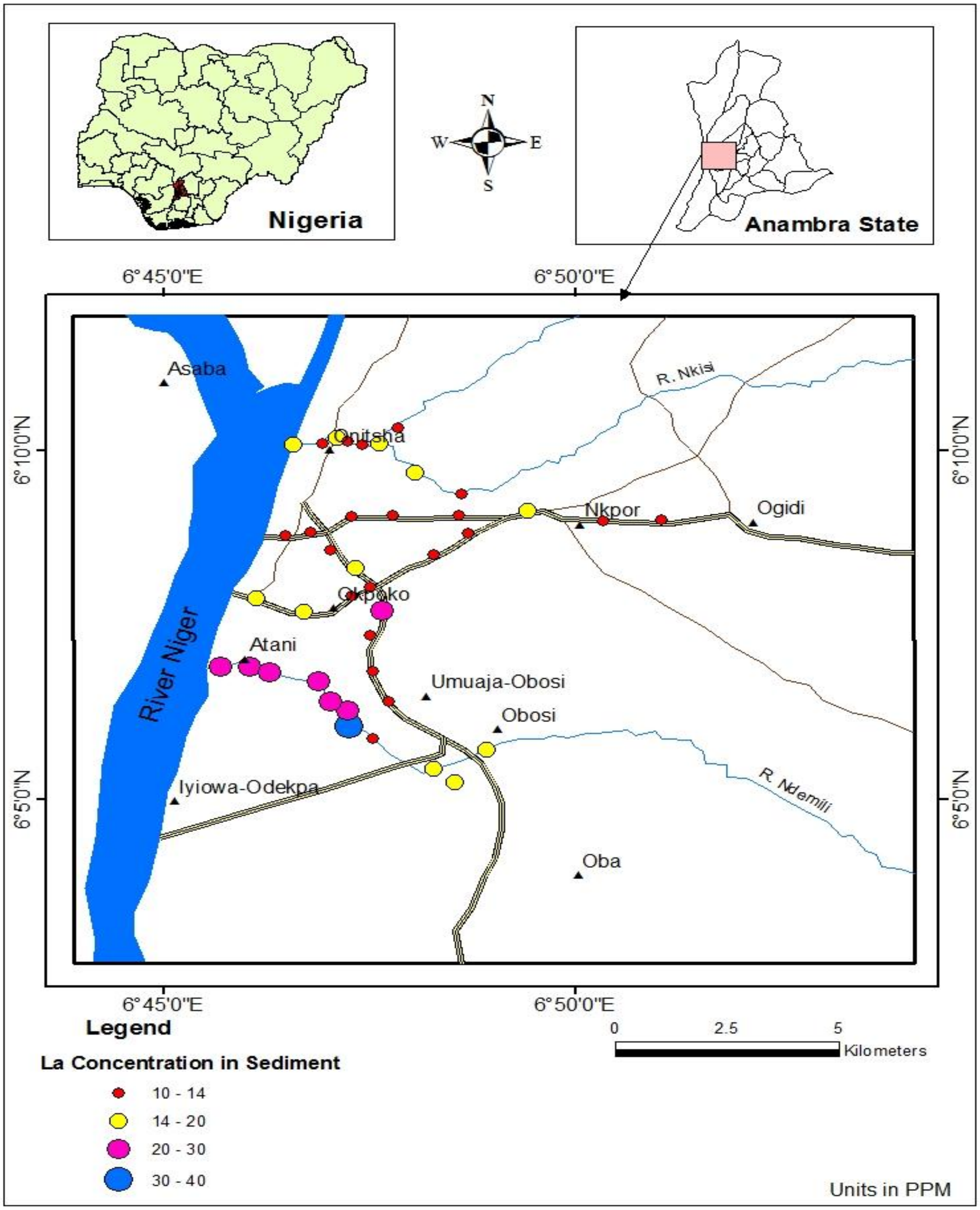


Fig.4.33: Spatial distribution of La in Sediments. (Concentration in ppm)

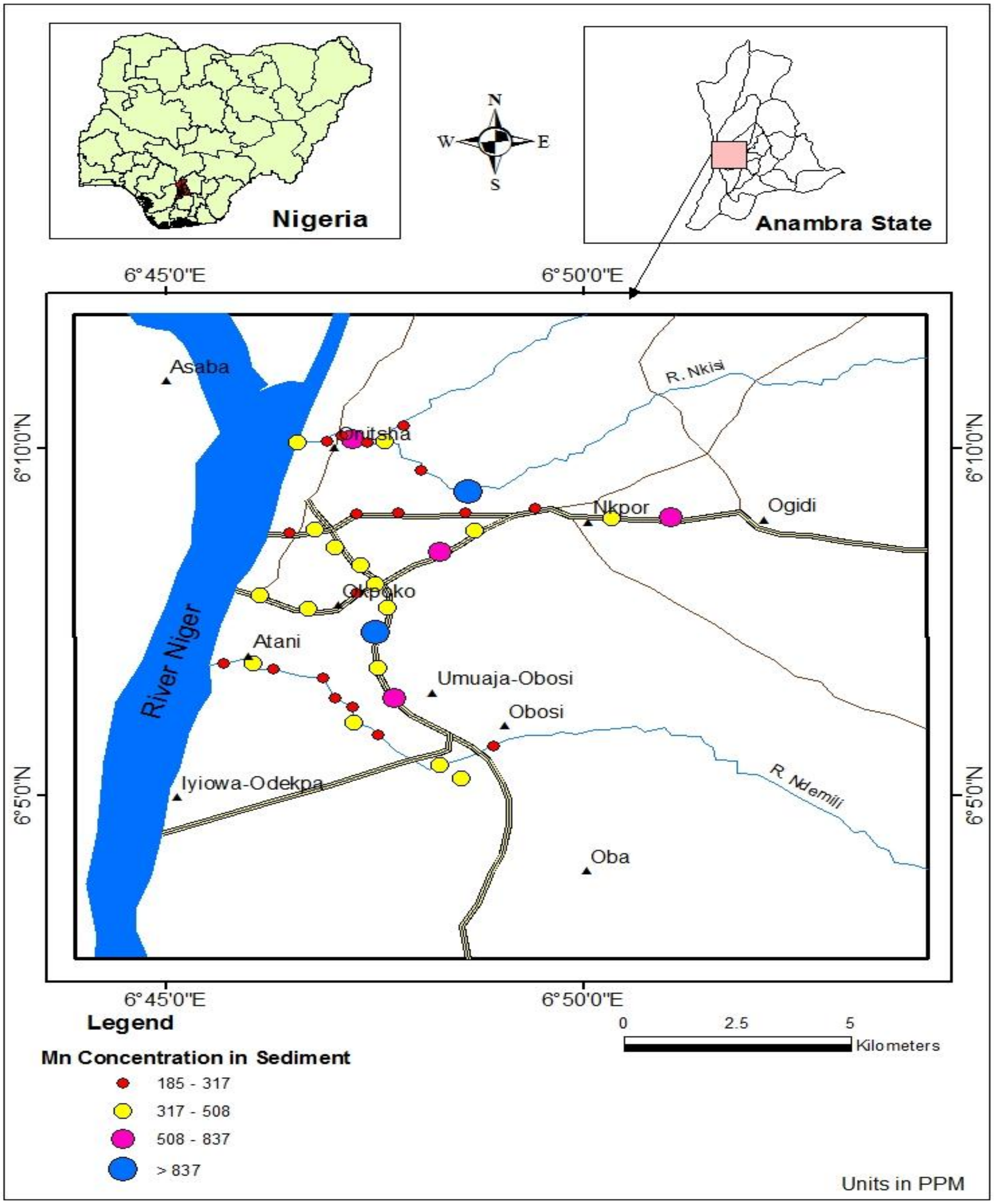


Fig. 4.34: Spatial distribution of Mn in Sediments. . (Concentration in ppm)

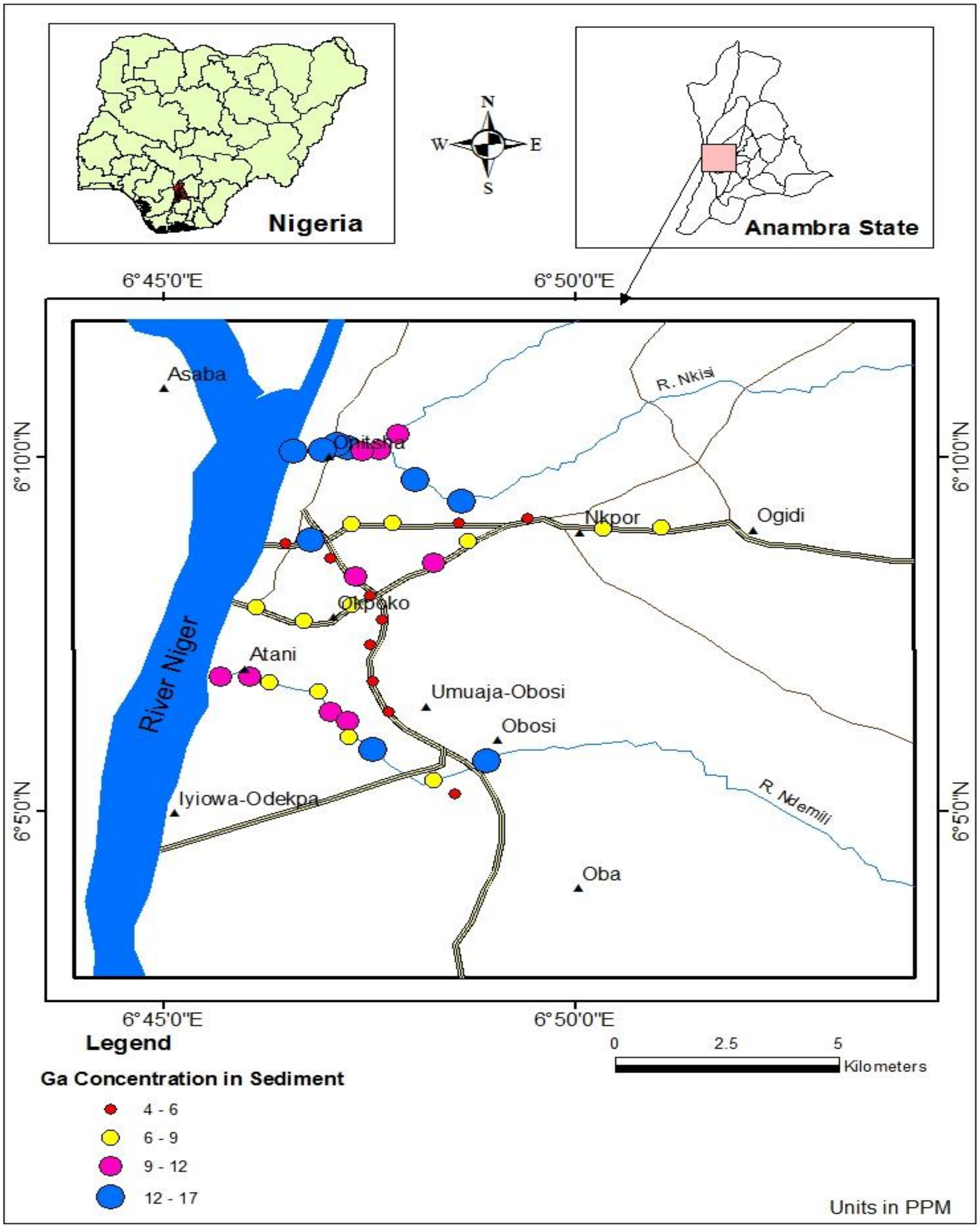


Fig. 4.35: Spatial distribution of Ga in Sediments. . (Concentration in ppm)

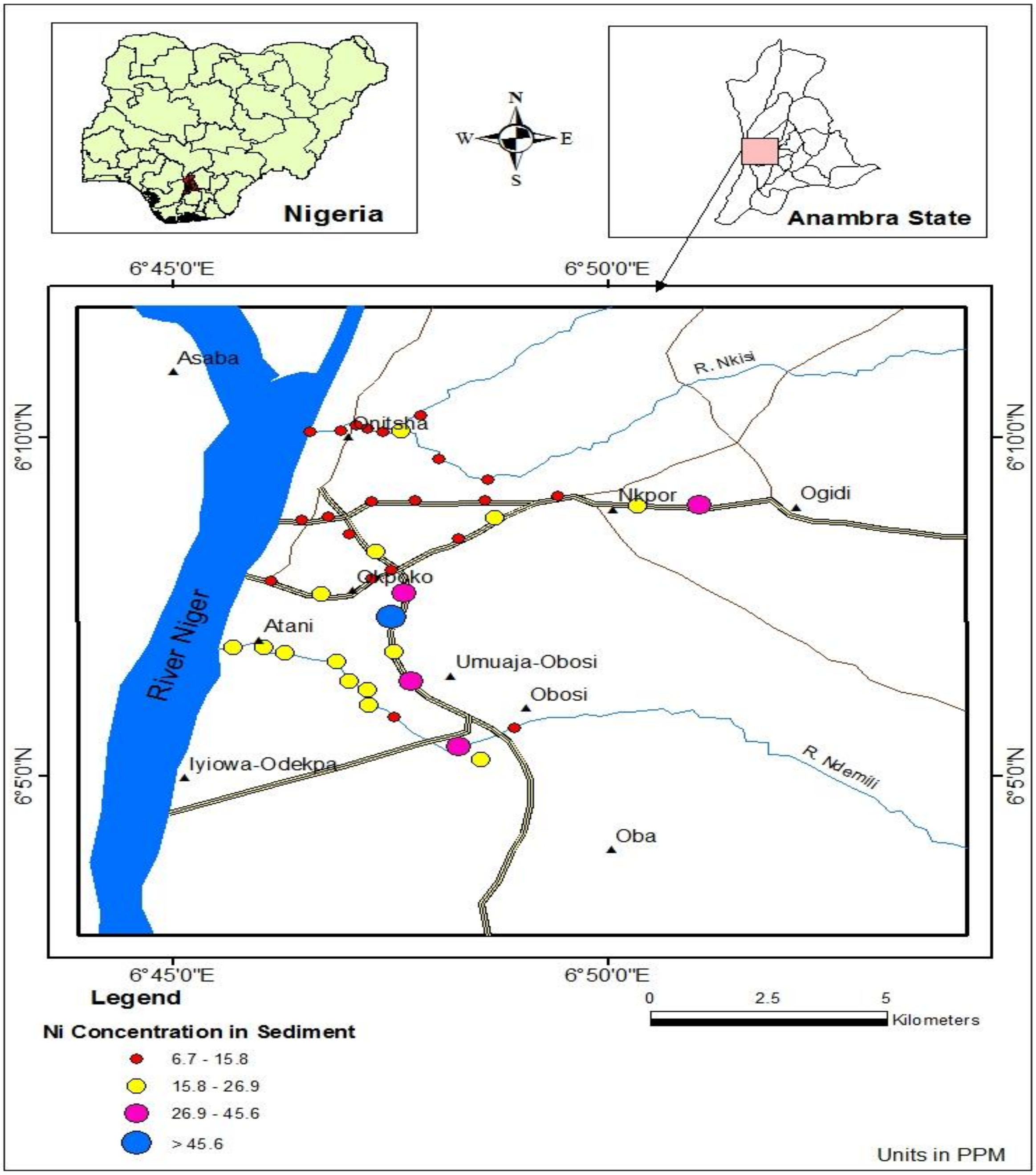


Fig. 4.36: Spatial distribution of Ni in Sediments. (Concentration in ppm)

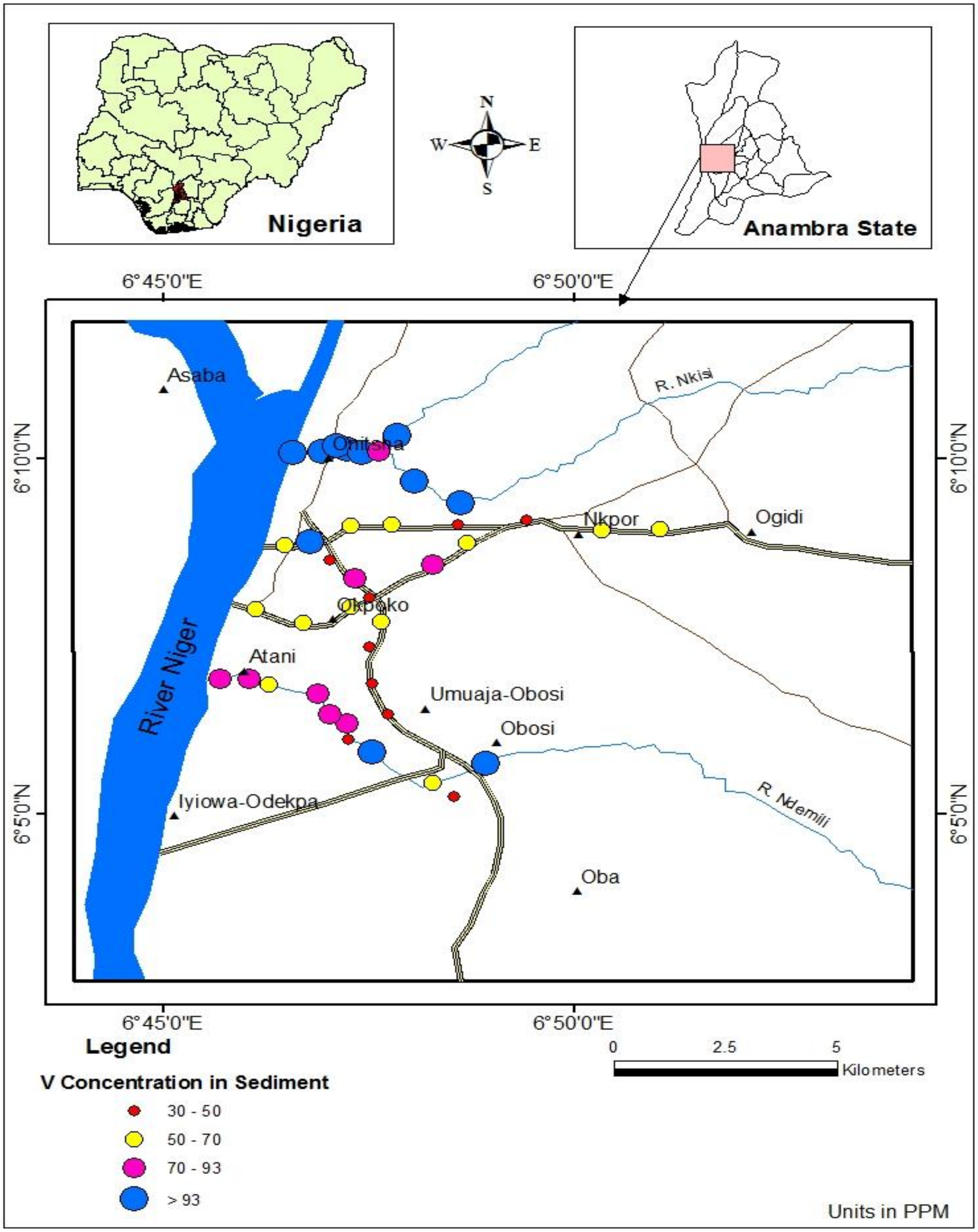


Fig. 4.37: Spatial distribution of V in sediments. (Concentration in ppm)

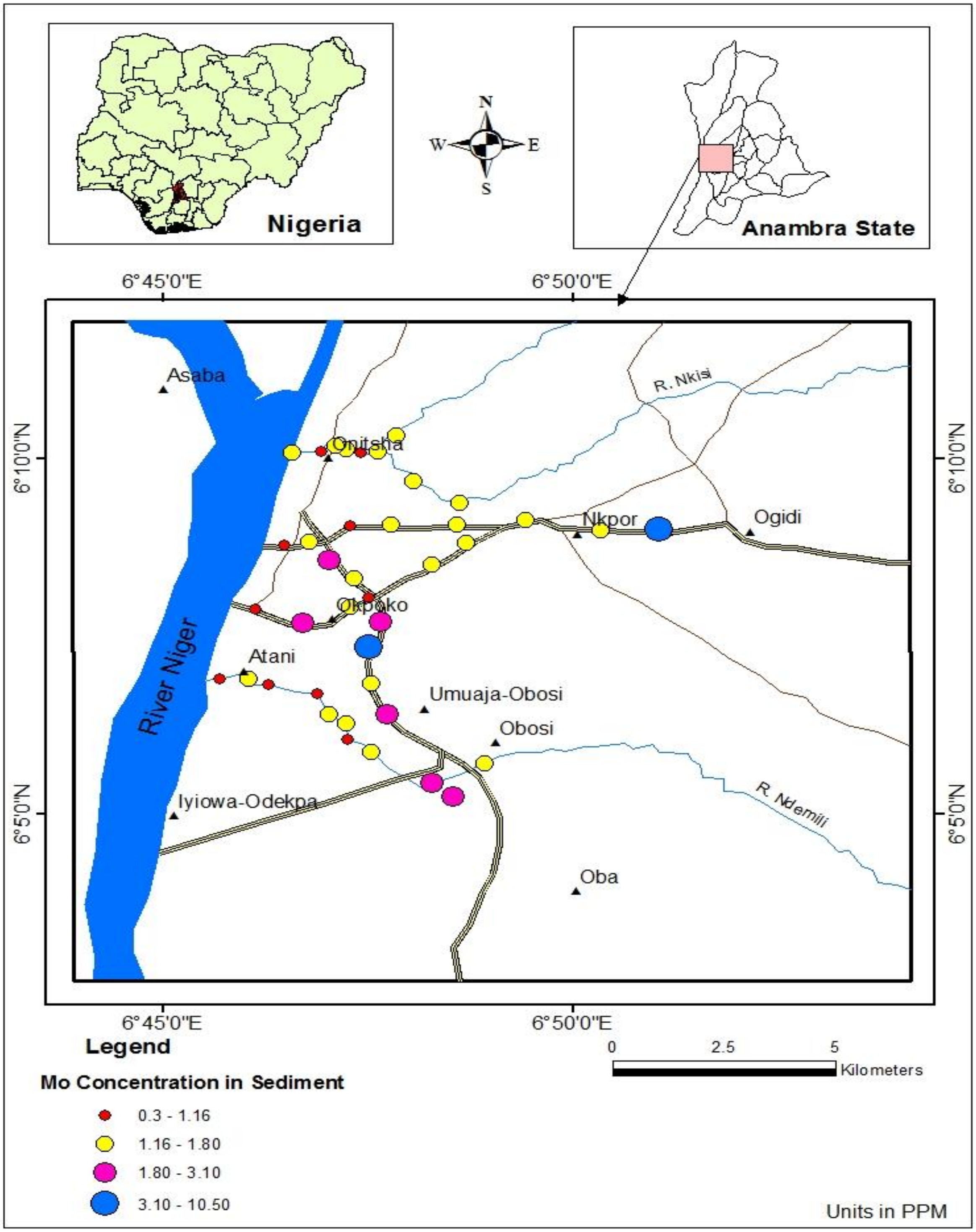


Fig. 4.38: Spatial distribution of Mo in Sediment. . (Concentration in ppm)

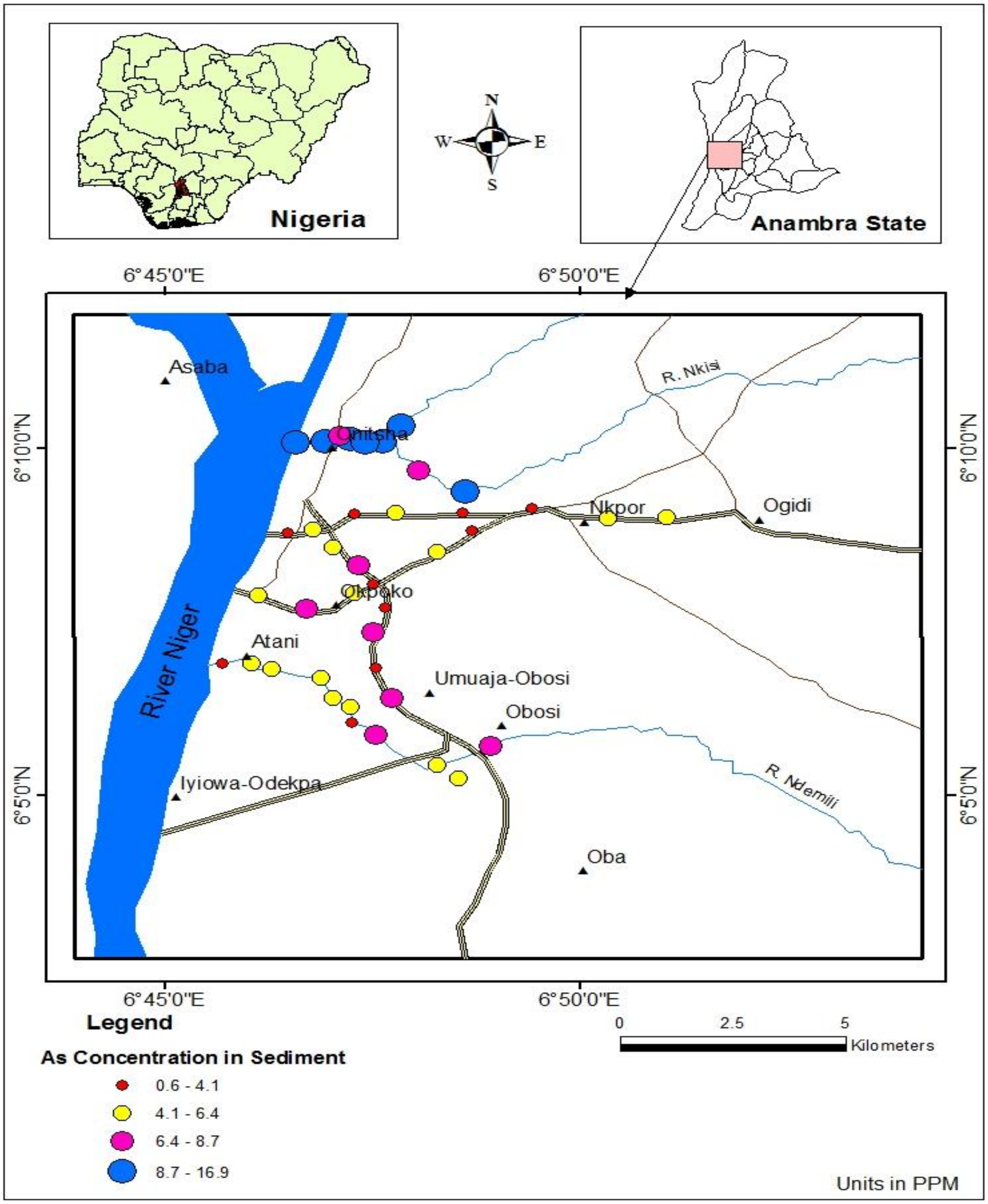


Fig. 4.39: Spatial distribution of As in Sediments. . (Concentration in ppm)

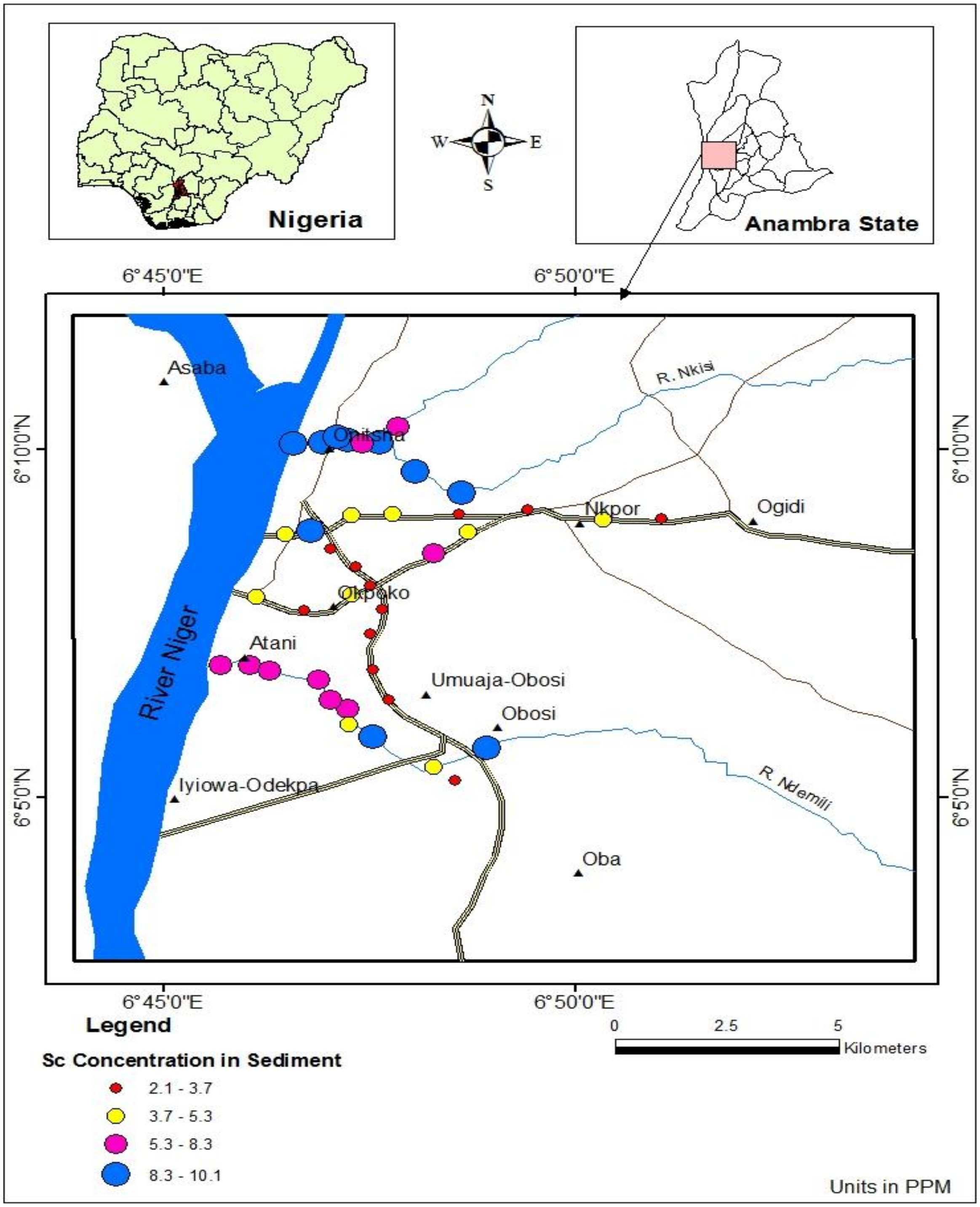


Fig.4.40: Spatial distribution of Sc in Sediments. (Concentration in ppm)

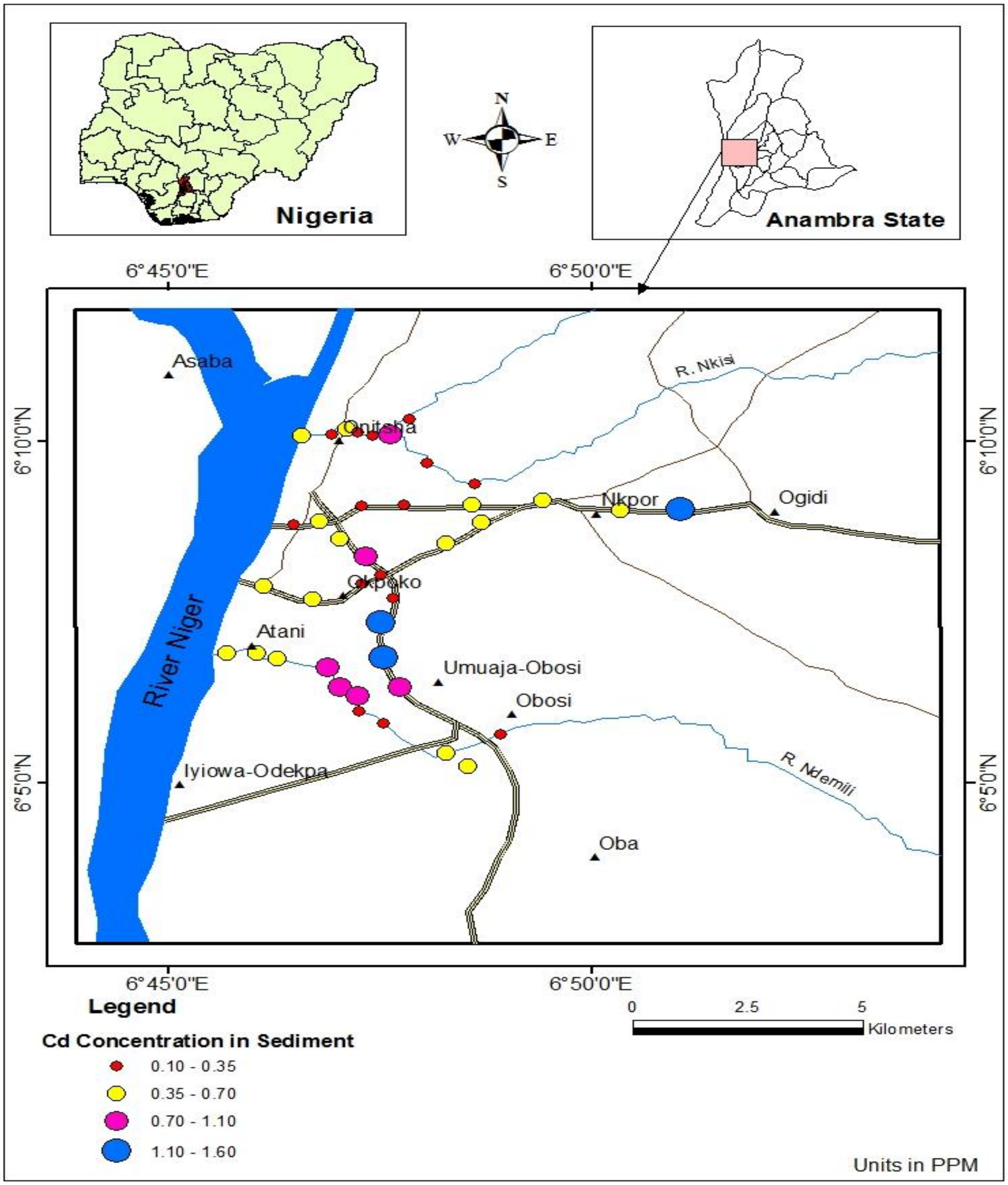


Fig.4.41: Spatial distribution of Cd in Sediments. (Concentration in ppm)

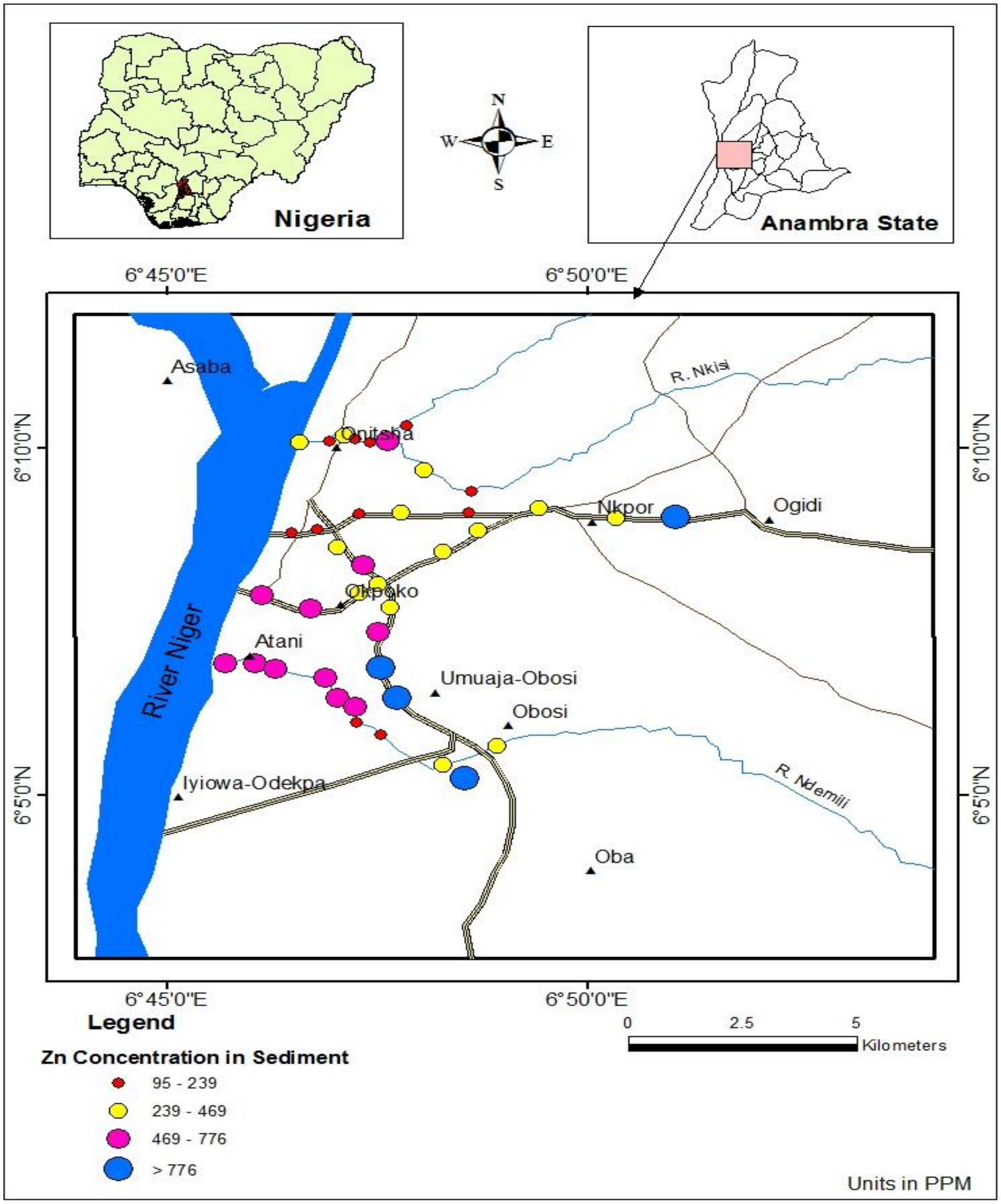


Fig.4.42: Spatial distribution of Zn in Sediments. (Concentration in ppm)

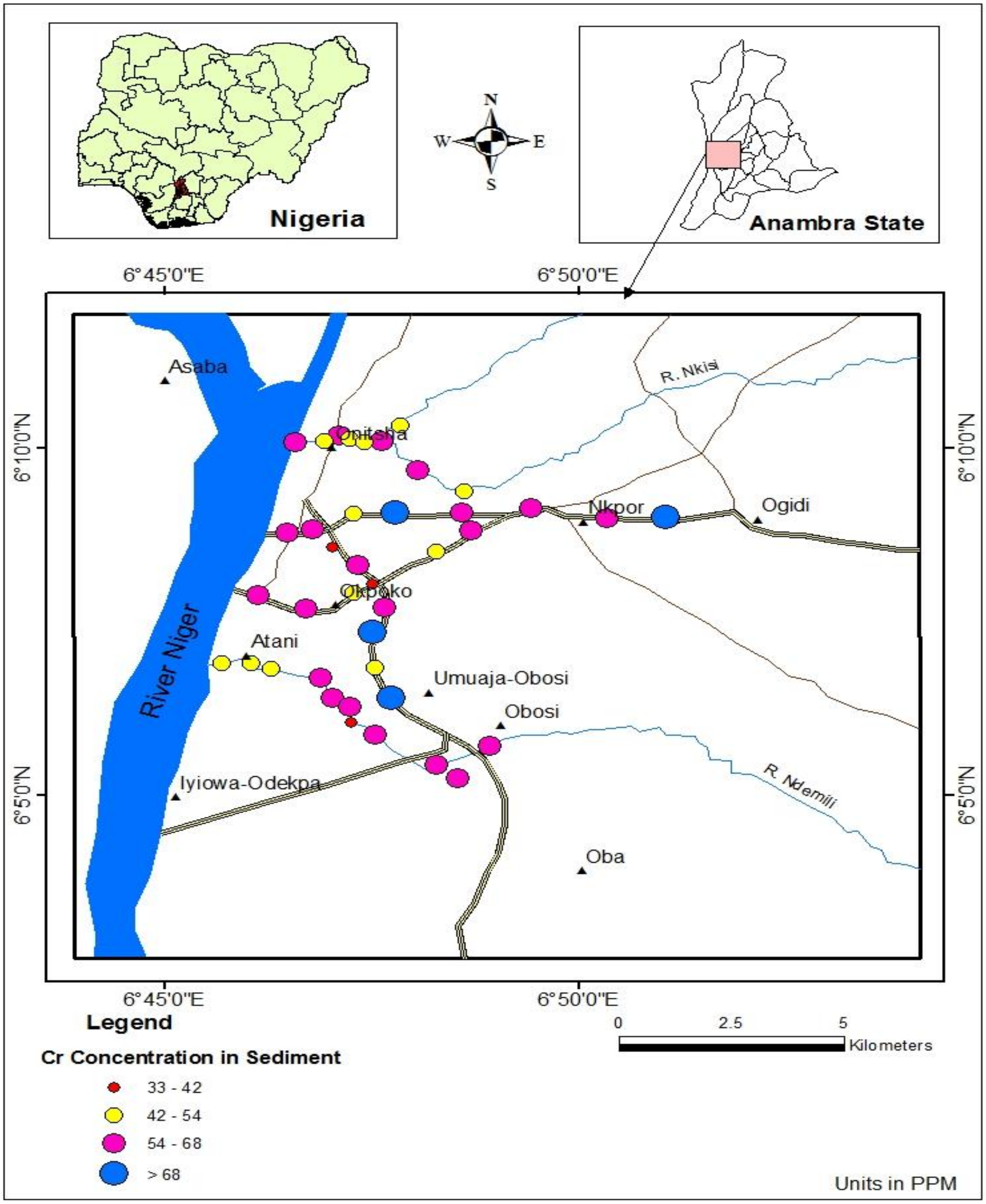


Fig. 4.43: Spatial distribution of Cr in Sediments. . (Concentration in ppm)

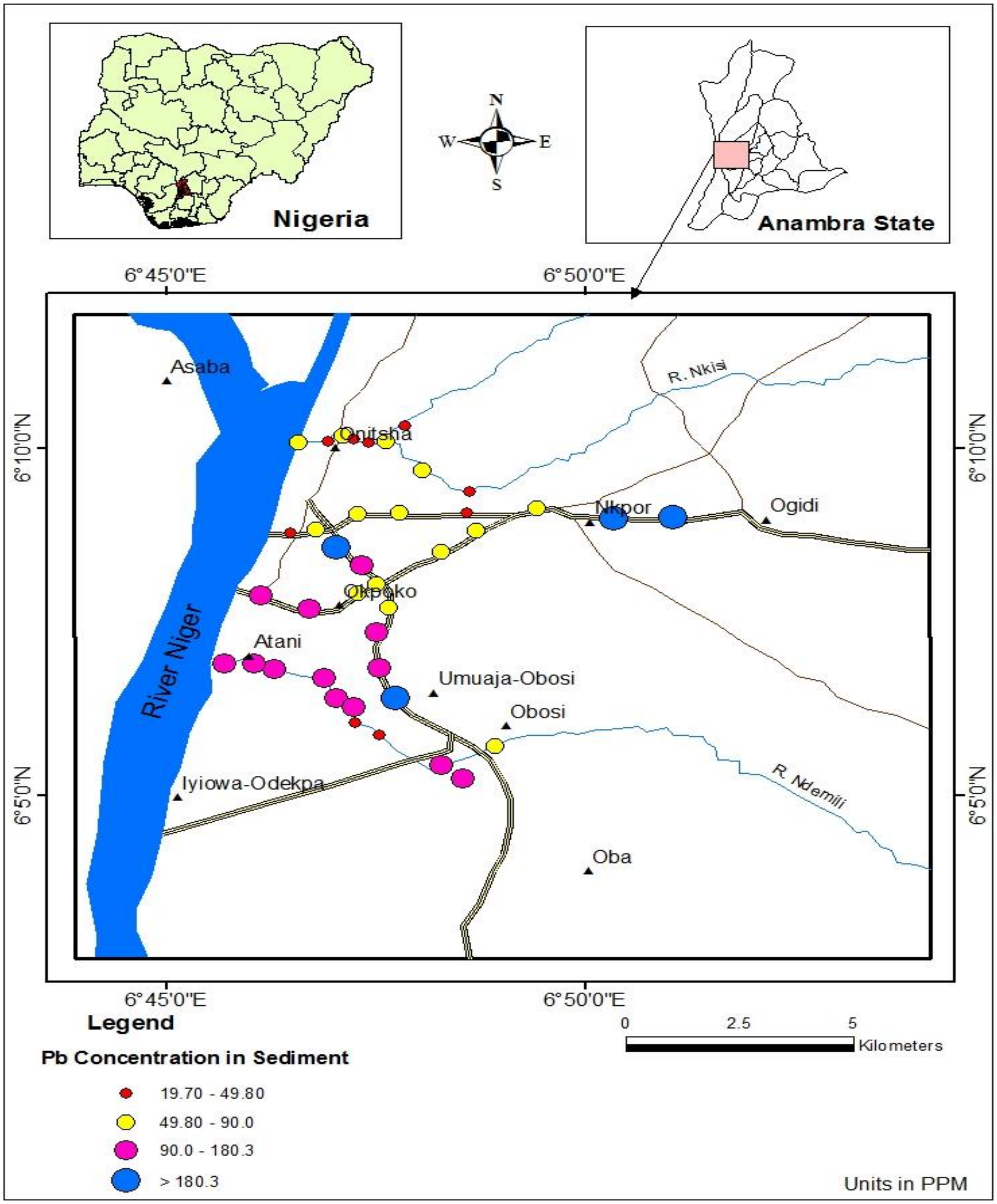


Fig. 4.44: Spatial distribution of Pb in Sediments. (Concentration in ppm)

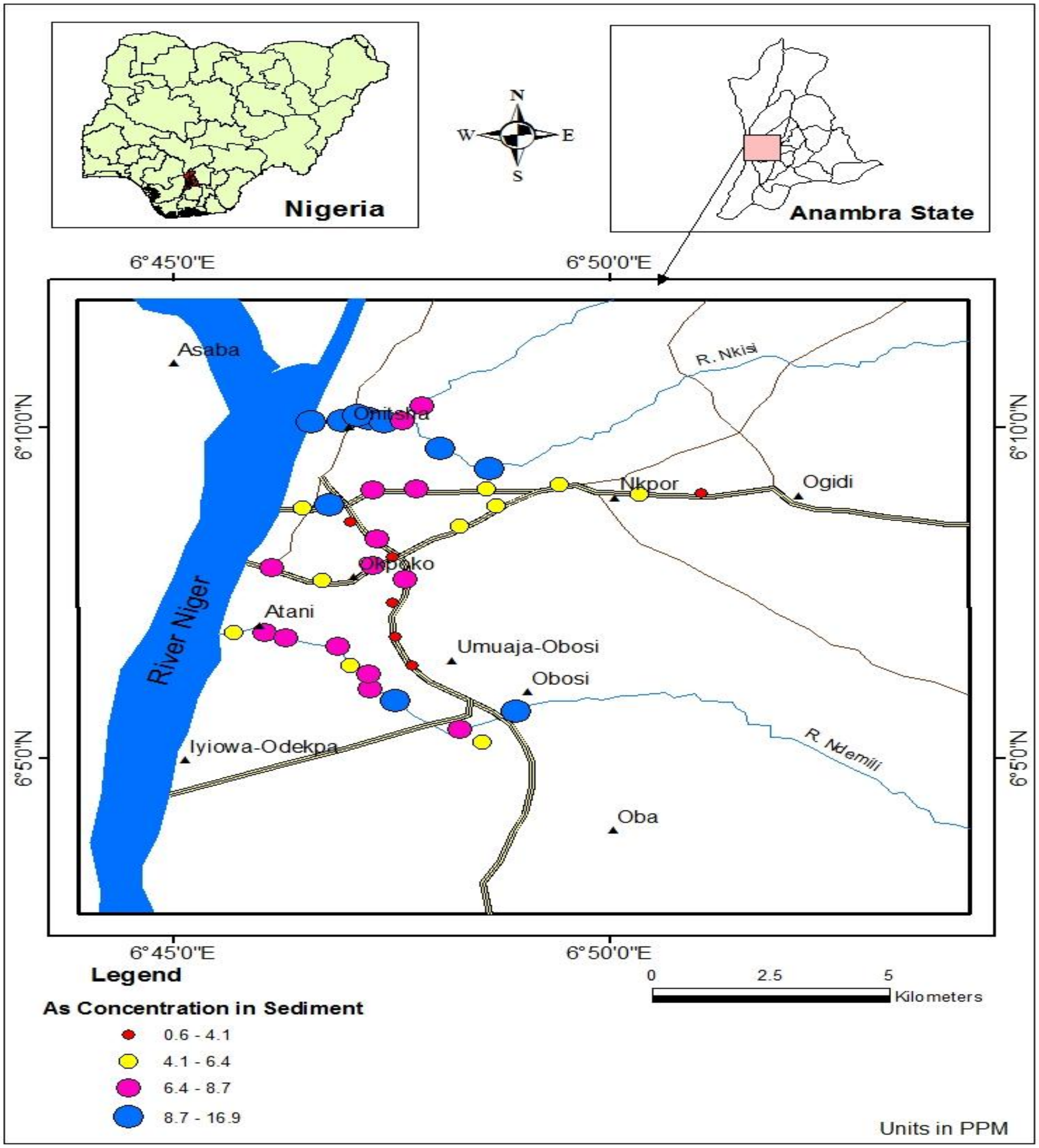


Fig. 4.45: Spatial distribution of As in Sediments. (Concentration in ppm)

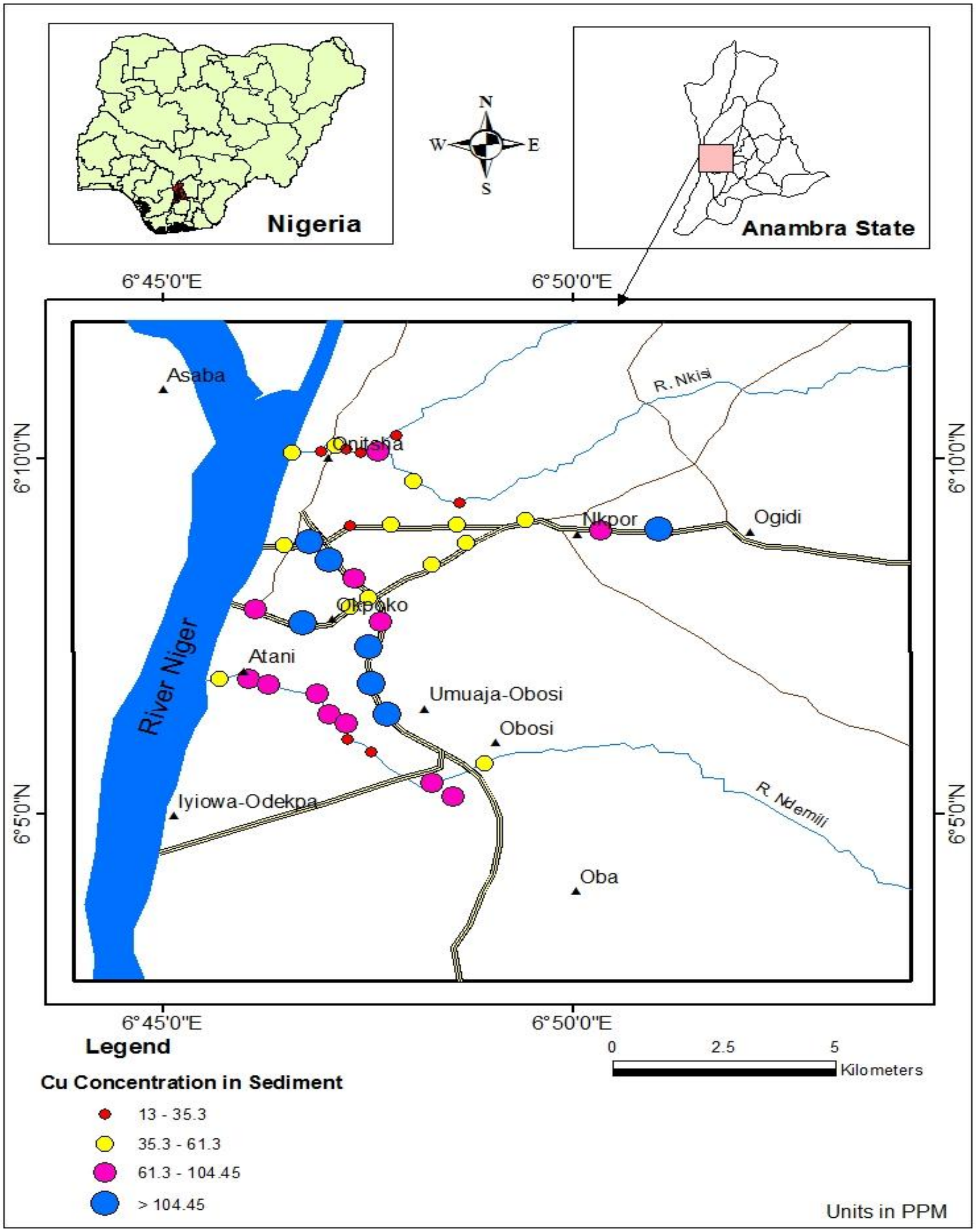


Fig. 4.46: Spatial distribution of Cu in Sediments. (Concentration in ppm)

### 4.5 Effect of land use on the distribution of trace elements

The highest concentration of Zn in the study area was found to be from the soils collected within the vicinity of FLG $3^A$ with (8395.0 ppm), with a mean concentration of 654.95 ppm standard deviation of ± 2008.57 ppm, (Table 4.5) This result showed that activities that enriched Zn content may have been used in the farm land and garden (FLG) land use in Onitsha; this include the use of fertilizer to enhance the garden, a practice that is common because the garden land are always been used continuously on annual bases. Again the land may have been enriched with Zn because of waste iron and steel materials that is been emptied in the farm area which contain corrosive protection materials. Relatively higher concentration of Zn (24.1 – 7568.1 ppm), mean (1081.6 ppm) was also found in soils collected from Mechanic and Metal works (MWM) land use. This area is such that contain used gasoline, diesel, engine oil, iron and steel materials, paint as well as other vehicular activities taking place in the area. This kind of anthropogenic activities greatly enriches Zn in the soil of the study area. comparing the mean concentration of the various land use which include; SOC (173.11 ppm), RA (422.6 ppm), MAP (2161.1 ppm), AWD (956.2 ppm), ID (482.15 ppm), NK (263.5 ppm) and RSD (502.49 ppm) and the CT, (14.9 ppm), it is found that most of the land use soils and sediments have been enriched with Zn concentration that calls for concern. fig. 4.47 is a boxplot showing the various statistical distribution of Zn in the various land use.

The highest concentration of Cr was observed in the soils collected from MWM (443.2 ppm) with mean and standard deviation of (78.3 ± 75.3) followed by RA ( 125.1 ppm), (58.5 ± 18.8).Relatively higher concentration of Cr in other land use as seen in fig. 4.54 compare to the soil collected from the control area (CT) area, i.e relatively pristine area of the metropolis. The relatively high concentration of Cr in the different land use may have been caused by anthropogenic activities such as Alloying additives in steel materials, textile and dyes materials etc, hence the samples collected within the vicinity of mechanic and metal workshops (MWM) land use recording the highest concentration of Cr.

The same pattern of metal enrichment was observed in Pb content in the soils of various land use. From the results, Pb content was found to be highest in the soils from MWM (2026.4 ppm) the mean and standard deviation in ppm of the various land use; for residential area (RA) (68.7,

± 66.2 ppm), school and office complexes (SOC) (61.01, ± 69.08), control samples (CT) (18.2, ± 6.2), farm land and gardens (FLG) (51.4, ± 84.7), market and abattoirs (MAP) (111.9, ± 97.1), active waste dump (AWD) (149.1, ± 136.8), mechanic and metal workshops (MWM) (379.1, ± 545.9), Ndemili river (ID) (106.9, ± 53.44), Nkisi river (NK) (50, ± 21.7) and Roadside drain sediments (RSD) (151.37, ± 134.07), Table 4.4, it is observed that while the soils from the control (CT) has the lowest concentration, all other land use have higher Pb concentration, indicative of differential influence of land use to the enrichment of Pb content in the soils and sediment. The enrichment of Pb in the environment may have been influenced by anthropogenic like petroleum/gasoline usage, paints, storage batteries, antiknock agent etc. hence the relatively high concentration of Pb content in the soils collected within the vicinity of MWM compare to other land use, Table 4.4, Fig. 4.53.

The mean concentrations of Mn and Ni in CT soils were far lower than the other land use areas (Table 4.4; Fig. 4.51 and Fig. 4.52), where MWM and RA recorded the highest mean concentrations of Mn (565.6, ± 417.7) for MWM, (596.5, ± 431.4) for RA. And Ni mean concentration for MWM (33.3 ± 55.7), RA (11.5, ±5.5) respectively. This suggests that the concentrations of these metals may have been enriched in the soils and sediments of the study area by activities relating to the materials used for construction of building, vehicular consumables, industrial emission, and combustion of petroleum products and the use of fungicides.

The concentration of Cd in the soils and sediments of different land use shows influence of land use activities on the presence of Cd in the soils and sediment. It was observed that the samples collected within the vicinity of mechanic and metal works (MWM) exhibited the highest concentration of Cd (10.3 ppm) followed by those from active waste dumps site (5.6 ppm), compare to the soils collected from the control areas in which the concentration of the element is below limit of detection, (Table 4.4 and Fig. 4.55). Other areas like the market and abattoirs (MAP), (2.0 ppm) the concentration of Cd is low to moderate. The areas with enriched content of Cd may have been as a result urban waste such as used electrical components, storage batteries and allows of metals and domestic burning of hydrocarbon rich materials.

The mean concentration of As in the control samples (CT) is (8.2 ppm) Table 4.4 and Fig. 4.55. The ferrogenised sandstone sample in the sedimentary profile was found to have high concentration of As, RK 1 (12.0 ppm) and RK 2 (27.0 ppm) relative to the other control samples CT 2 (3.8ppm), CT 5 (3.5 ppm) and CT 6 (0.5 ppm). The enrichment of As in the ferrogenised sandstone may have been as a result of secondary geogenic enrichment of the As in the ferogenised rock samples. The other land use also showed differential mean concentration, with MWM (5.8 ppm) showing relatively higher concentration of As compare to other land use Table 4.4 and fig. 4.54.

The mean concentration of Cu and La also vary with respect to the different land use, Table4.4, Fig 4.47 and Fig. 4.56. For La it was found that the mean concentration in the control samples was relatively high; CT (17.9 ppm mean) compare to the result in other land use, RA (16.1 ppm mean value), MAP (16.7 ppm), AWD (17.6 ppm), MWM (15.0 ppm), ID (24.5 ppm), NK (14.7 ppm) and RSD (13.89 ppm). From the result the sediment samples from Ndemili River (ID) exhibited the highest mean value, while the control samples as ealiear reported recorded high mean value. This suggests that the La in the soil may have been enriched by geogenic effect as against anthropogenic activities. For Cu, it was found that there were considerably higher mean concentration of Cu the samples collected from the vicinity of (150.4 ppm mean value), MAP (108.6 ppm mean value), SSD (86.4 ppm), ID (64.4 ppm), RA (38.1 ppm), NK (37.6 ppm) FLG (33,8 ppm) and SOC (25.6 ppm) as against the result of soil from the control area CT (7.1 ppm) mean values respectively. It shows great influence of anthropogenic effect on the relatively high concentration of Cu in most of the land use, especially in MWM and AWD areas relative to the control samples and SOC vicinity.

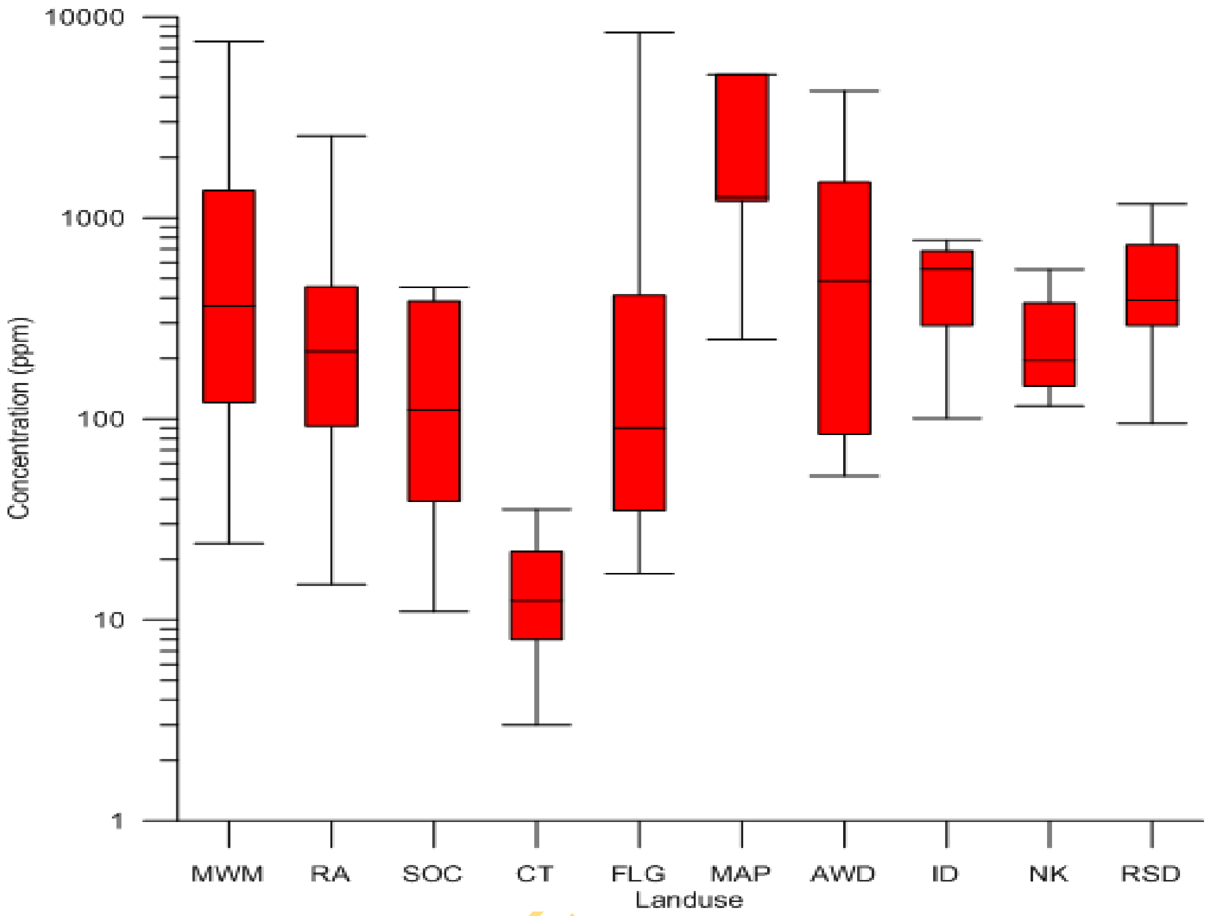


Fig. 4.47: Boxplots of the total concentrations (ppm) of Zn in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

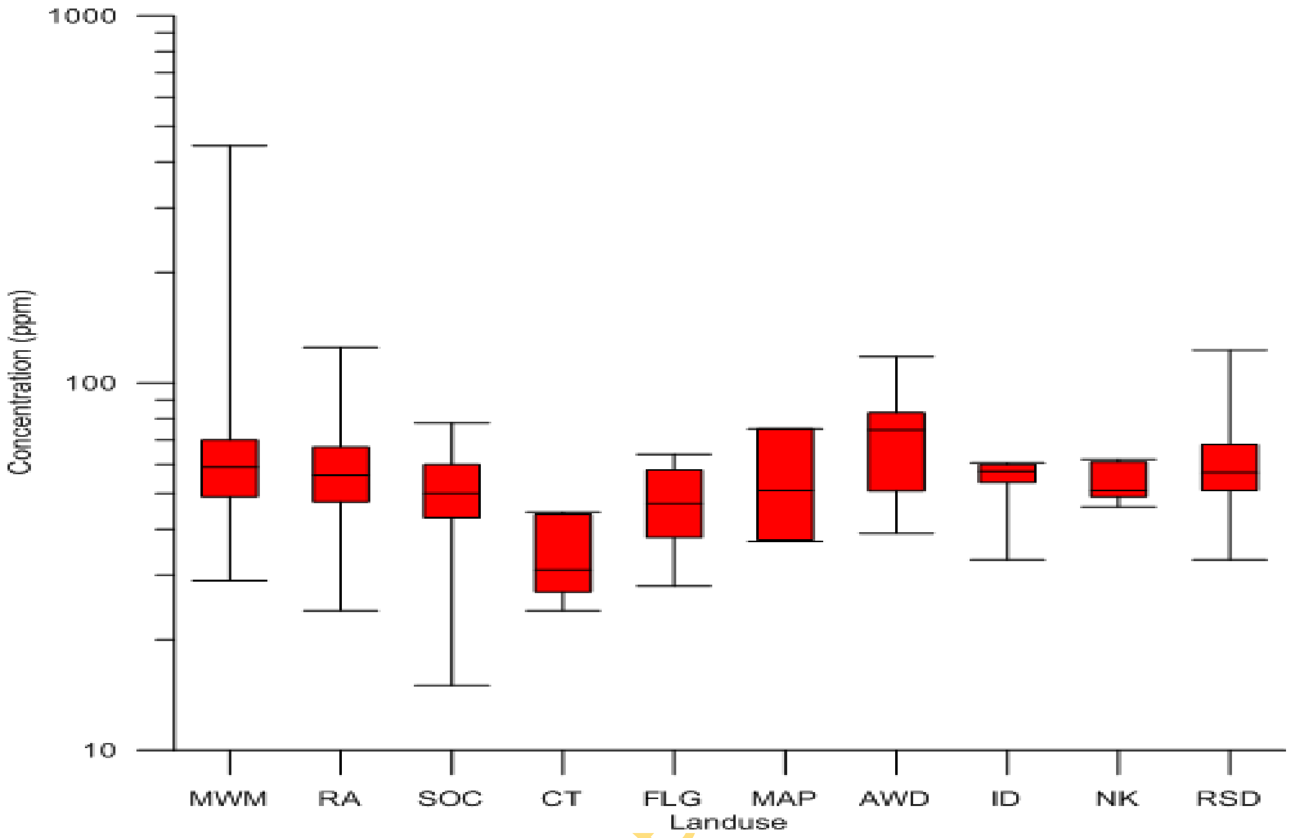


Fig. 4.48: Boxplots of the total concentrations (ppm) of Cr in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution

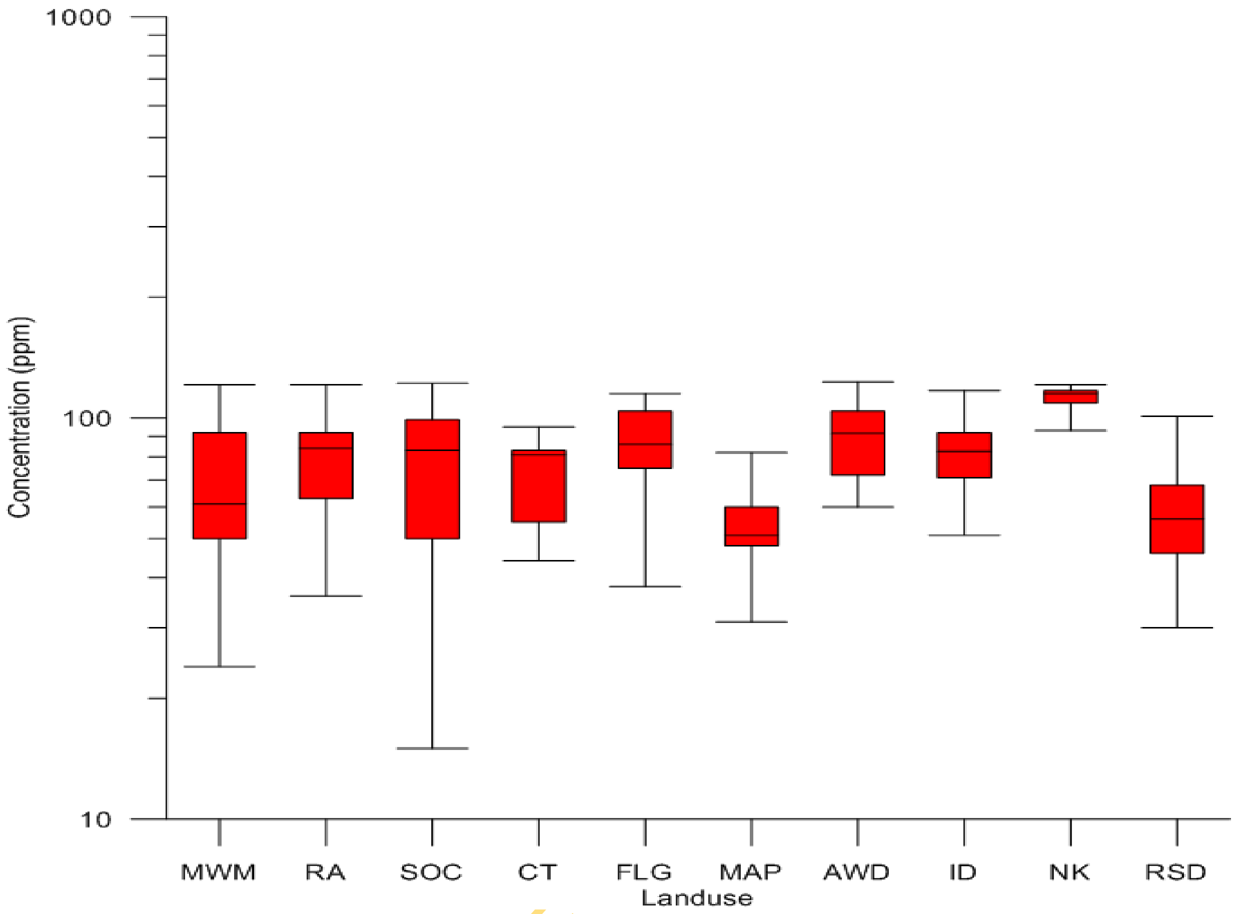


Fig4.49: Boxplots of the total concentrations (ppm) of V in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

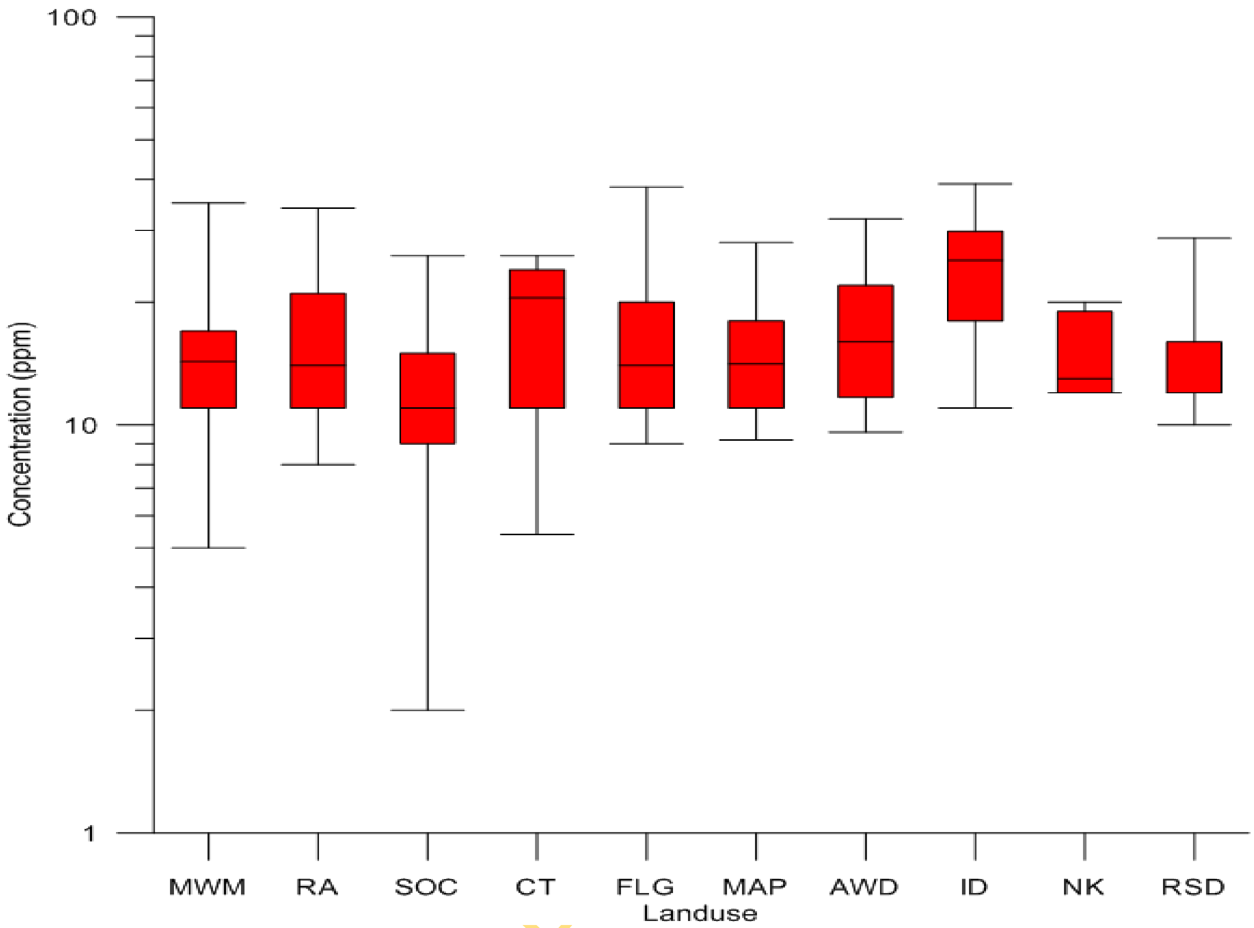


Fig. 4.50: Boxplots of the total concentrations (ppm) of La in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

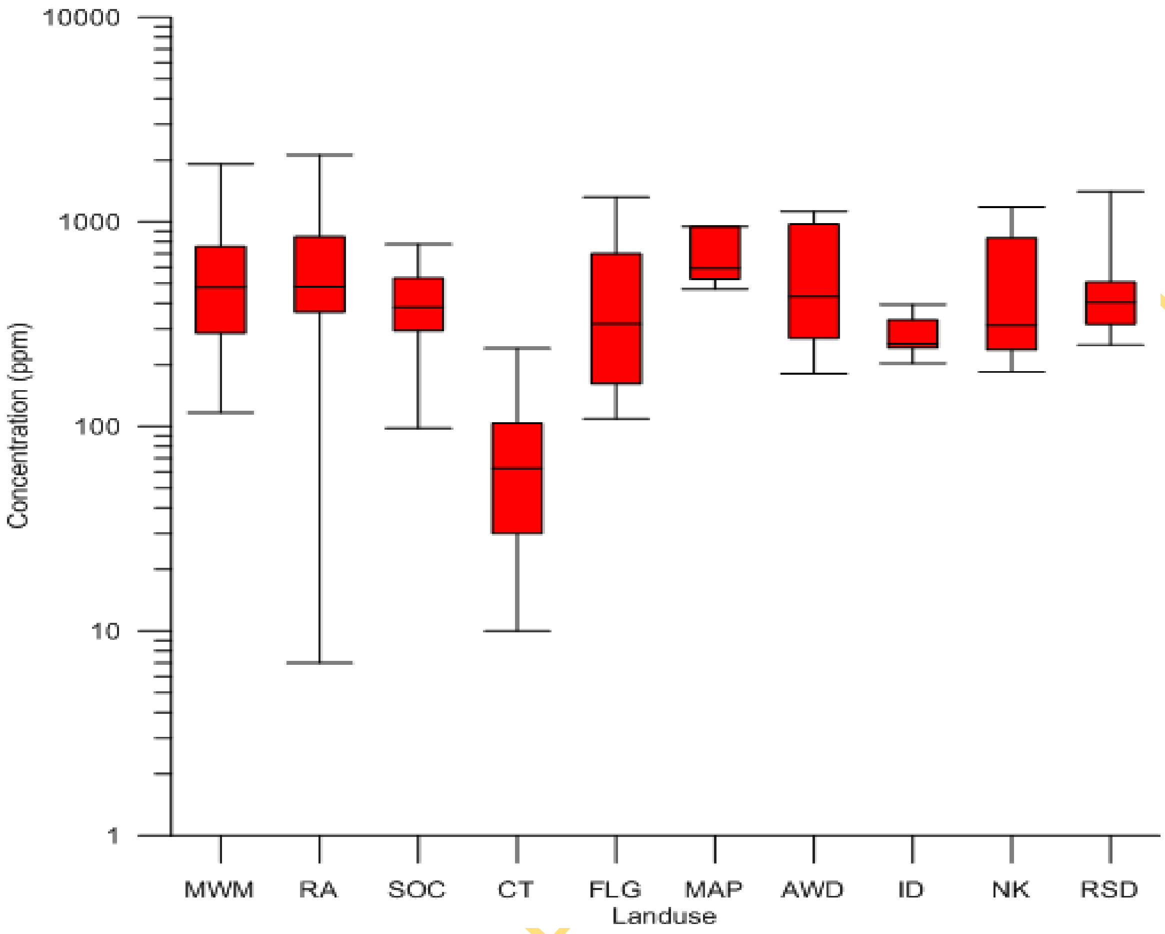


Fig4.51: Boxplots of the total concentrations (ppm) of Mn in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

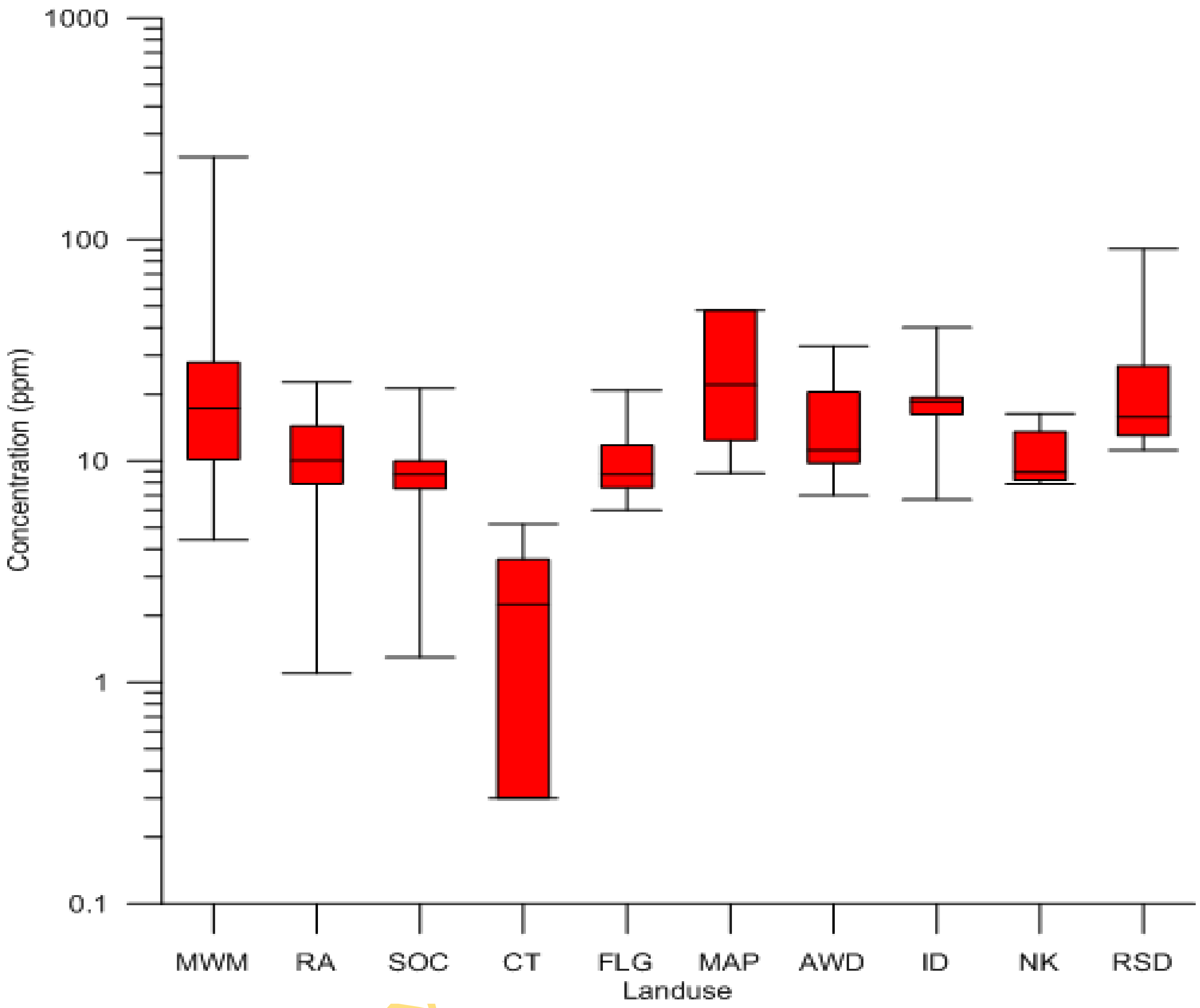


Fig. 4.52: Boxplots of the total concentrations (ppm) of Ni in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

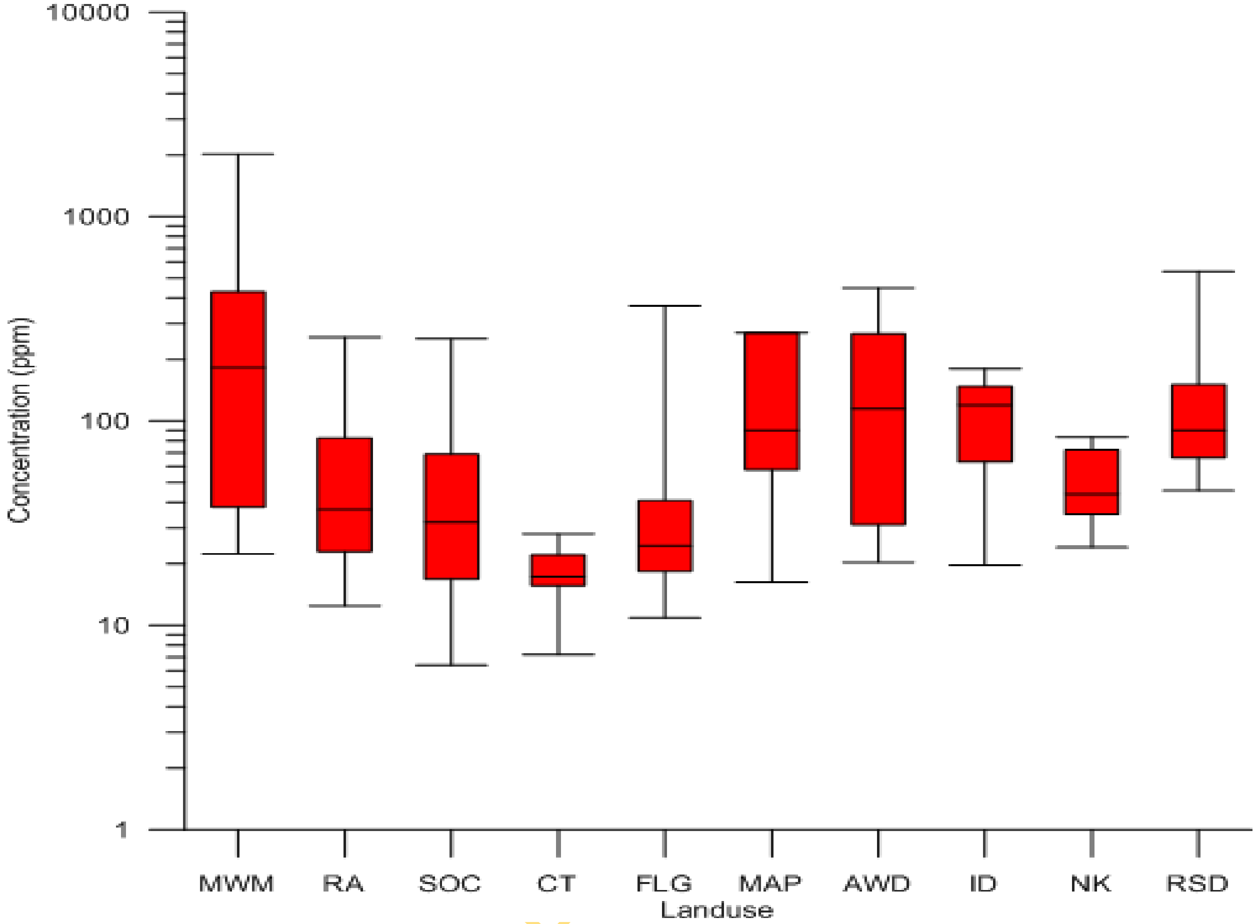


Fig. 4.53: Boxplots of the total concentrations (ppm) of Pb in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

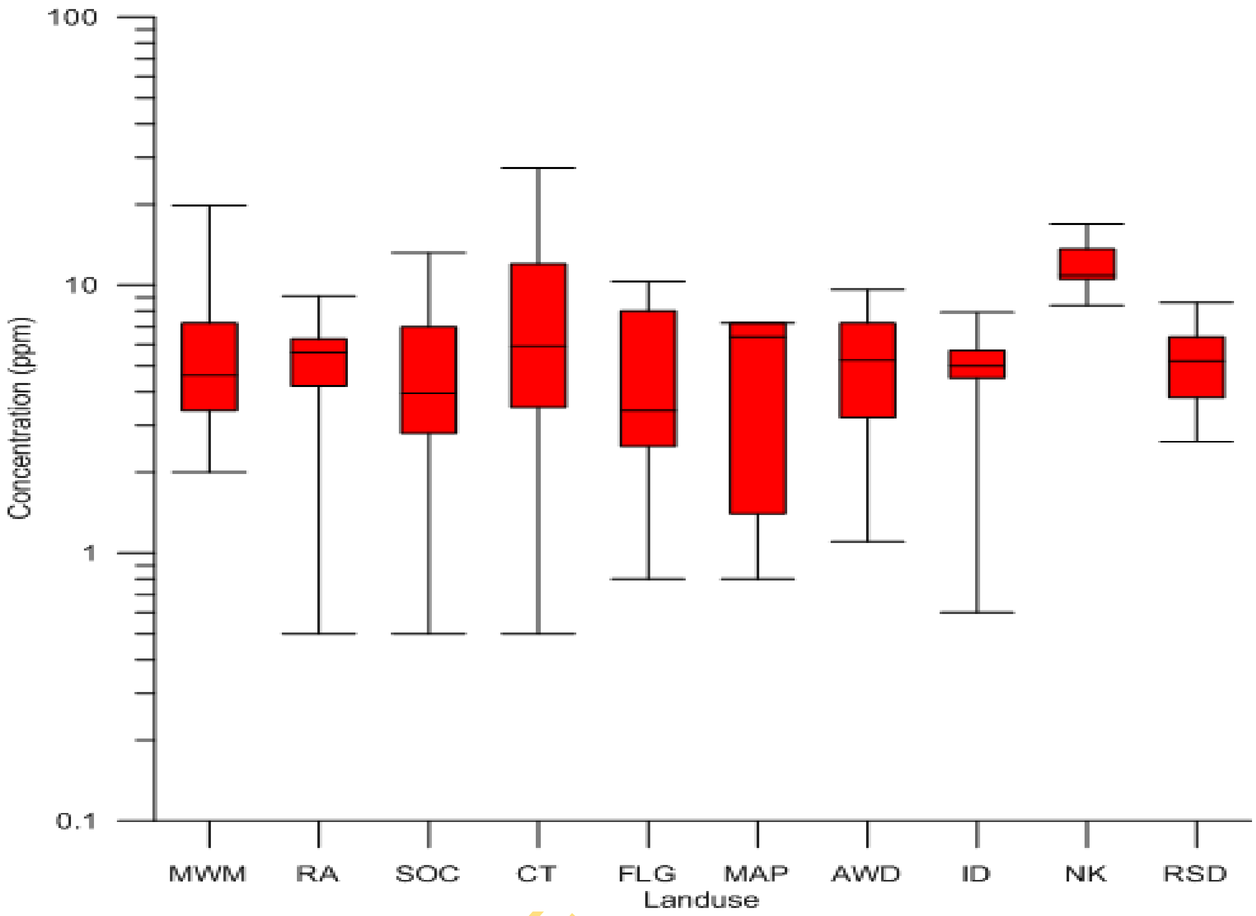


Fig. 4.54: Boxplots of the total concentrations (ppm) of As in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

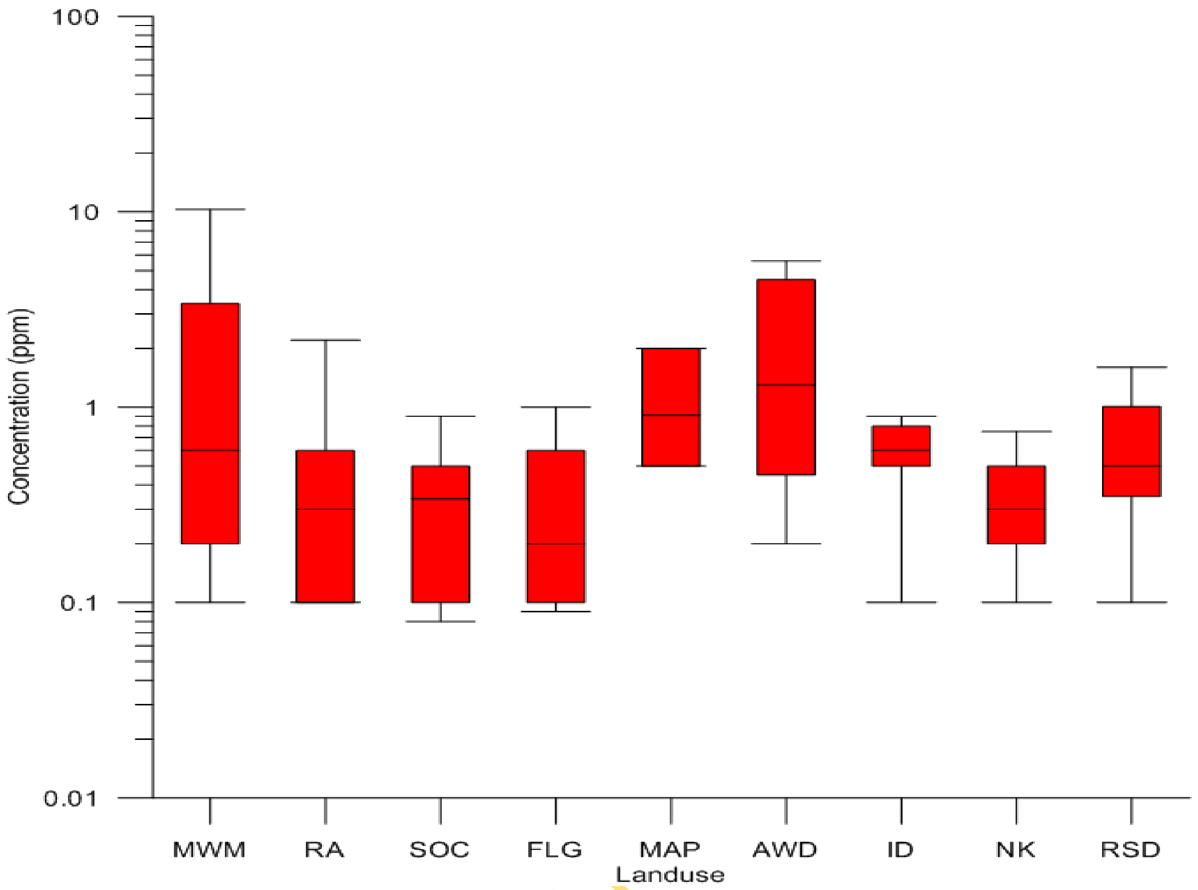


Fig. 4.55: Boxplots of the total concentrations (ppm) of Cd in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

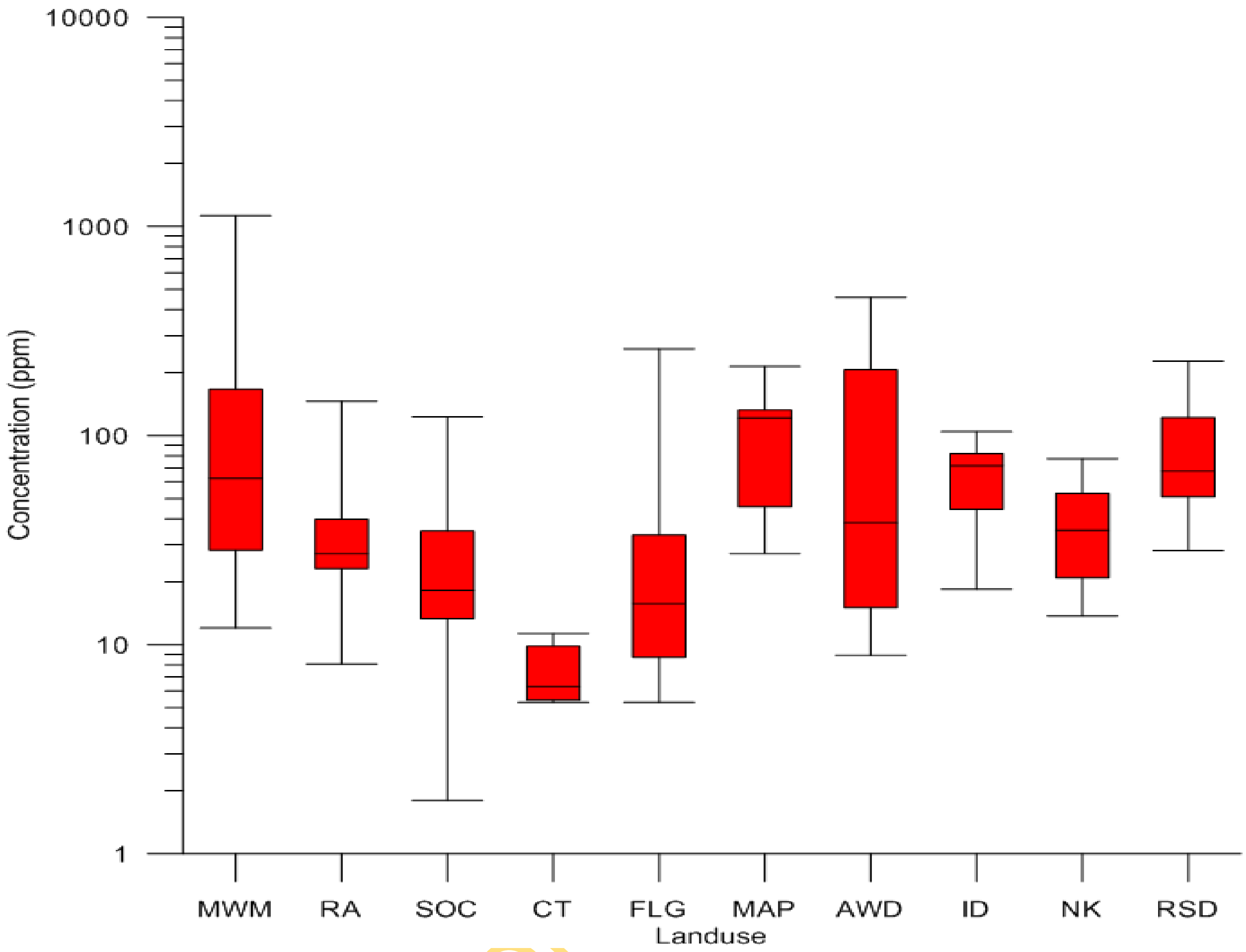


Fig. 4.56: Boxplots of the total concentrations (ppm) of Cu in different land use. The central box represent 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

## 4.6 Comparison between the Top Soils and Sub soils metal content of Onitsha Area

A comparative analyses of some selected trace element was carried out using the boxplot to evaluate the variation that exist between the soils collected at a depth of 0 – 30 cm and >30 – 100cm depth. The trace element composition in both the top soils and sub soils for Mo, Cu, Pb, Zn, Ni, Co, Mn, As, Cd, and Cr shows varying concentration of these elements from top to sub soils, (Table 4.5, and Figure 4.57). The mean concentration of Zn showed that topsoil had (847.12 ppm mean) compare to the subsoil (259.00 ppm mean) thus suggesting that the top soil is much more enriched with Zn content at the top soil relative to the sub soil. Mean content of Pb in the top soil is (167.99 ppm) and is higher than the value in the subsoils (98.66 ppm). Similar metal content characteristics were observed in almost all the element investigated, Table 4.5, Figure 4.63, which implies that the relatively high concentration of most of these elements may have been enriched by urban and industry related activities hence the wide variation between the top soil and subsoils to in some instance two to three fold higher in the top soil than the subsoil.

Table 4.5: Descriptive statistics of selected trace elements (ppm) in Top soils and Sub soils from Onitsha area

| | Top Soils (0 – 30cm) | | | | Sub Soils > 30cm – 100cm | | | |
|---|---|---|---|---|---|---|---|---|
| Elements | Min | Max | Mean | Std. Dev | Min | Max | Mean | Std. Dev |
| Mo | 0.2 | 46.88 | 2.05 | 5.2 | 0.2 | 3.1 | 1.07 | 0.48 |
| Cu | 5.3 | 1123.2 | 88.53 | 175.9 | 1.8 | 181.8 | 28.68 | 37.58 |
| Pb | 7.2 | 1730.5 | 167.99 | 292.8 | 6.4 | 2026.4 | 98.66 | 335.72 |
| Zn | 3.0 | 8395.0 | 847.12 | 1542.0 | 11.0 | 2899.0 | 259 | 543.78 |
| Ni | 0.3 | 236.6 | 19.35 | 34.84 | 1.3 | 35.0 | 9.81 | 5.53 |
| Co | 0.2 | 136.5 | 8.17 | 16.38 | 0.6 | 22.0 | 4.38 | 4.15 |
| Mn | 7.0 | 2127.0 | 514.46 | 392.0 | 98.0 | 1148.0 | 451.78 | 295.15 |
| As | 0.5 | 27.3 | 5.61 | 4.01 | 0.8 | 13.2.0 | 5.24 | 2.55 |
| Cd | 0.08 | 10.3 | 1.4 | 2.17 | 0.1 | 2.4 | 0.42 | 0.61 |
| Cr | 24 | 443.2 | 62.16 | 48.62 | 15.0 | 83.0 | 53.22 | 15.0 |

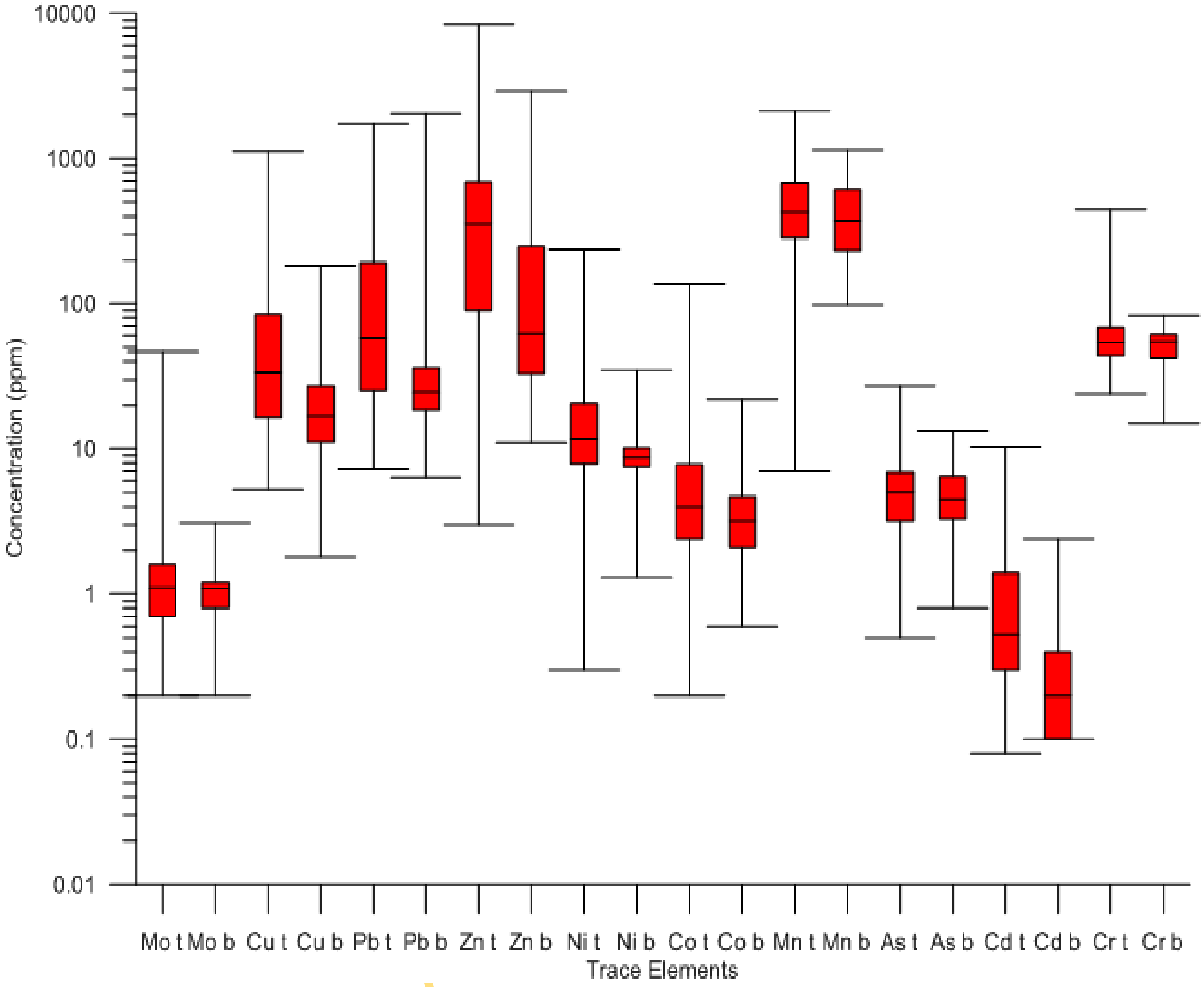


Fig. 4.57: Boxplots of concentrations (ppm) of selected trace element in top soils (0 – 30cm) and subsoils (> 30 – 100cm). The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution. Please note that subscript‘t’ to the elements represent topsoil, while subscript ‘b’ to the elements represents subsoil.

## 4.7 **Comparison of the mean concentration of potentially harmful elements in soils in selected cities of the world with this study**

The mean concentrations of some potentially harmful elements in soils of some urban cities in the world and the study are presented in Table 4.6. From the data in Table 4.6, it will be observed that, there remarkeblyhigher concentration of some of the elements in the study area (Onitsha) compare with most of these cities to an extent thatraisesconcern. For example, the mean concentration of Zn in Onitsha (present area of study) is higher than it is in all the referenced cities. Similar trend is exhibited by Pb. Except Benin City, the mean Pb concentration in the study area is higher than all other cities (Table 4,6). The mean concentration of As in this study is higher than other cities refrenced except that of Idrija (Slovenia) were that of Idrija is more than 4 fold higher than that this study. Similar trend is being observed in Cr were the mean concentration of Cr in the study area is more than most of the cities under comparison except Ibadan (Table 4.6) were the mean concentration in the Ibadan soil is alittle higher than this study both with very close magin of concentration. The same patterns of consideration variation in concentration are found the other elements, Table 4.6.

Table 4.6: Comparison of mean concentration of selected potentially harmful elements in soils of some urban areas of the world with this study area. (All values are in ppm)

| City | As | Cd | Co | Cr | Cu | Mn | Mo | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Idrija[a] | 20.2 | 0.6 | 11.6 | 24.4 | 31.5 |  | 1.4 | 19.6 | 49.4 | 120 |
| Berlin[b] | 3.9 | 0.35 | 5 | 25.1 | 31.2 |  |  | 7.7 | 76.6 | 129 |
| Ibadan[c] | 3.9 | 8.4 |  | 64.4 | 46.8 | 1097 |  | 20.2 | 95.1 | 228.6 |
| Norway[d] | 3.0 | 0.24 |  | 73 | 42 |  |  | 48 | 52 | 151 |
| Murcia[e] |  | 0.13 |  | 16.3 | 8.9 | 135 |  | 11.1 | 21.9 | 16.6 |
| Benin City[f] | 1.6 | 3.01 |  | 45.26 | 119.74 | 425.29 |  | 13.71 | 232.31 | 533.1 |
| Kowloo[g] |  | 0.62 | 3.33 | 23.1 | 23.3 |  |  | 12.4 | 94.6 | 125 |
| Onitsha soil | 5.61 | 1.4 | 8.17 | 62.16 | 88.53 | 514.46 | 2.05 | 19.35 | 167.99 | 847.12 |

[a] Bavec, et al., 2015 [d] Andersson, et al., 2010 [c] Odewande and Abimbola (2008)

[e] Acosta, et. al., 2011 [f] Olatunji et al., 2014 [g] Lee., et al., 2006

## 4.8 Comparison of the mean concentration of sediments of selected cities in the world with this study.

Similarly, Table 4.7 shows the mean concentration of some potentially harmful elements in urban cities of the world with this study. From the results, Mean concentration of As the two rivers and the roadside drian sediment studied is higher than the mean value reported by Olatunji and Abimbola, 2010 in the lagos lagoon. The mean concentration of Cd in the study area is lower than most of the cities referenced except for the Lagos lagoon but with close level of concentration, Table 4.7. the mean lead (Pb) concentration in the study area is similar to most of the cities referenced for comparison except cities like Seoul and Uijeongbu City sediments were their Pb mean concentration is significantly higher than the study area sediments to between 2 to 3 folds. However, the results of Pb in the area is of concern.

Zn mean concentration in this study is found to be lower than cities like Seoul and Kottuli (Indian) were the mean Zn concentration is 4 to 5 fold higher than the results in the three areas of this study. But significantly higher than most other cities sediments as referenced Table 4.7. similarlar variation in mean concentration are found in the other elements Table 4.7, were influence of human population, urbanization and industrialization plays significant role in the relative variation of the enrichment of these elements.

Table 4.7: Comparison of mean concentration of selected potentially harmful elements in sediments of some urban areas of the world with this study area.

| City | As | Cd | Co | Cr | Cu | Mn | Mo | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| [a]Seoul City | - | 4.3 | - | 182.1 | 445.6 | - | - | 89.6 | 214.3 | 2665 |
| [b]Uijeongbu City | - | 1.2 | - | 41 | 128 | - | - | 29 | 534 | 334 |
| [c]Birmingham | - | 1.62 | - |  | 466.9 |  |  | 41.1 | 48 | 534 |
| [d]Lagos Lagoon | 2.99 | 0.27 | 9.52 | 31.52 | 36.04 | 494.98 | - | 12.66 | 20.27 | 72.33 |
| [e]Kottuli (Indian) | - | - | - | 1.71 | 492.39 | 127.8 | - | 2.78 | 43.46 | 2848 |
| [f]Aqaba City | - | 2.5 | 18.1 | 36.2 | 53 | 96.5 | - | 90.5 | 206 | 153 |
| [g]Jordan | - | 1.87 | 32.4 | 29.2 | 139.4 |  | - | 66 | 270.5 | 350.7 |
| [h]Calcuta | - | 3.12 | 15.6 | 54 | 44 |  | - | 42 | 536 | 159 |
| NdeMilli Rv. | 5.02 | 0.57 | 7.19 | 54.62 | 64.42 | 282.2 | 1.22 | 18.73 | 106.95 | 482.15 |
| Nkisi Rv. | 11.4 | 0.3 | 3.9 | 53.6 | 37.6 | 443.6 | 1.4 | 10.7 | 50 | 263.5 |
| RSD* | 5.29 | 0.65 | 6.73 | 61.38 | 86.44 | 451.38 | 2.34 | 23.65 | 151.37 | 502.49 |

[a] Lee et al., 2005

[b] Chon et al., 1998

[c] Charlesworth et al., 2003

[d] Olatunji and Abimbola, 2010

[e] Harikumar and Jisha, (2010)

[f] Al-Khashman (2007),

[g] Al-Mumani, 2009

[h] Chatterjee and Banerjee (1999)

RSD* Roadside drain Sediment

### 4.9 Interelemental Relationship for soils and sediments

The determined trace elements results for both the top soils and sub soils were further subjected to statistical interpolation to ascertain the relationship between the various elements. Inter element relationship; Pearson Correlation (PC) and Principal Component Analysis (PCA) were carried out using Origin, Grapher 8 and SPSS computer packages. For the elemental relationship, there is a weak coefficient of determination (R) between Ni and Zn (R = 0.209) and between Zn and Cu (R = 0.3368), while there is strong correlation between Cu and Mo (R = 0.6015), Cr Vs Ni (R = 0.6705) and Ni and Cu (R = 0.9099), (Fig. 4.58a – Fig. 4.58e). From the result, relatively fair to strong affinity level of the elements were observed, it could be suggested that these elements were influenced by analogous sources of enrichment across the top and sub soils studied. The matrix correlation coefficient for the data is presented in (Table 4.8) There is wide variation in the correlation coefficient (r) between element pairs. For example, the r values ranged from −0.01 between Hg and Cr to 0.95 between Ni and Cu. Fairly strong to very strong positive correlations occurred among Cu, Zn, Ni, Cd, Pb, V, Mn, Mo, Cr, Sc, Co and Ga. Considerably high correlations were found between Ni and Cu (r = 0.95), Cr and Mo (r = 0.93), Ni and Mo (r = 0.83), Cr and Ni (r = 0.82), and Sc and V (r = 0.83). Other elements also showed fair to strong correlation as summarized in (Table 4.1.6).

Similarly, the result obtained from the two PCA and three component plot, (Table 4.9, Table 4.10 and Figure 4.59) further clarified elemental association in four and three component factors of association, respectively. Factor analyses revealed four groups of trace elements, (Table 4.9); the first group is made up of Mo, Cu, Pb, Zn, Mn, Cd, As and Cr accounting for 37.0% total variance of eigen value. These elements might have been enriched by same sources, such as from domestic waste, leaded gasoline, industrial emission, waste batteries and vehicular wastes. Though some of the elements like Mo and Cd are relatively low in some locations in concentration, their presence nevertheless as earlier stated, could be tied to close or similar sources with the other elements. The second group is made up of V, Sc and Ga, accounting for approximately 17.8% of the total variance. These elements might have been enriched in the soil by activities such as vehicular waste, Iron and Steel work as well as tool making. The third group consists of Zn and Co, which accounted for 9.6% of the total variance. These two elements might have been enriched, by activities relating to soil leachate from automobile activities and other urban consumables like additives in chemical products, gasoline usage, metal smelting and metal plating. The fourth group is La and Hg, with a total eugen value of 8.1%. This occurrence may have been as a result of smelting of non ferrous materials, electronics waste, incinerator from the urbanized area and other vehicle washout. Table 4.10; shows summary of factor Analyses of the trace elements in the soils from the study area.

Further application of the three component plot of principal component analyses (PCA) enabled us to find out further that in similar ways, the same trace elements clustered close to each other as seen in the factor analyses earlier analysed i.e. those elements that are likely to be from analogous sources cluster together as seen in Fig. 4.59. For the three component loading, Mo, Cu, Pb, Ni, Mn, Cd, Cr and As loaded close to each other which suggest similar source of enrichment in the soil. While V, Sc and Ga loaded a bit far away from other element, which suggest in similar term that these elements may have been enriched by same source. Zn and Co loaded close to each other and La and Hg also exhibit close association. These close associations also suggested that these elements may have same source of enrichment in the soil.

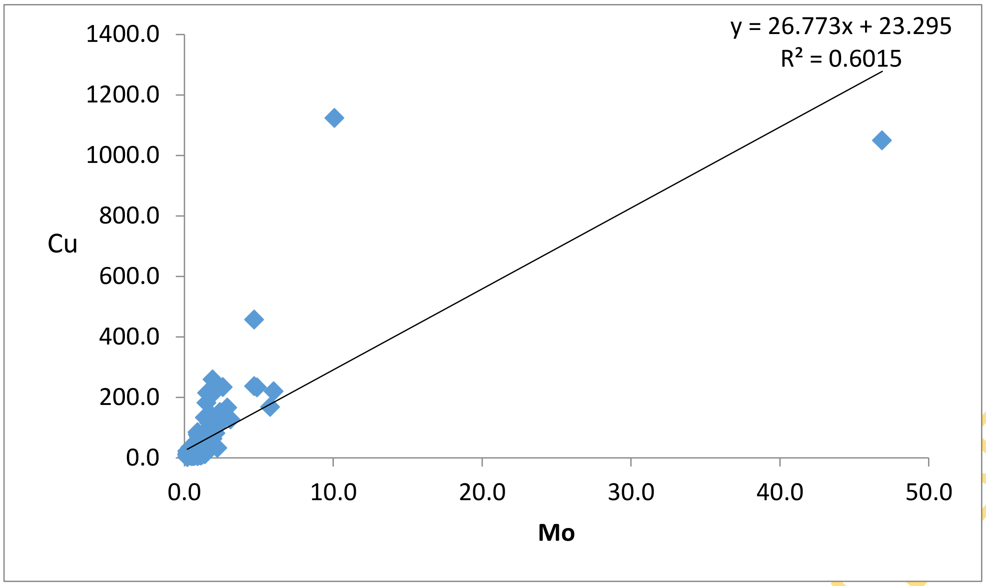


Fig. 4.58a: Bivariate plot of Cu and Mo in soils of the study area

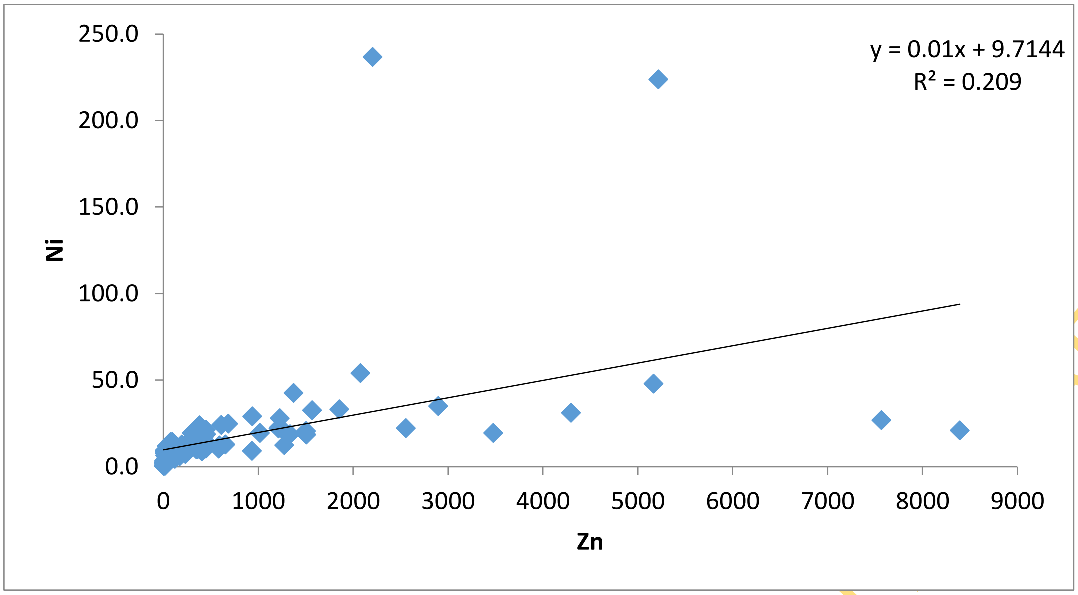


Fig. 4.58b: Bivariate plot of Ni and Zn in soils of the study area

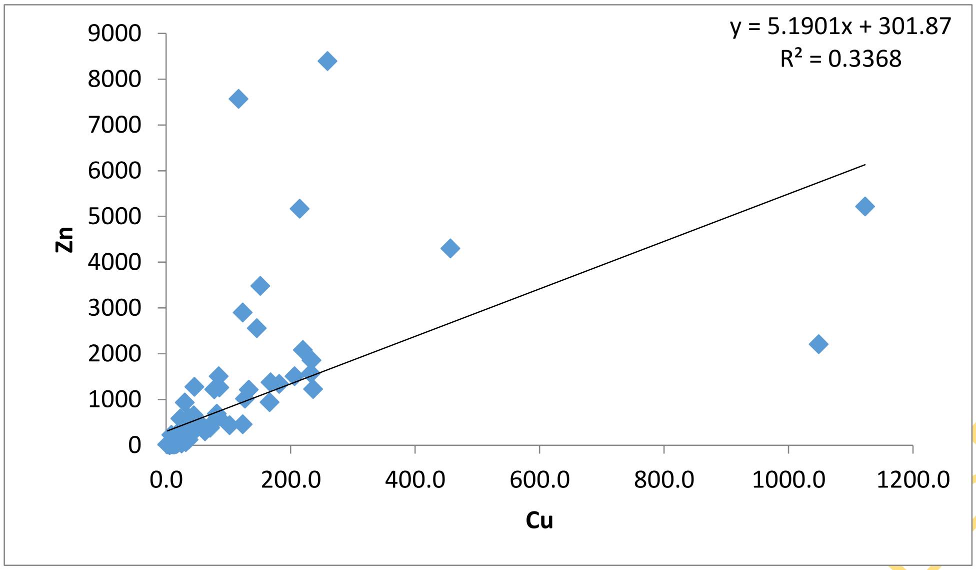


Fig. 4.58c: Bivariate plot of Zn and Cu in soils of the study area.

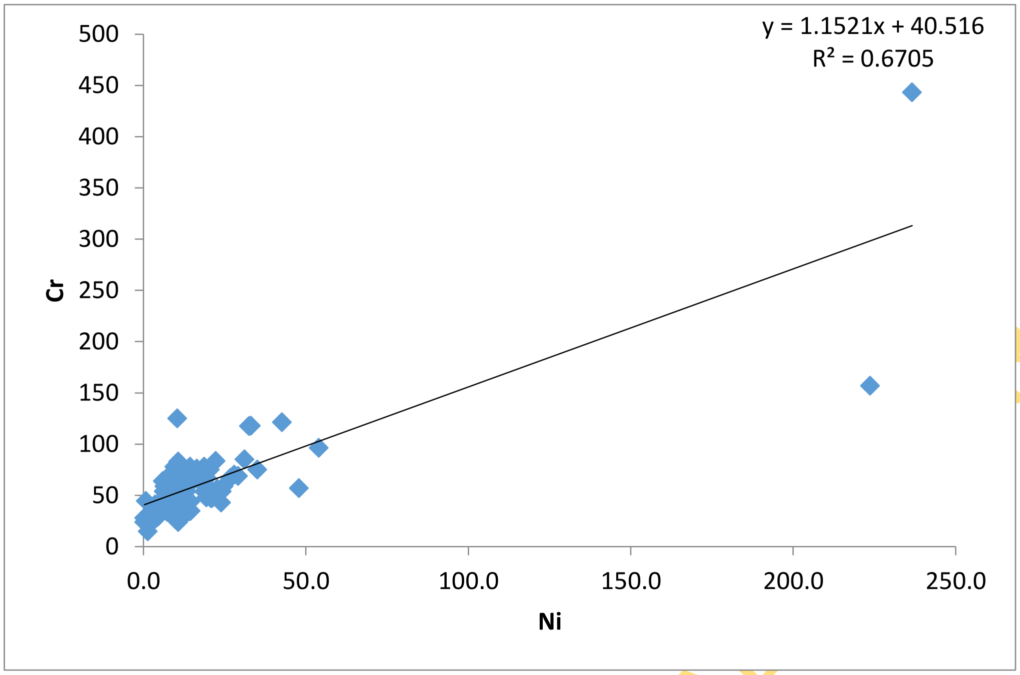


Fig. 4.58d: Bivariate plot of Cr and Ni in soils of the study area.

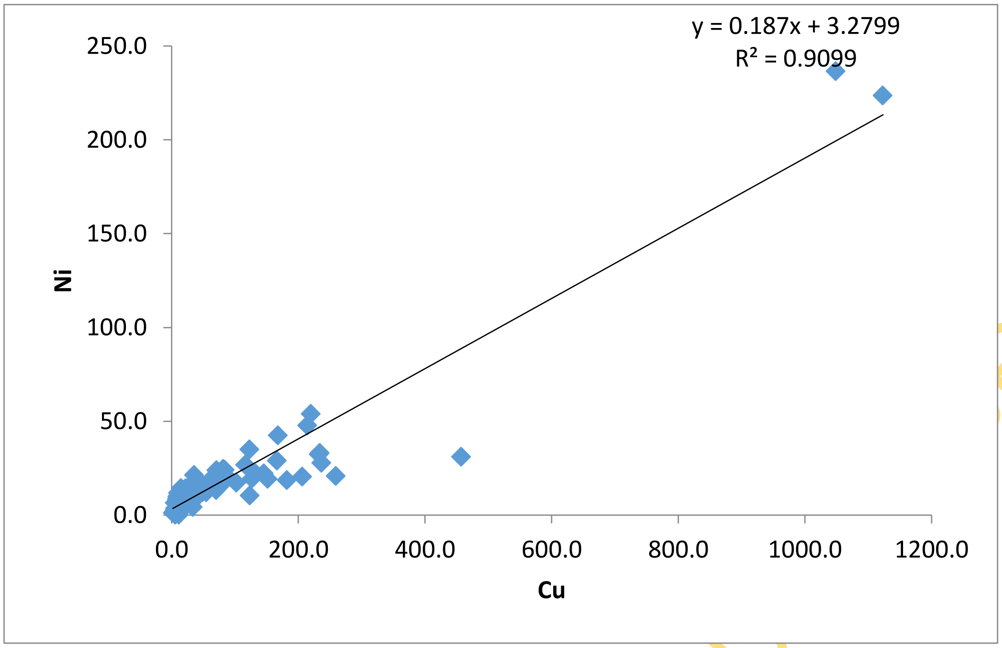


Fig. 4.58e: Bivariate plot of Ni and Cu in soils of the study area

Table 4.8: Correlation coefficients of elements in the soils of the study area.

| | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mo | 1 | | | | | | | | | | | | | | |
| Cu | **0.78** | 1 | | | | | | | | | | | | | |
| Pb | 0.28 | 0.47 | 1 | | | | | | | | | | | | |
| Zn | 0.25 | **0.58** | 0.31 | 1 | | | | | | | | | | | |
| Ni | **0.83** | **0.95** | 0.4 | 0.46 | 1 | | | | | | | | | | |
| Co | 0.16 | 0.39 | 0.13 | **0.75** | 0.26 | 1 | | | | | | | | | |
| Mn | 0.44 | **0.56** | 0.34 | 0.35 | **0.55** | 0.23 | 1 | | | | | | | | |
| As | 0.43 | 0.44 | 0.18 | 0.24 | 0.41 | 0.18 | 0.1 | 1 | | | | | | | |
| Cd | 0.42 | **0.72** | **0.56** | **0.68** | **0.65** | 0.24 | 0.46 | 0.37 | 1 | | | | | | |
| V | -0.11 | -0.2 | -0.18 | -0.23 | -0.19 | -0.14 | -0.08 | 0.1 | -0.26 | 1 | | | | | |
| La | -0.13 | -0.09 | -0.08 | -0.1 | -0.1 | -0.02 | 0 | -0.25 | -0.08 | -0.06 | 1 | | | | |
| Cr | **0.93** | **0.77** | 0.34 | 0.27 | **0.82** | 0.14 | **0.5** | 0.43 | 0.48 | 0.04 | -0.19 | 1 | | | |
| Hg | -0.02 | 0 | 0.02 | 0.04 | 0.02 | 0 | 0.1 | 0.01 | 0.04 | -0.05 | 0.11 | -0.01 | 1 | | |
| Sc | -0.13 | -0.25 | -0.22 | -0.29 | -0.22 | -0.18 | -0.14 | 0.02 | -0.33 | **0.83** | 0.22 | -0.05 | -0.18 | 1 | |
| Ga | -0.11 | -0.19 | -0.17 | -0.18 | -0.18 | -0.13 | 0.06 | -0.06 | -0.23 | 0.9 | -0.02 | 0.05 | 0.1 | **0.77** | 1 |

Table 4.9: Principal Component Analyses of the Trace Elements in the study area

| Element | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| Mo | **0.79** | 0.28 | -0.39 | 0.03 |
| Cu | **0.94** | 0.13 | -0.02 | 0.04 |
| Pb | 0.56 | -0.06 | 0.03 | 0.13 |
| Zn | 0.67 | -0.15 | 0.65 | -0.16 |
| Ni | 0.91 | 0.17 | -0.18 | 0.09 |
| Co | 0.45 | -0.13 | 0.71 | -0.24 |
| Mn | 0.62 | 0.17 | 0.10 | 0.37 |
| As | 0.46 | 0.36 | -0.07 | -0.40 |
| Cd | 0.80 | -0.05 | 0.20 | 0.09 |
| V | -0.33 | 0.89 | 0.18 | -0.08 |
| La | -0.17 | -0.07 | 0.18 | 0.71 |
| Cr | 0.79 | 0.41 | -0.32 | 0.03 |
| Hg | 0.04 | -0.06 | 0.13 | 0.52 |
| Sc | -0.40 | 0.81 | 0.15 | 0.06 |
| Ga | -0.30 | 0.85 | 0.25 | 0.12 |
| Total | 5.5 | 2.7 | 1.4 | 1.2 |
| % of Variance | 37.0 | 17.8 | 9.6 | 8.1 |
| Cumulative % | 37.0 | 54.8 | 64.4 | 72.4 |

Table 4.10: Summary of Elemental Associations of the four-factor model and the Eigen value in (%).

| Factor | Elemental Association | Eigenvalues % |
|---|---|---|
| R-1 | Mo-Cu-Pb-Zn-Ni-Mn-Cd-Cr- As | 37.0 |
| R-2 | V-Sc-Ga | 17.8 |
| R-3 | Zn-Co | 9.6 |
| R-4 | La-Hg | 8.1 |

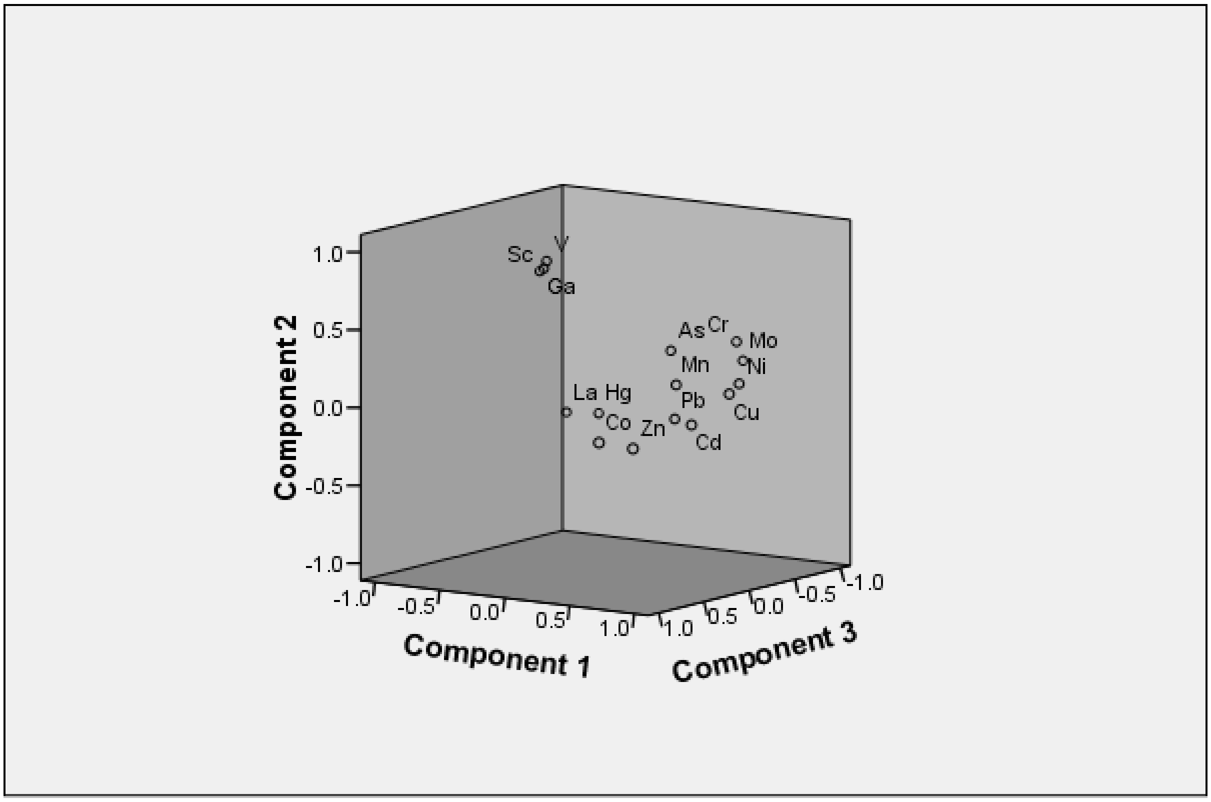


Fig. 4.59: Plot of the three principle component for the trace elements in soils of the study area

Similarly, the results of trace elements determined from the various sediments samples in the study area, which include the Ndemilli river (ID), Nkisi river (NK) and Roadside drian sediments (RSD) were further subjected to statistical interpolation as it was done for the soils, to ascertain the relationship between the various elements. Inter element relationship; Pearson Correlation (PC) and Principal Component Analysis (PCA) were carried out using Origin, Grapher 8 and SPSS software packages. For the elemental relationship, there is a fair coefficient of determination (R) between Zn and Pb (R = 0.232) and between Pb and Cu (R = 0.3052), while there is strong correlation between Cu and Mo (R = 0.5338) and Ni Vs Cr (R = 0.608), (Figure 4.60a – Figure 4.60d). As earlier suggested for the soils, the results of the inter elemental relationship for sediments from their relatively fair to stronge affinity level of the elements, it could be said that these elements were influenced by analogous sources of enrichment across the sediments of the Ndemilli river, Nkisi river and road deposited sediments studied. The correlation matrix for the sediments data obtained (Table 4.11) shows a wide variation in the correlation coefficient (r) between element pairs. For example, the r values ranged from −0.02 between Hg and As to 0.96 between Sc and V. Fairly strong to very strong positive correlations occurred among As, Cu, Zn, Cd, Pb, V, Mn, Mo, Cr, Sc, Co and Ga. Considerably high correlations were found between Sc and V (r = 0.96), Ga and Sc (r = 0.94), Sc and Th (r = 0.91), Ni and Mo (r = 0.90), V and Th (r = 0.88), Cd and Cu (r = 0.83) and Cr and Ni (r = 0.78). Other elements also showed fair to strong correlation as summarized in (Table 4.11).

The result obtained from the two PCA and three component plot, (Table 4.11, Table 4.12 and Figure 4.61) for the sediments, further clarified elemental association in three component factors of association, respectively. Factor analyses revealed three groups of trace elements, (Table 4.12); the first group is made up of Mo, Cu, Pb, Zn, Ni, Co, Cd, Cr and Hg accounting for 47.39% total variance of eigen value. These elements might have been enriched by same sources that empty into the drians both the natural and man made drians, such as from domestic and industrial waste, leaded gasoline, industrial emission, waste batteries and wastes from vehicular activities.. The second group is made up of Mn, As, Th, V, Cr, Sc and Ga, accounting for approximately 19.60% of the total variance. These elements might have been enriched in the sediments through drains from interaction with soils that may have been contaminated by activities such as Vehicular waste, Iron and Steel work as well as tool making. The third group is only made up of La, which accounted for 10.45% of the total variance. This element might have been enriched, by activities relating to soil leachate from automobile activities and other urban consumables like additives in chemical products and metal plating. Table 4.13; shows summary of factor Analyses of the trace elements in the sediments in both the natural and artificial drains from the study area.

Further application of the three component plot of principal component analyses (PCA) enabled us to find out further that in similar ways, the same trace elements clustered close to each other as seen in the factor analyses earlier analysed i.e. those elements that are likely to be from analogous sources cluster together as seen in Fig. 4.61. For the three component loading, Mn, Cr, Mo, Hg, Ni, Cu, Co, Zn, Cd and Pb loaded close to each other which suggest similar source of enrichment in the sediments. While Sc, V, Ga and Th loaded a bit far away from other element, which suggest in similar term that these elements may have been enriched by same source. As and La isolated completely from the two main groups of association and cluster, showing possibly different source of enrichment in the sediments.

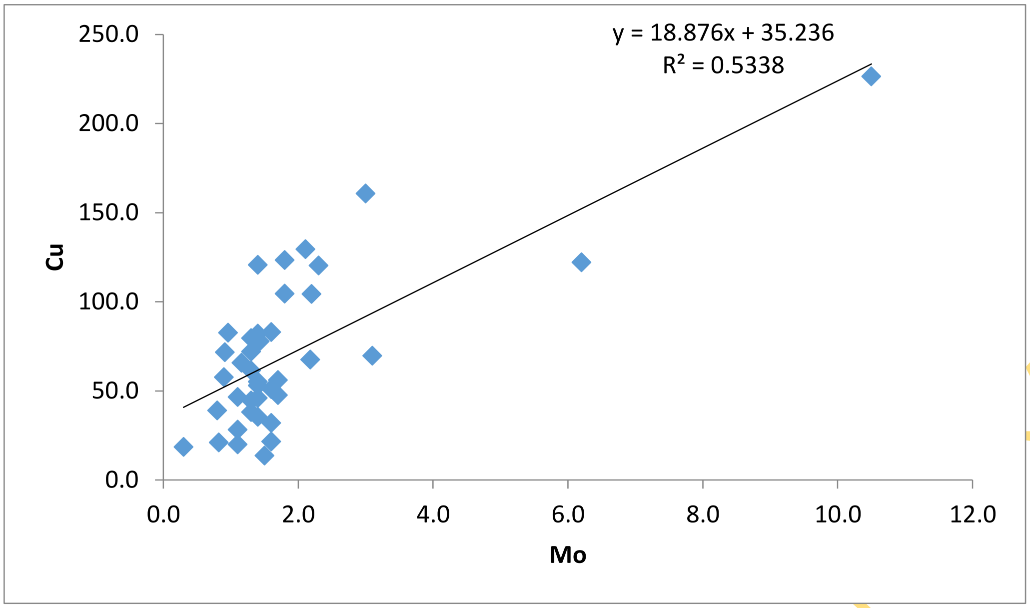


Fig. 4.60a: Bivariate plot of Cu and Mo in sediments of the study area

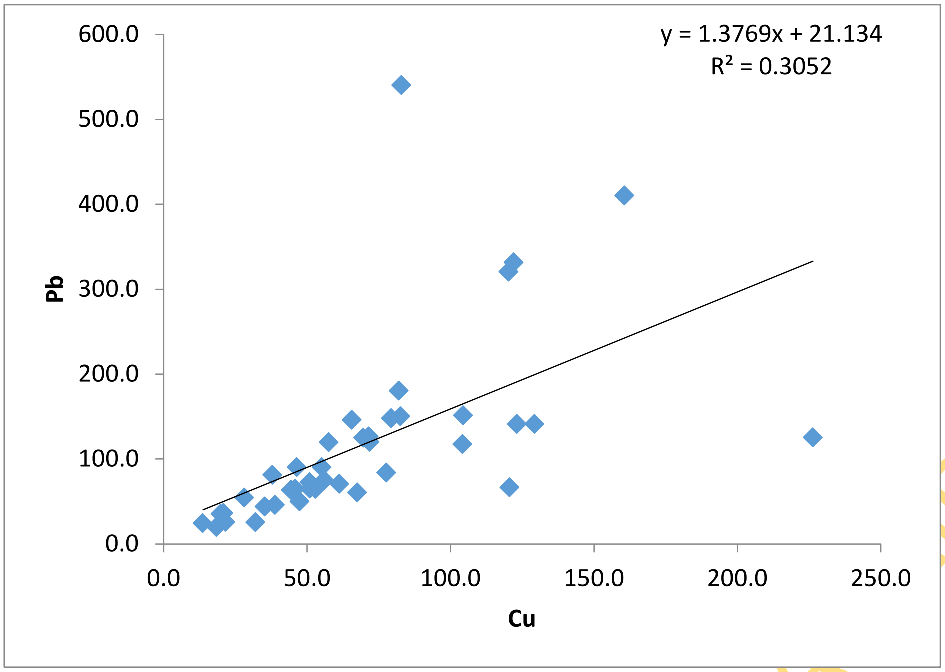


Fig. 4.60b: Bivariate plot of Pb and Cu in sediments of the study area

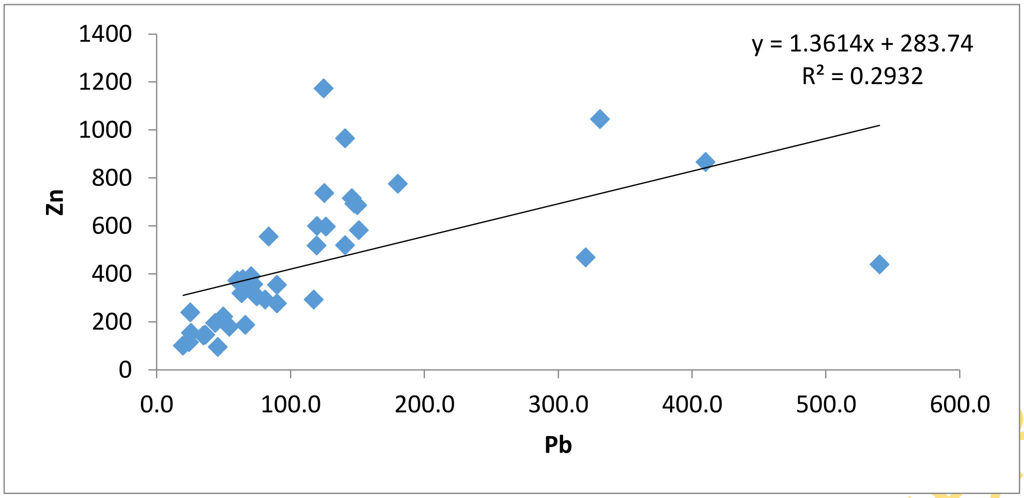


Fig. 4.60c: Bivariate plot of Zn and Pb in sediments of the study area

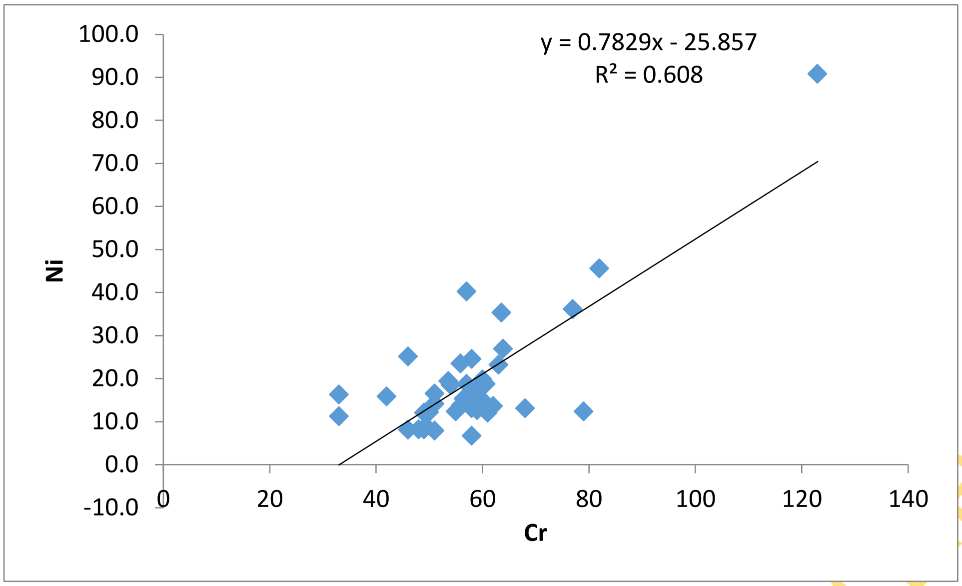


Fig. 4.60d: Bivariate plot of Ni and Cr in sediments of the study area

Table 4.11: Correlation coefficients of elements in the sediments of the study area

| | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Th | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mo | 1 | | | | | | | | | | | | | | | |
| Cu | **0.73** | 1.00 | | | | | | | | | | | | | | |
| Pb | 0.28 | **0.55** | 1.00 | | | | | | | | | | | | | |
| Zn | 0.45 | **0.63** | **0.54** | 1.00 | | | | | | | | | | | | |
| Ni | **0.90** | **0.81** | 0.32 | **0.50** | 1.00 | | | | | | | | | | | |
| Co | **0.66** | **0.67** | 0.35 | **0.55** | **0.82** | 1.00 | | | | | | | | | | |
| Mn | **0.70** | 0.41 | 0.09 | 0.16 | **0.61** | 0.48 | 1.00 | | | | | | | | | |
| As | 0.11 | -0.13 | -0.15 | -0.17 | -0.10 | -0.26 | **0.43** | 1.00 | | | | | | | | |
| Th | -0.35 | -0.55 | -0.53 | -0.57 | -0.48 | -0.49 | -0.10 | **0.57** | 1.00 | | | | | | | |
| Cd | **0.67** | **0.83** | **0.58** | **0.81** | **0.74** | **0.62** | 0.34 | -0.13 | -0.63 | 1.00 | | | | | | |
| V | -0.34 | -0.48 | -0.39 | -0.41 | -0.46 | -0.50 | -0.12 | **0.66** | **0.88** | -0.45 | 1.00 | | | | | |
| La | -0.24 | -0.08 | -0.09 | 0.12 | 0.02 | 0.38 | -0.23 | -0.33 | 0.04 | -0.02 | 0.05 | 1.00 | | | | |
| Cr | **0.82** | **0.63** | 0.22 | 0.41 | **0.78** | **0.54** | **0.50** | 0.11 | -0.20 | **0.57** | -0.18 | -0.17 | 1.00 | | | |
| Hg | 0.46 | **0.62** | 0.19 | **0.62** | **0.55** | 0.47 | 0.32 | -0.02 | -0.38 | **0.76** | -0.23 | 0.09 | 0.41 | 1.00 | | |
| Sc | -0.36 | -0.47 | -0.43 | -0.42 | -0.43 | -0.42 | -0.09 | **0.61** | **0.91** | -0.46 | **0.96** | 0.18 | -0.19 | -0.21 | 1.00 | |
| Ga | -0.30 | -0.36 | -0.36 | -0.31 | -0.33 | -0.31 | -0.09 | **0.51** | **0.85** | -0.35 | **0.92** | 0.26 | -0.15 | -0.13 | **0.94** | 1 |

Table 4.12: Principal Component Analyses of the Trace Elements in the study area

| Element | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Mo | 0.77 | 0.48 | -0.24 |
| Cu | 0.86 | 0.23 | 0.05 |
| Pb | 0.57 | -0.13 | 0.03 |
| Zn | 0.73 | 0.05 | 0.33 |
| Ni | 0.86 | 0.36 | 0.01 |
| Co | 0.78 | 0.17 | 0.33 |
| Mn | 0.45 | 0.59 | -0.35 |
| As | -0.32 | 0.76 | -0.31 |
| Th | -0.80 | 0.51 | 0.04 |
| Cd | 0.87 | 0.19 | 0.19 |
| V | -0.75 | 0.59 | 0.14 |
| La | -0.05 | -0.09 | 0.89 |
| Cr | 0.63 | 0.53 | -0.13 |
| Hg | 0.62 | 0.30 | 0.32 |
| Sc | -0.74 | 0.60 | 0.25 |
| Ga | -0.65 | 0.60 | 0.38 |
| Total | 7.58 | 3.14 | 1.67 |
| % of Variance | 47.39 | 19.60 | 10.45 |
| Cumulative % | 47.39 | 66.99 | 77.44 |

Table 4.13: Summary of Elemental Associations of the three-factor model and the Eigen value in (%).

| Factor | Elemental Association | Eigenvalues % |
|---|---|---|
| R-1 | Mo-Cu-Pb-Zn-Ni-Co-Cd-Cr-Hg | 47.39 |
| R-2 | Mn-As-Th-V-Cr-Sc-Ga | 19.60 |
| R-3 | La | 10.45 |

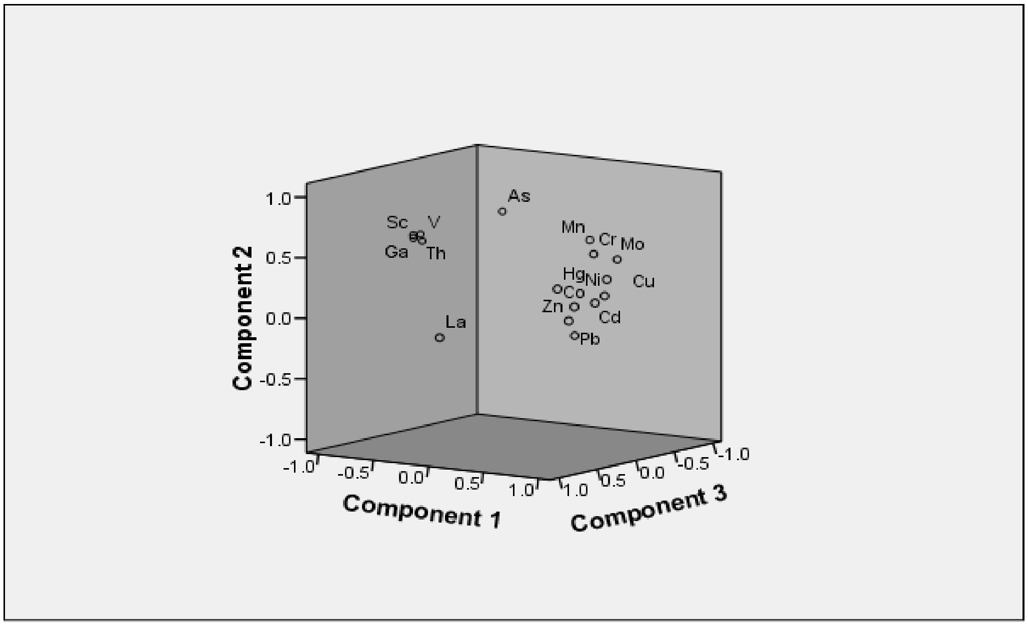


Fig. 4.61: Plot of the three principal components for the trace elements in sediments of the study area

## 4.10 Environmental Assessment of the Study area

### 4.10.1 Geo-accumulation Index Assessment

The summary and detailed results of the calculated Geo-accumulation Index Assessment (I-geo) values from selected metals in the Onitsha metropolis according to different landuse activities are presented in Figure 4.69 – Figure 4.74 and Appendix 4(a and b). The selected metals presented in boxplot include Cu, Mn, Pb, Ni, As and Zn. The results of the I-geo of these summarised elements reveal that the soils and sediments from different landuse vary from practically unpolluted, as exhibited by most of the samples collected from control area ( CT ) to highly polluted landuse, as exhibited by soils and sediments from MWM, AWD, ID and RSD. The summary of results for Cu content in the study area show that MWM range from slightly polluted to extremely polluted. The same I-geo characteristics are being exhibited by soils collected from MAP, AWD, RSD, ID, NK, RA and FLG for Cu, were most of the soils and sediment range from uncataminated to heavily contaminated, Appendix 4 (a and b). Pb I-geo in the various land use show that MWM exhibited the highest pollution status in most of the samples analysed, Figure 4.64, relative to other land use with charateristics of moderate to heavily contaminated as against the I-geo characteristics of practicaly uncomtaminated to mederately contaminated for samples of the control samples. The summary of results of the I-geo characteristics for Cu, Mn, Ni, Zn and As are presented in Figure 4.62, Figures 4.63 4.65, 4.64 and 4.65 respectively. this results are in agreement with other published work with similar studies (Odewande and Abimbola, 2008; Abimbola et al. 2006; Olatunji and Abimbola, 2010), were enrichment and pollution status of most of these potentially harmful elements are influenced by factor like urbanisation, landuse type among others

Similarly, the I-geo results for soils and sediments in the study area were presented in Arv GIS geo spatial maps for visual interpretation as seen in Figure 4.68 to Figure 4.75 for Co, Mo, Zn, As, Cu, Mn, Ni and Pb, for the soil in the study area and Figure 4.76 to Figure 4.81 for the same element representing the I-geo for sediments. It was observed that most of the elements with relatively high I-geo are from location with high human influences especially urban waste disposal, industrial activities, high human populated areas as well as areas with huge vehicular activities, exhibiting moderate to extremily contaminated characteristics.

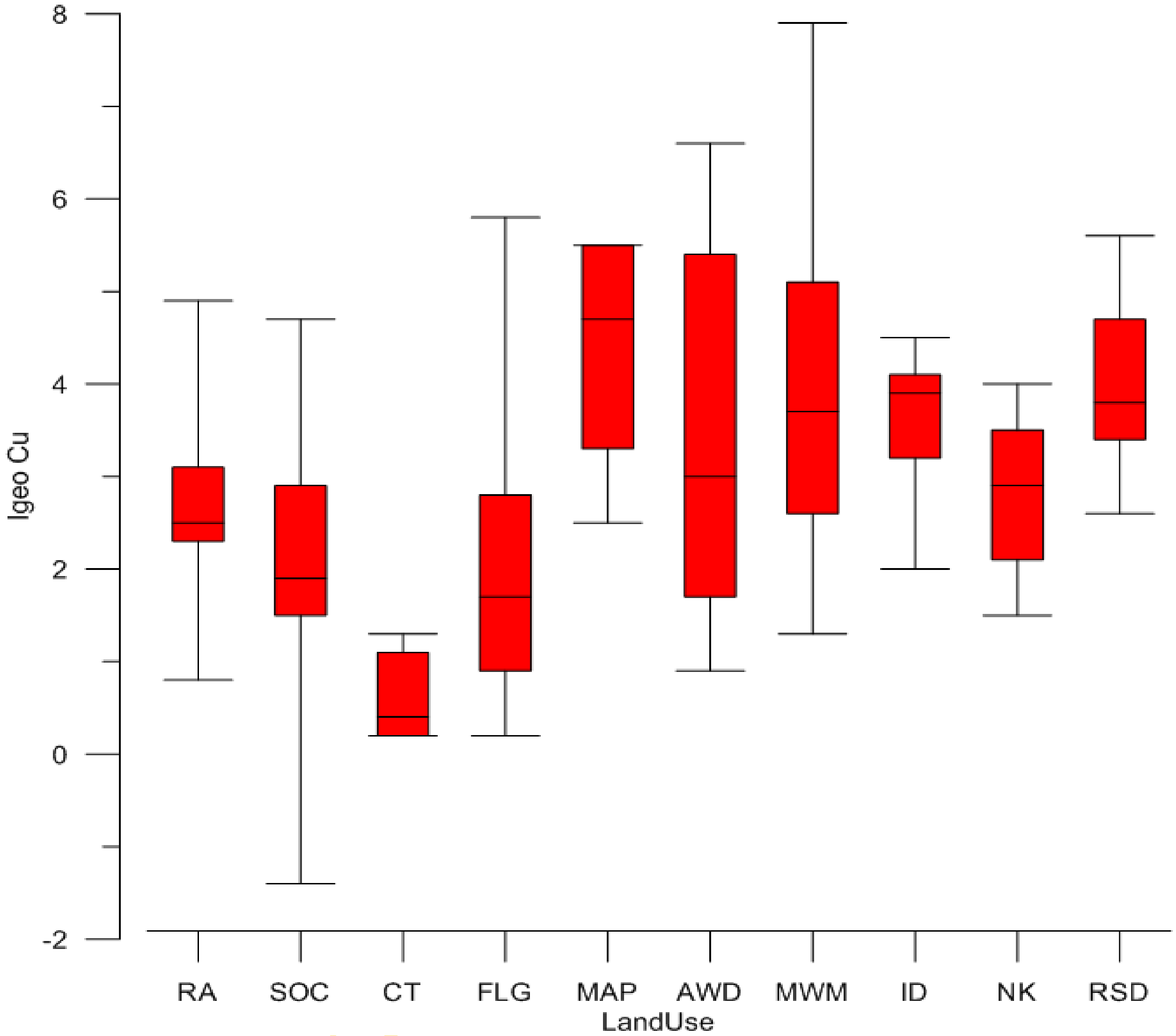


Fig. 4.62: Geo-accumulation index plot for Cu in different land use. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

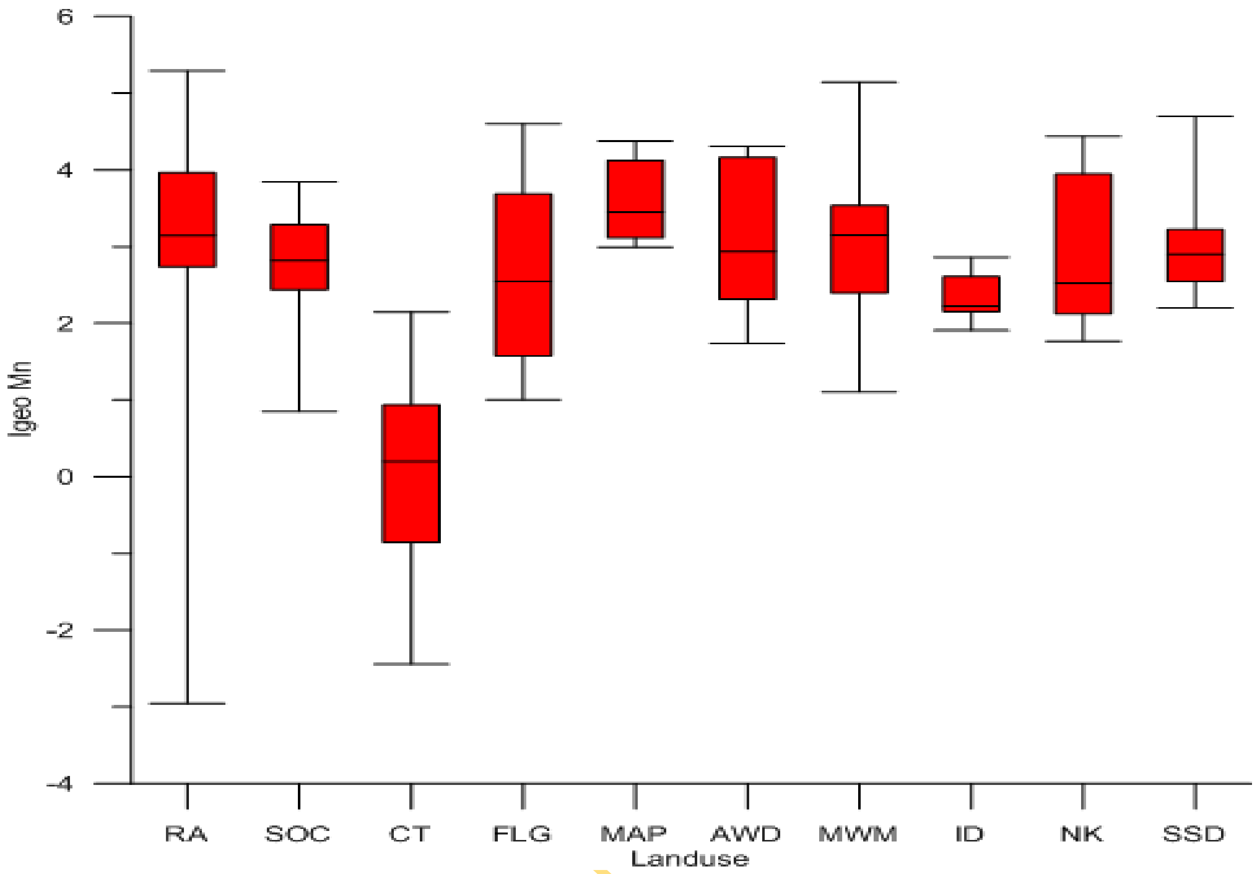


Fig. 4.63: Geo-accumulation index plot for Mn in different land. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

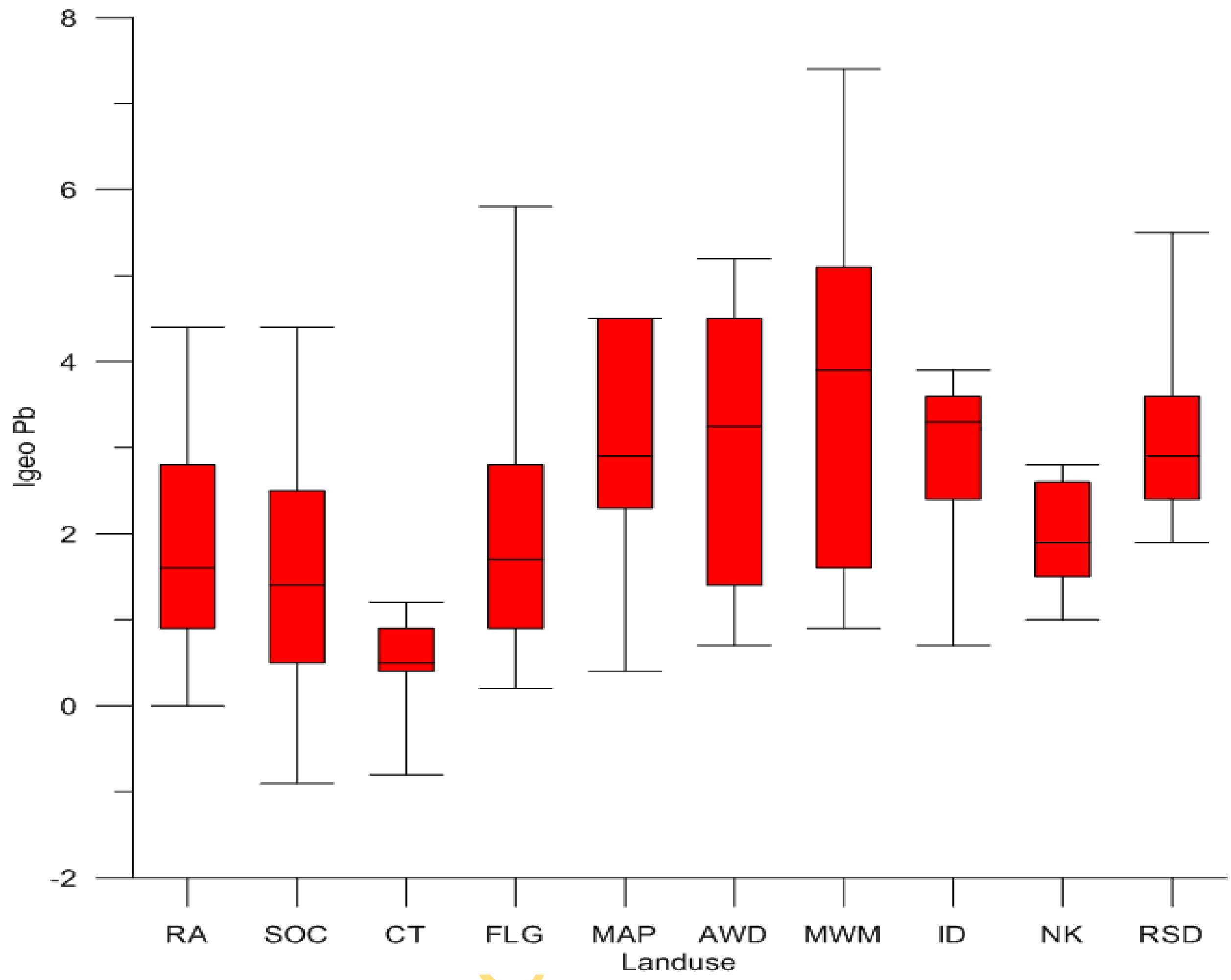


Fig. 4.64: Geo-accumulation index plot for Pb in different land. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median:the whiskers extend to the Max and Min of the distribution.

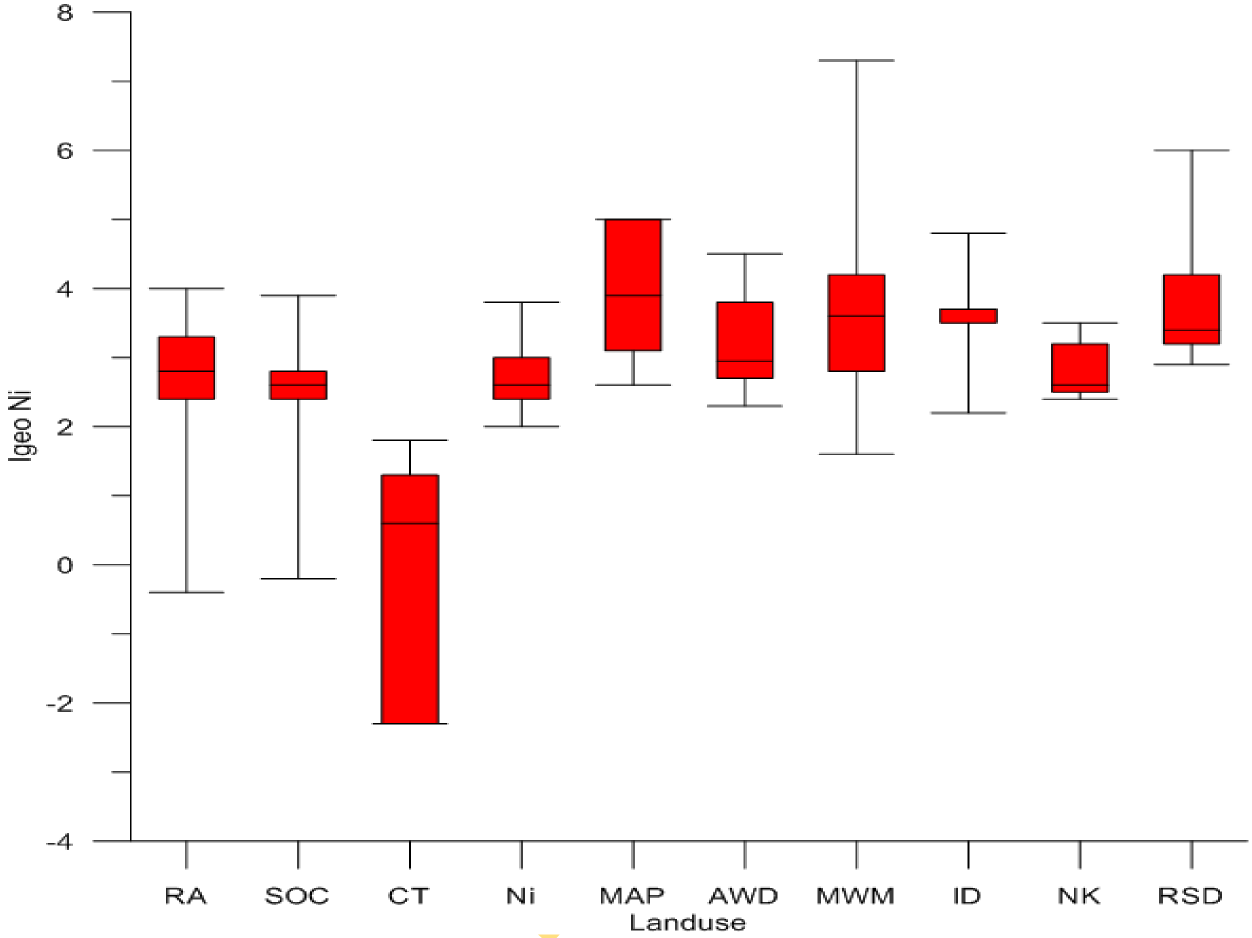


Fig. 4.65: Geo-accumulation index plot for Ni in different land use. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

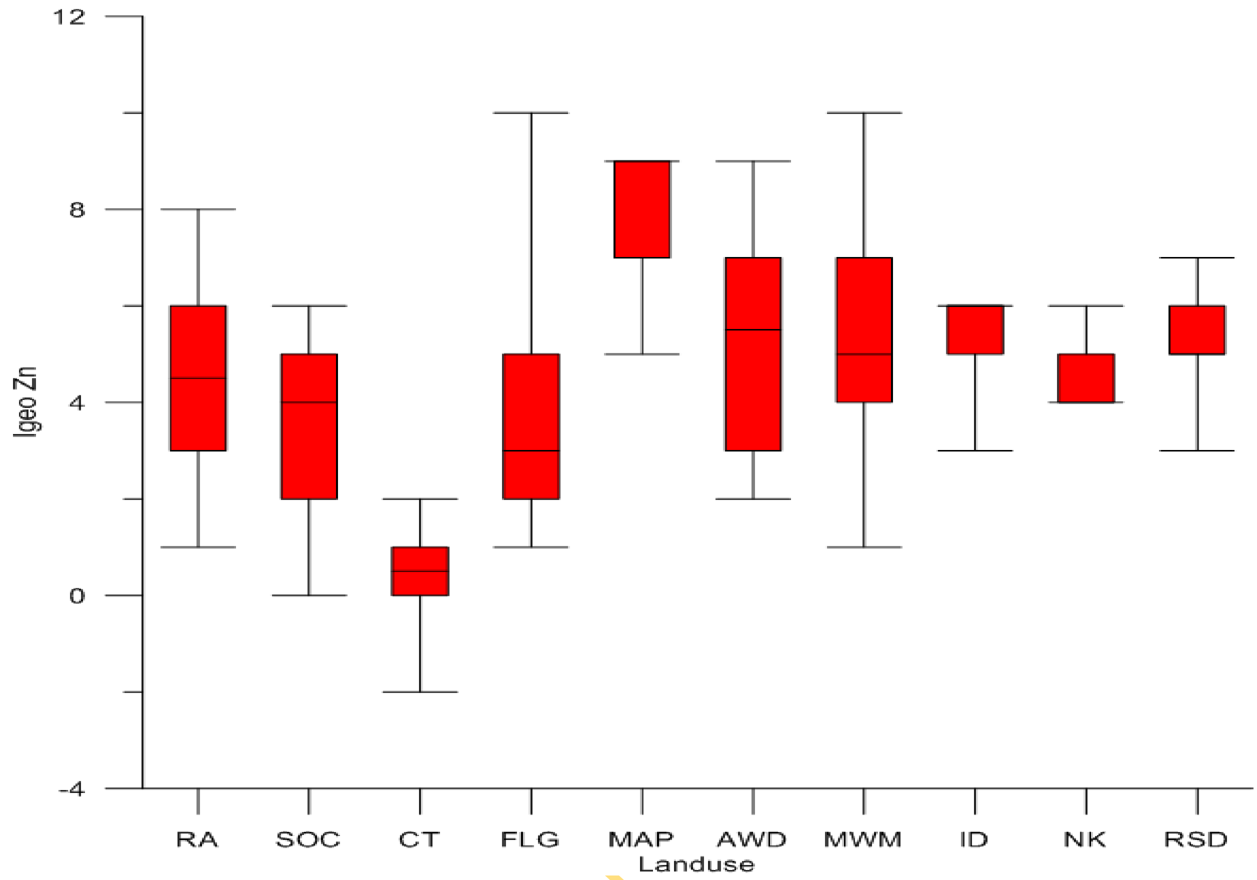


Fig. 4.66: Geo-accumulation index plot for Zn in different land use. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

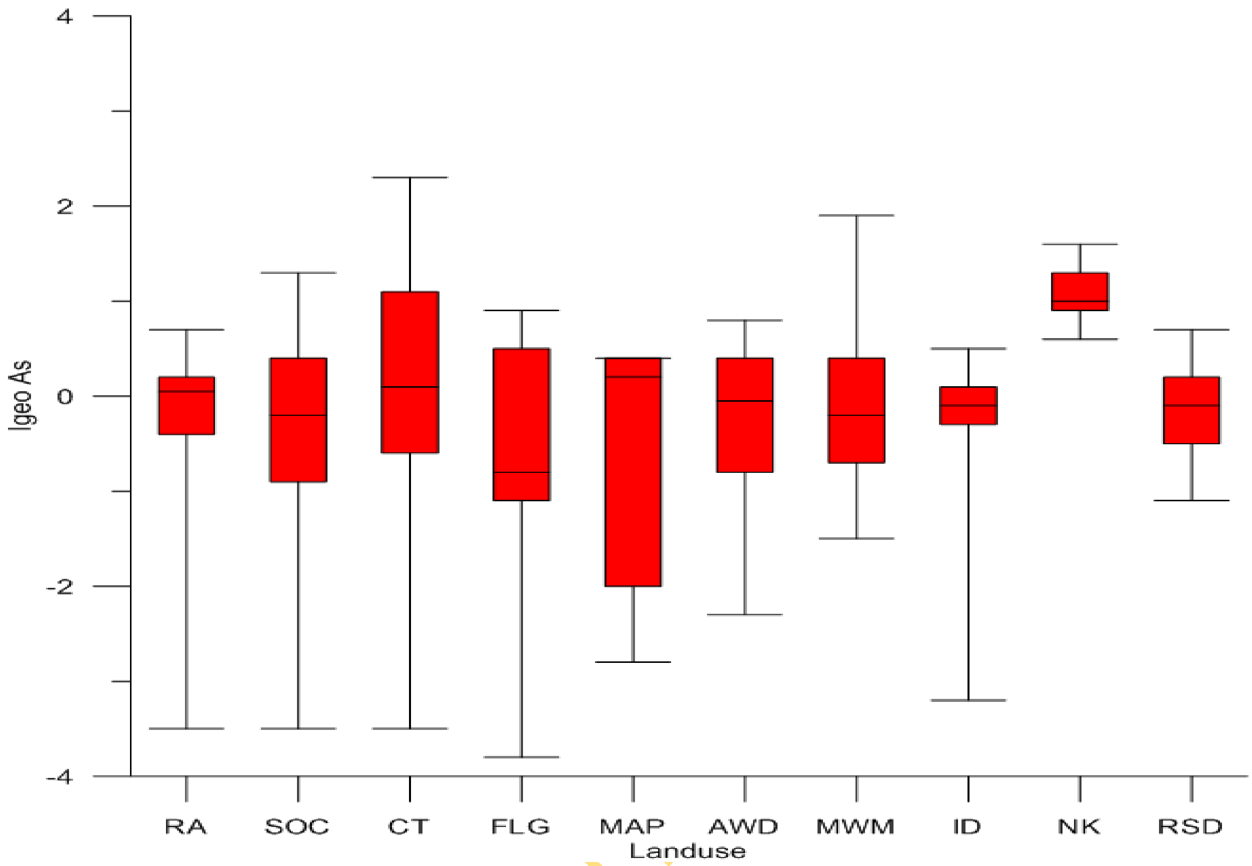


Fig. 4.67: Geo-accumulation index plot for As in different land use. The central box represents 50% of the distribution, between the 25th and 75th percentiles. The line bisecting the central box is the median: the whiskers extend to the Max and Min of the distribution.

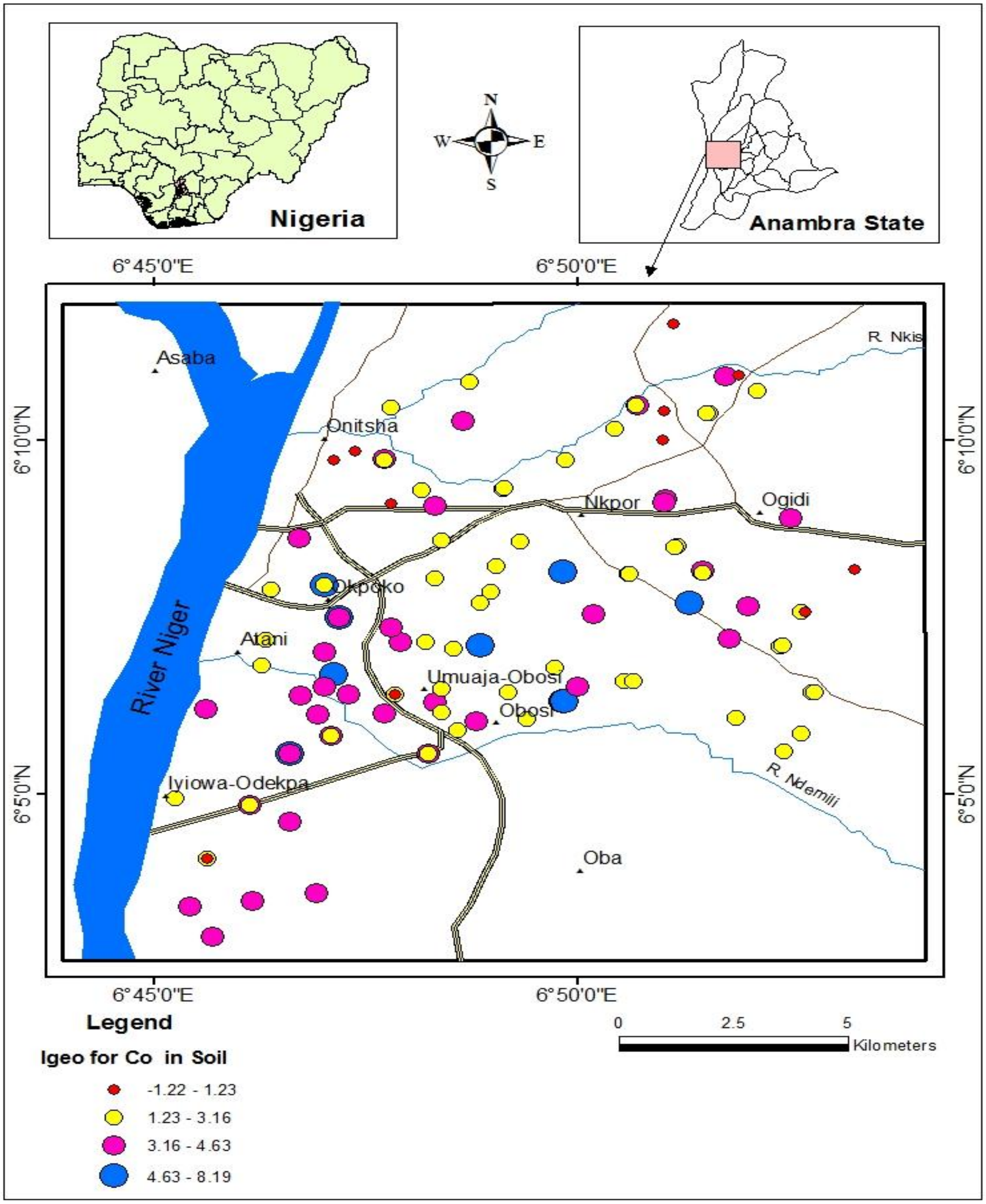


Fig. 4.68: Geo-accumulation index plot for Co in soils

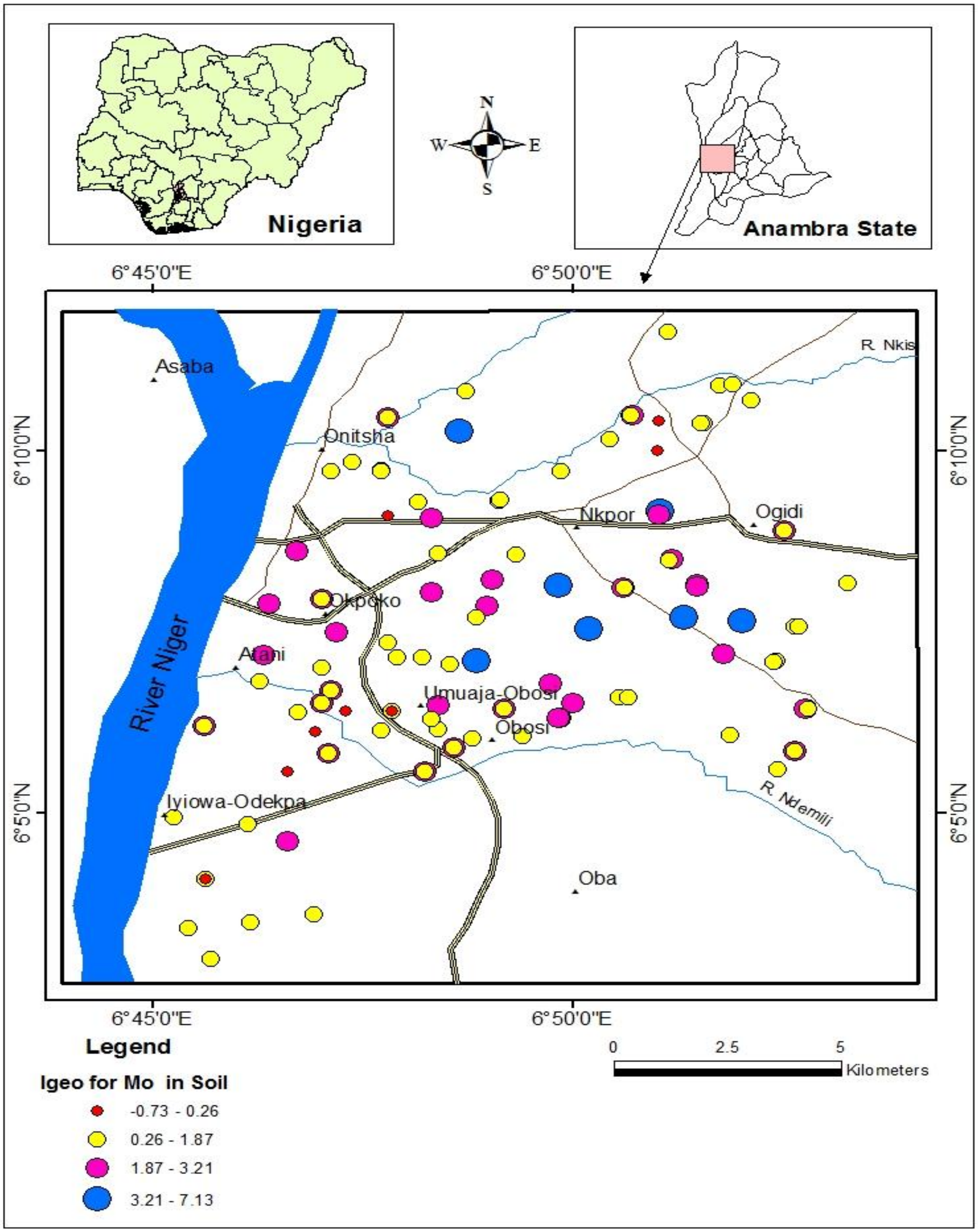


Fig. 4.69: Geo-accumulation index plot for Mo in soils

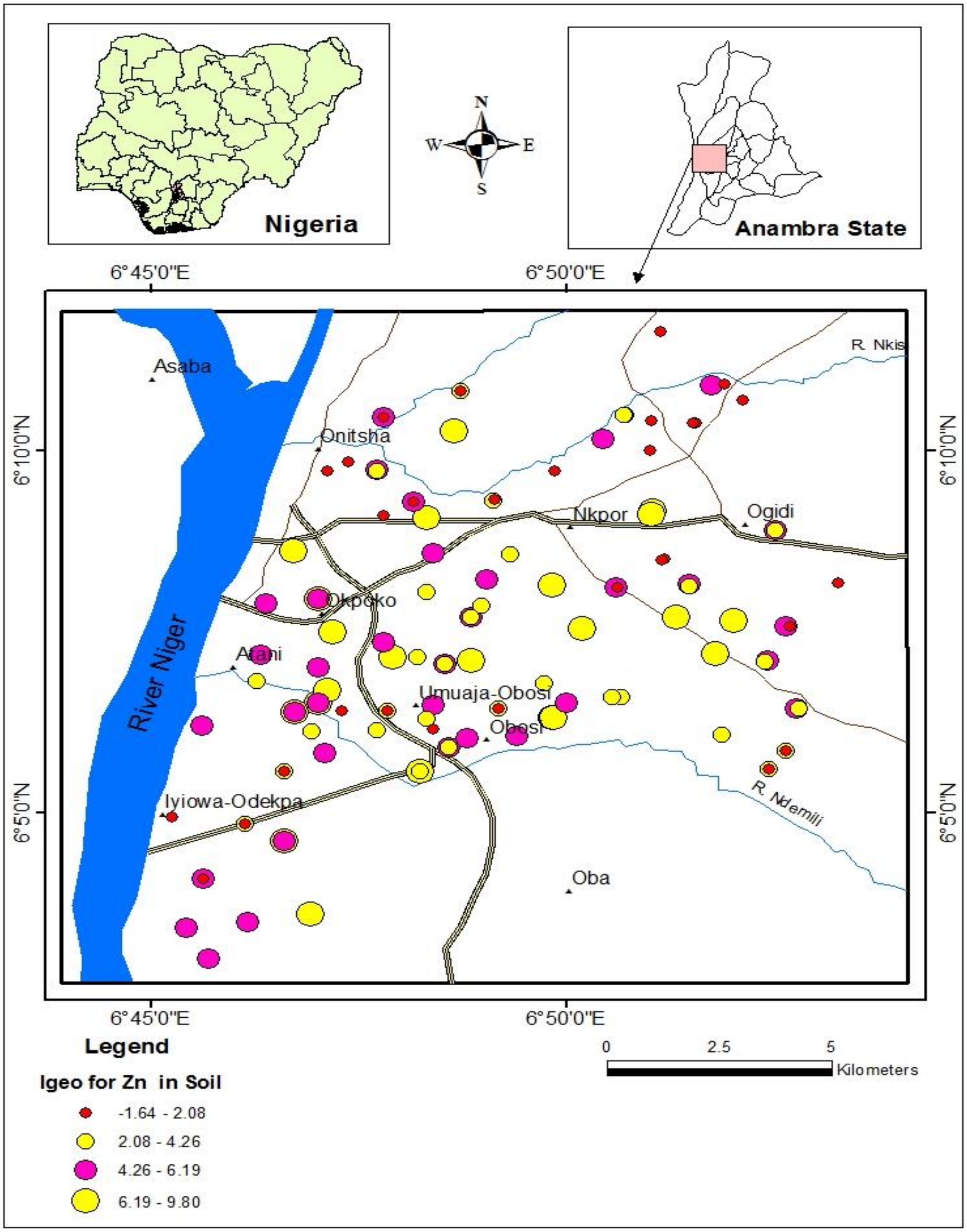


Fig. 4.70: Geo-accumulation index plot for Zn in soils

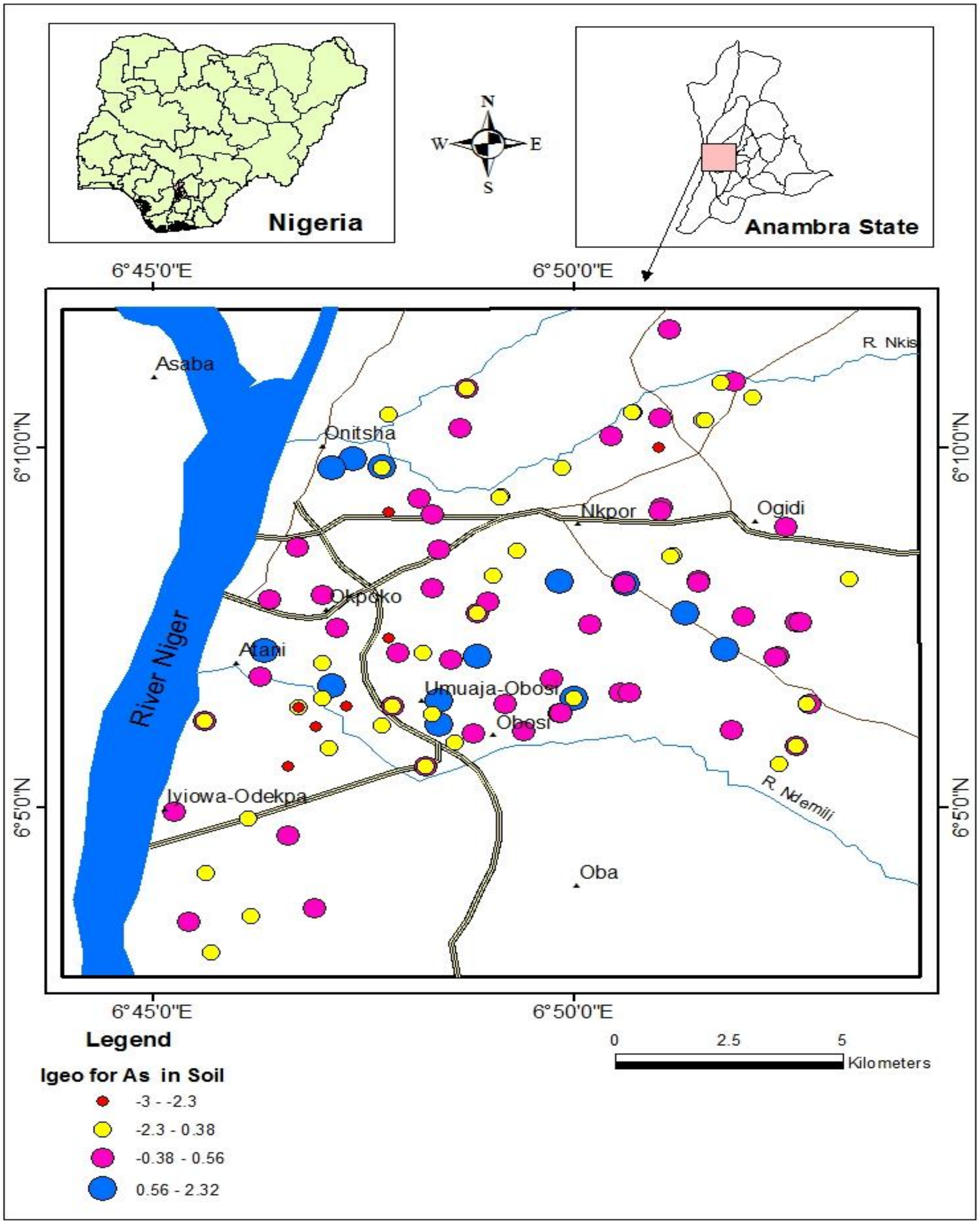


Fig. 4.71: Geo-accumulation index plot for As in soils

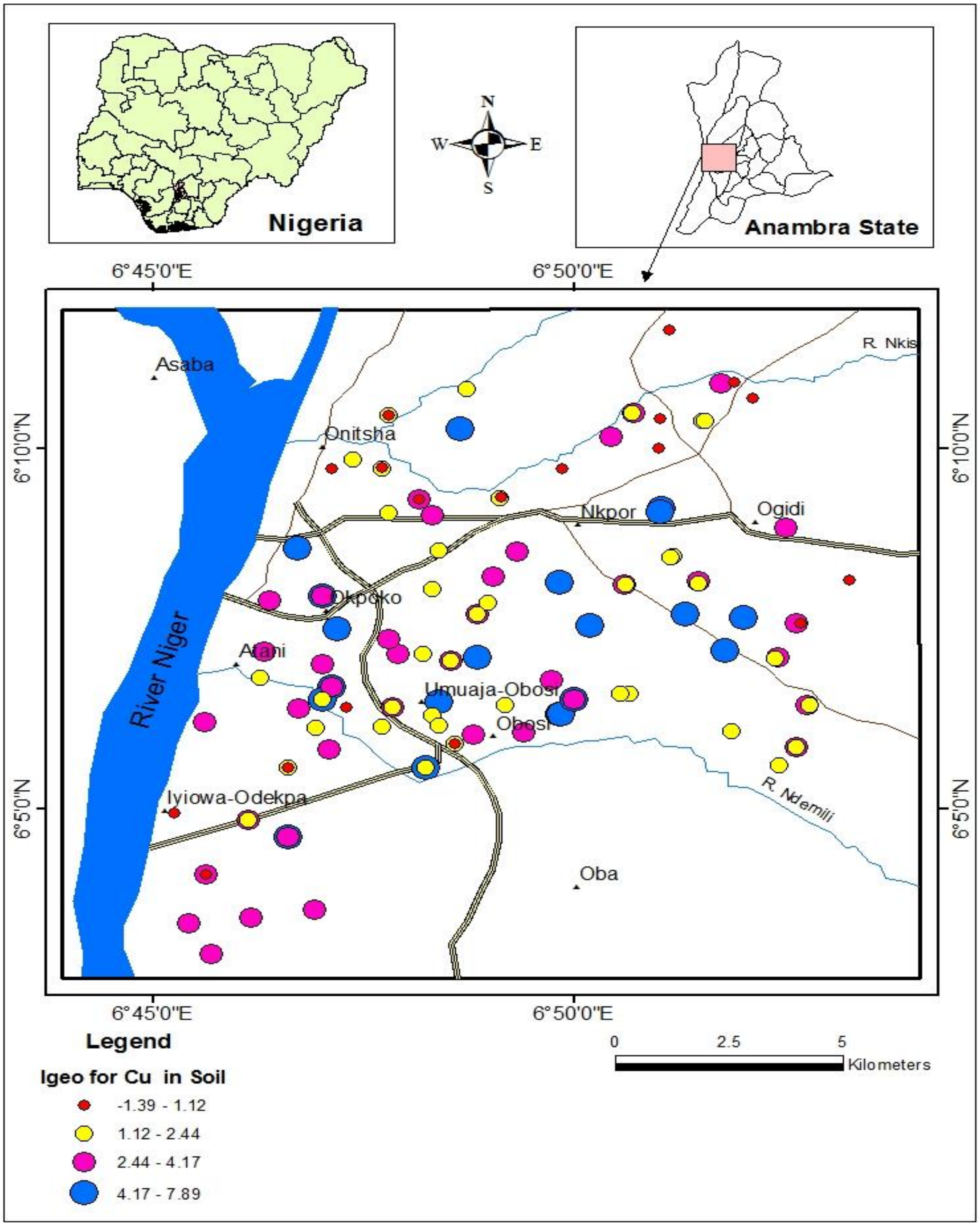


Fig. 4.72: Geo-accumulation index plot for Cu in soils

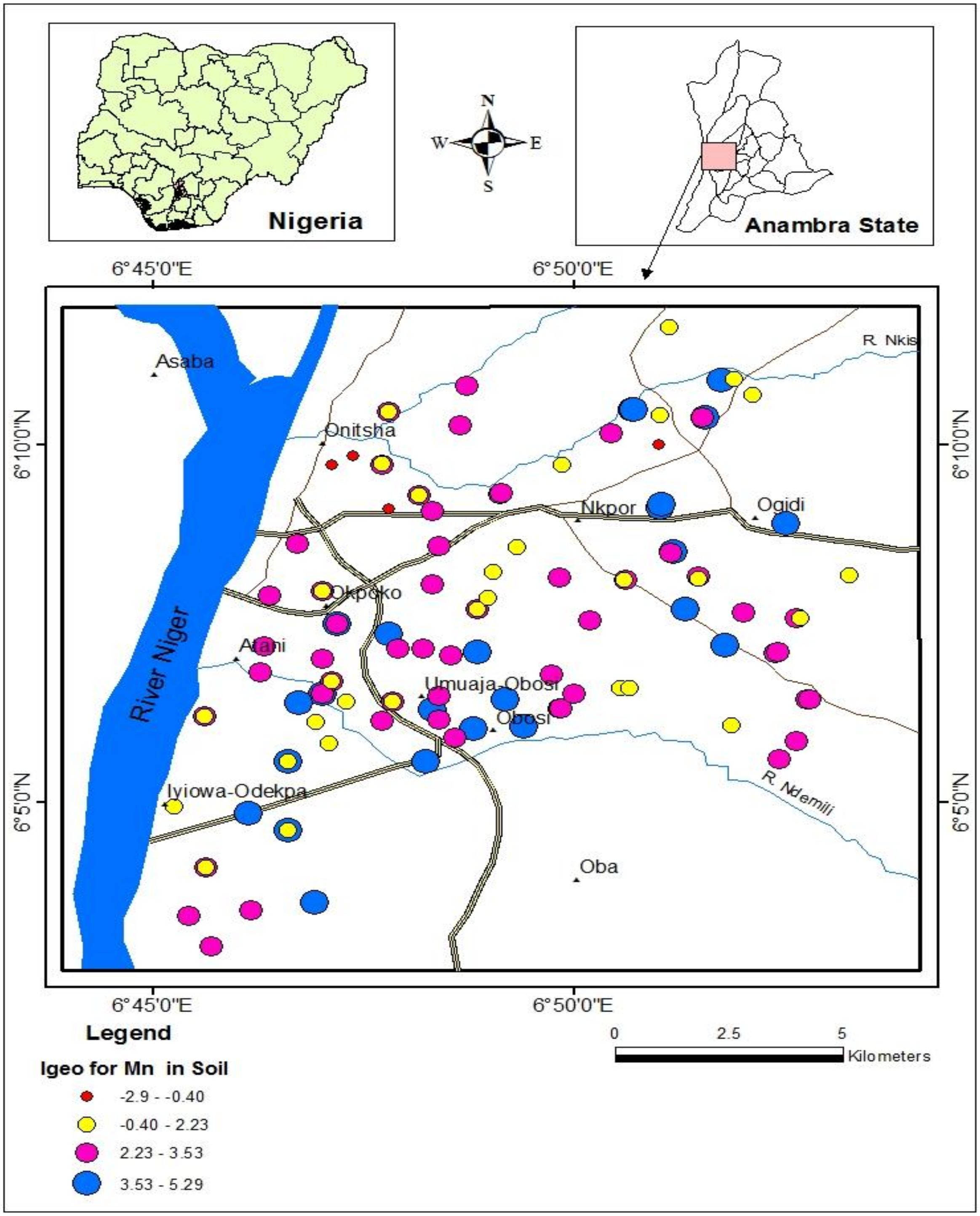


Fig. 4.73: Geo-accumulation index plot for Mn soils

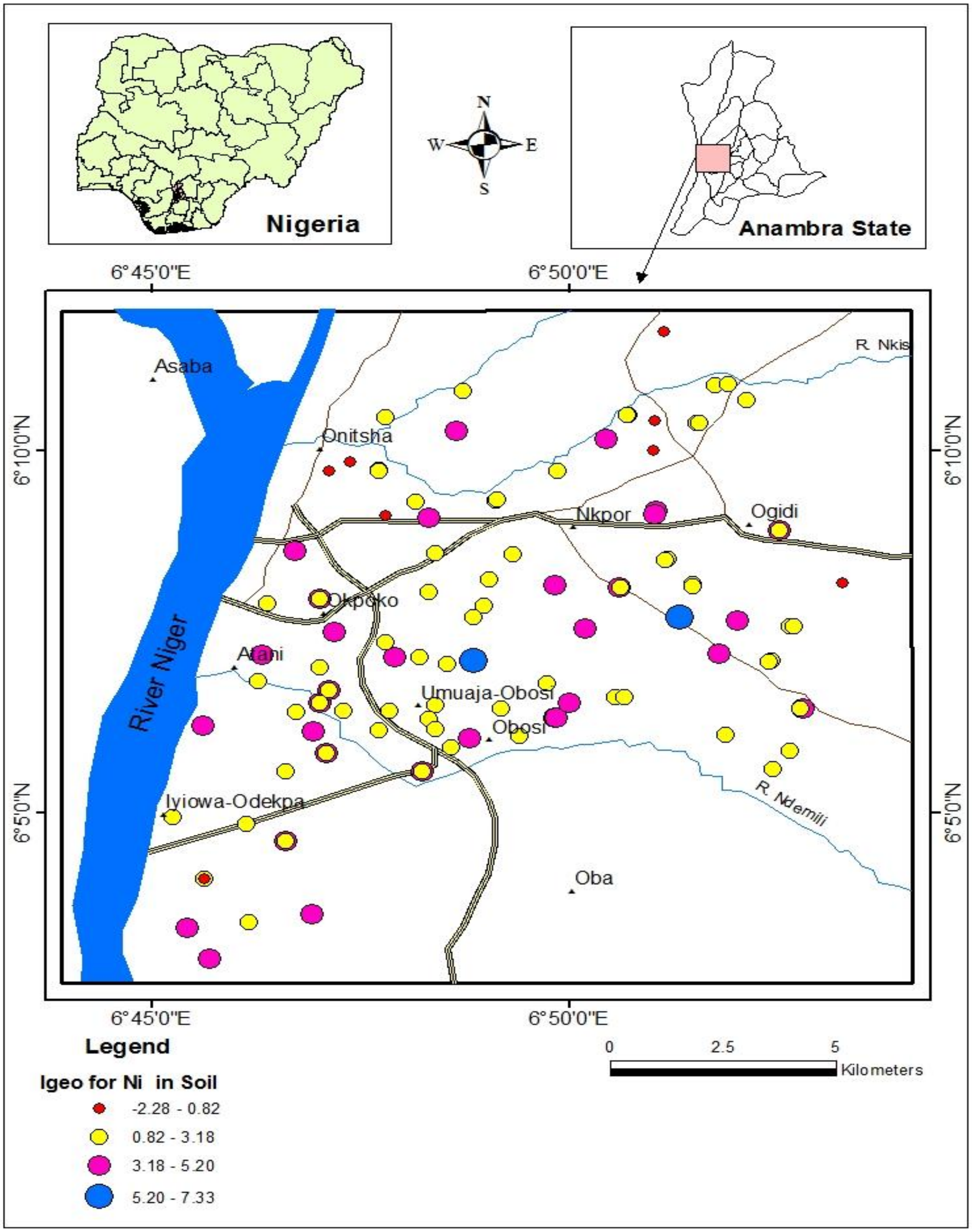


Fig. 4.74: Geo-accumulation index plot for Ni in soils

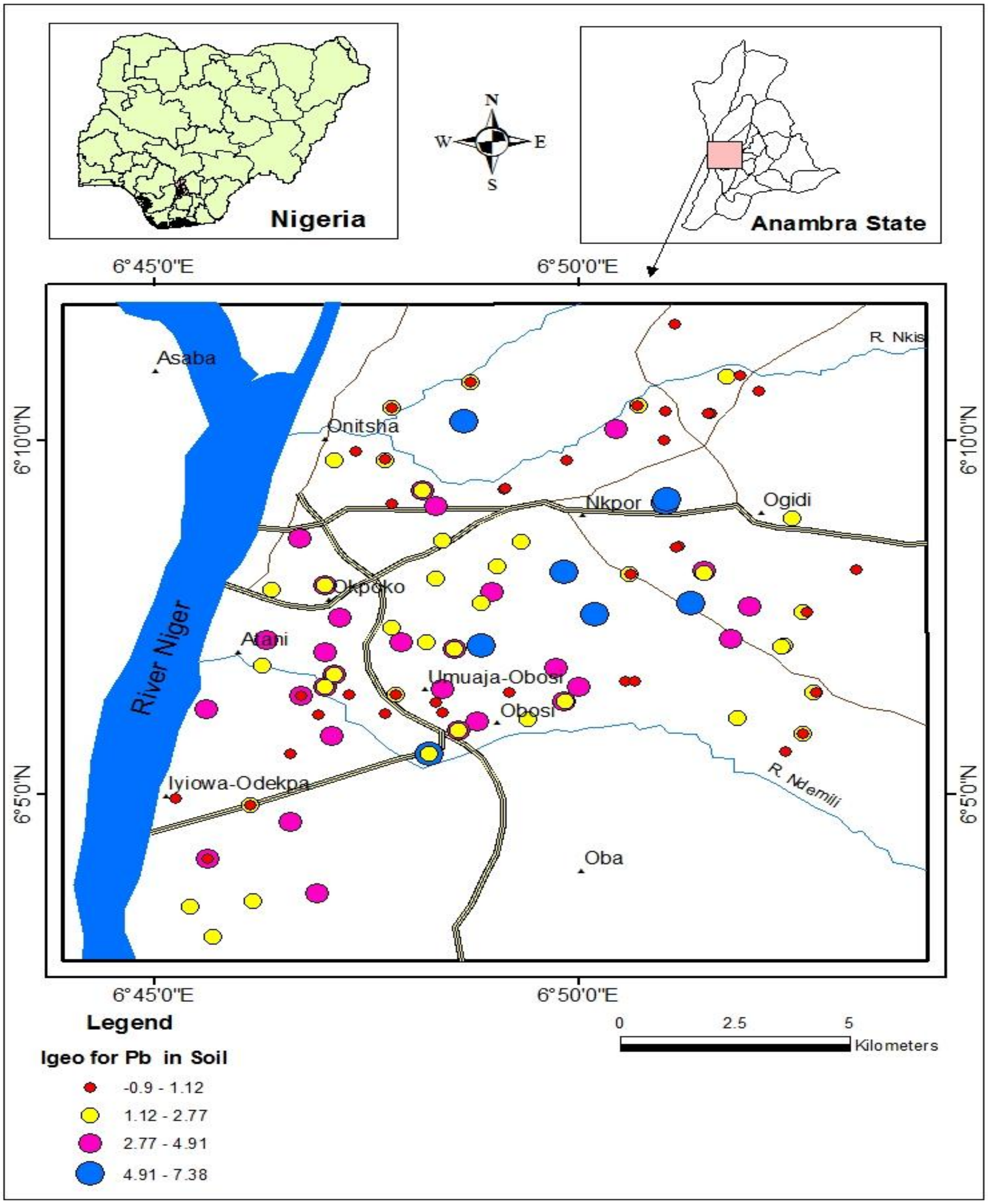


Fig. 4.75: Geo-accumulation index plot for Pb in soils

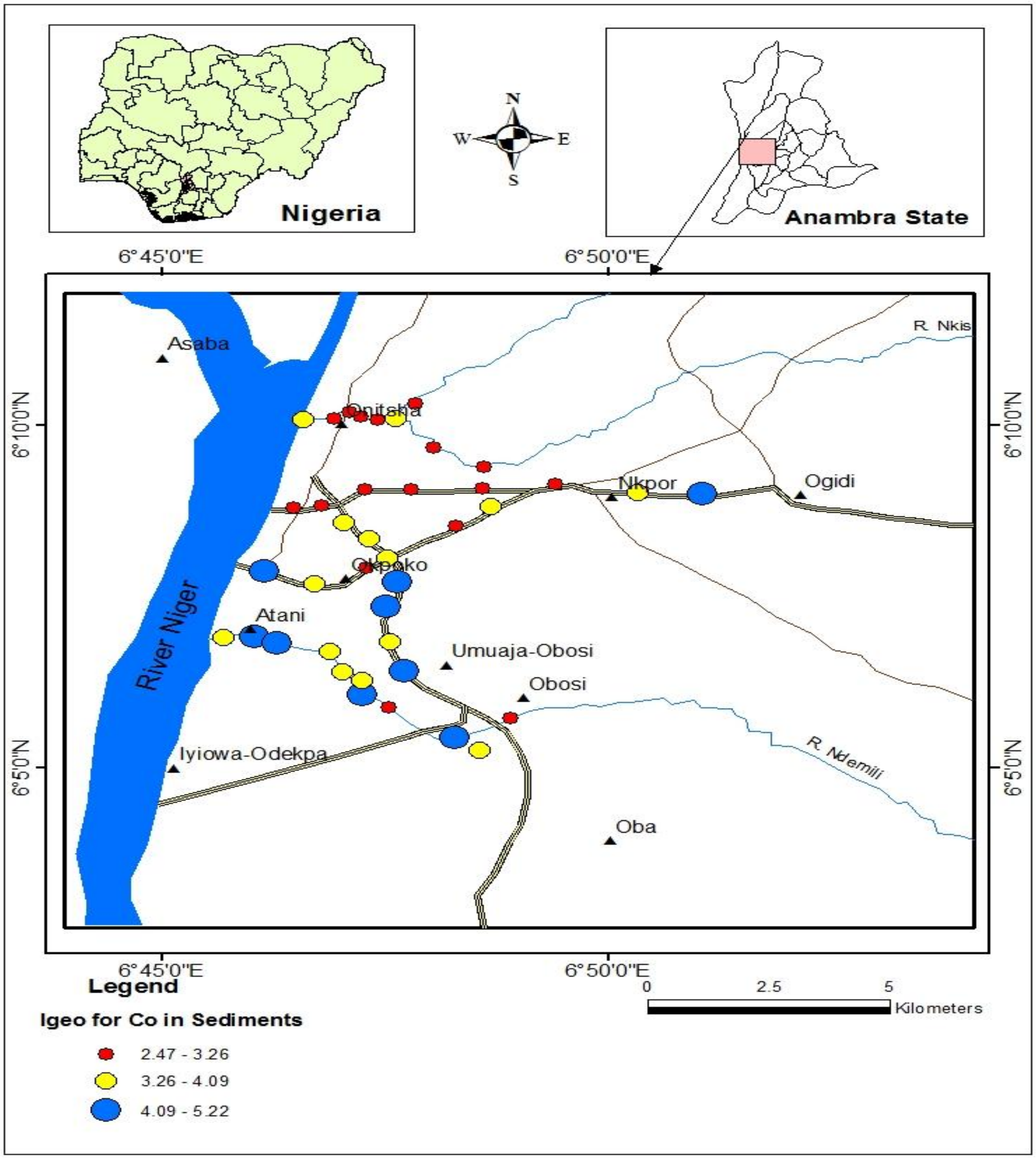


Fig. 4.76: Geo-accumulation index plot for Co in Sediments

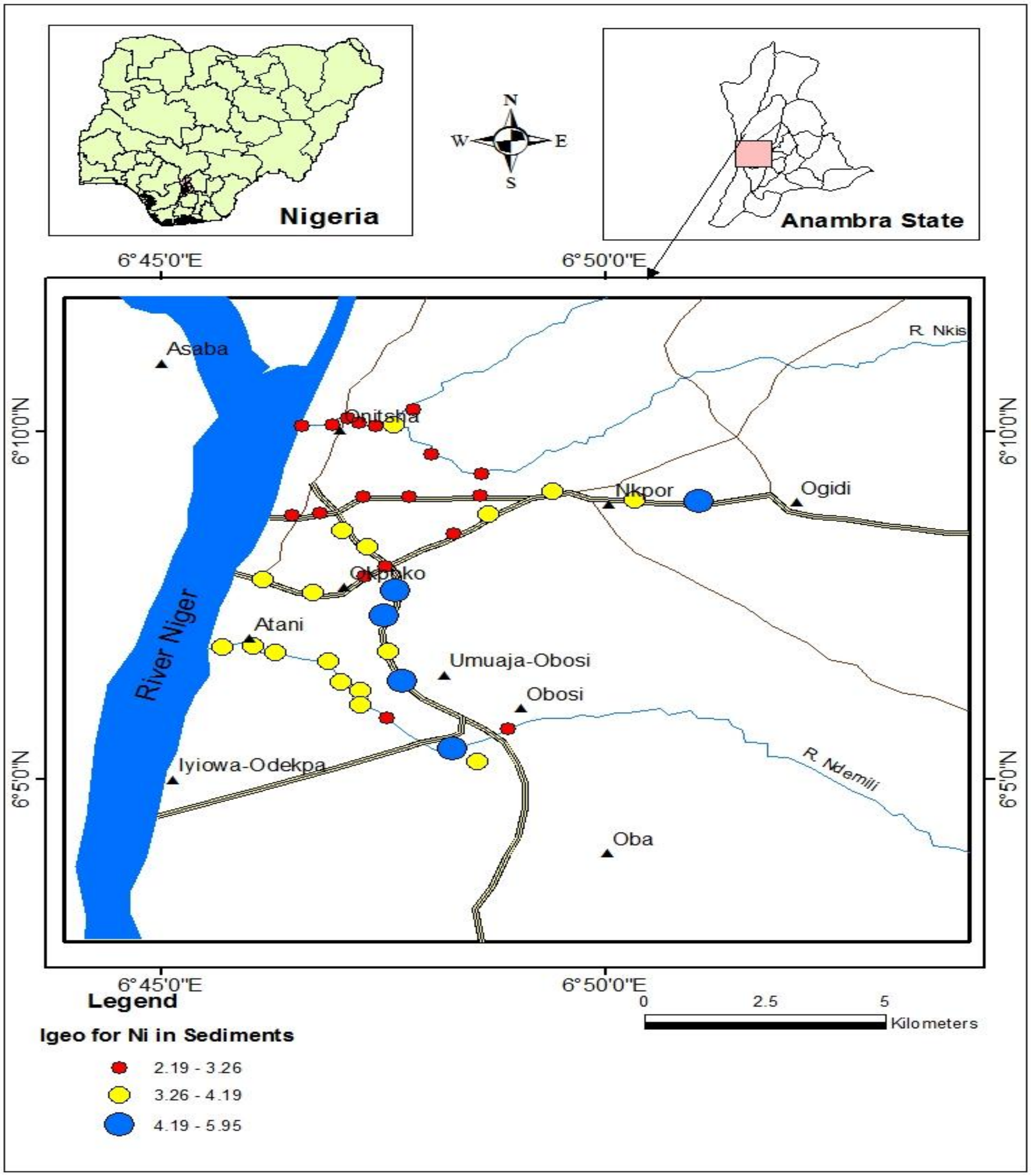


Fig. 4.77: Geo-accumulation index plot for Ni in Sediments

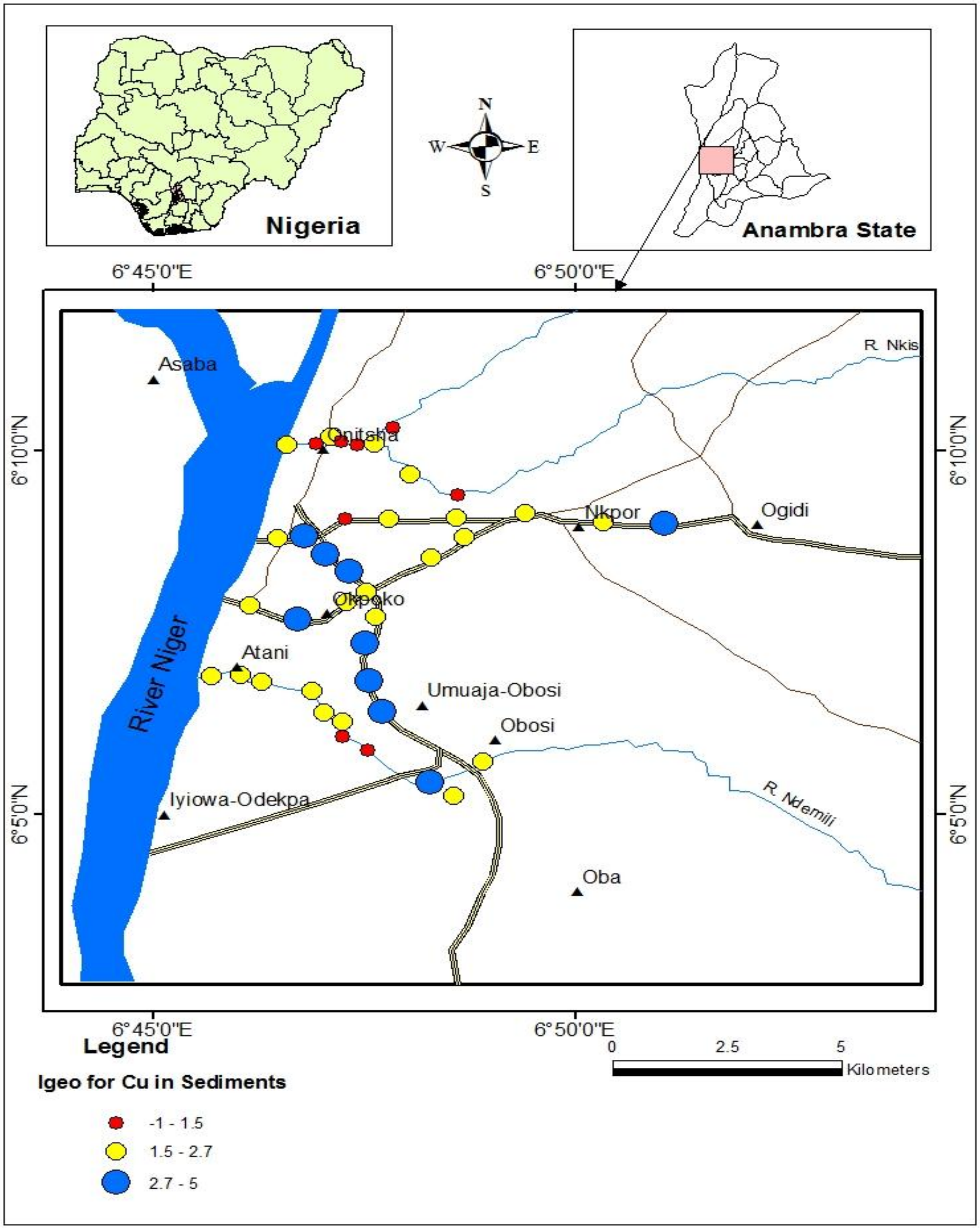


Fig. 4.78: Geo-accumulation index plot for Cu in Sediments

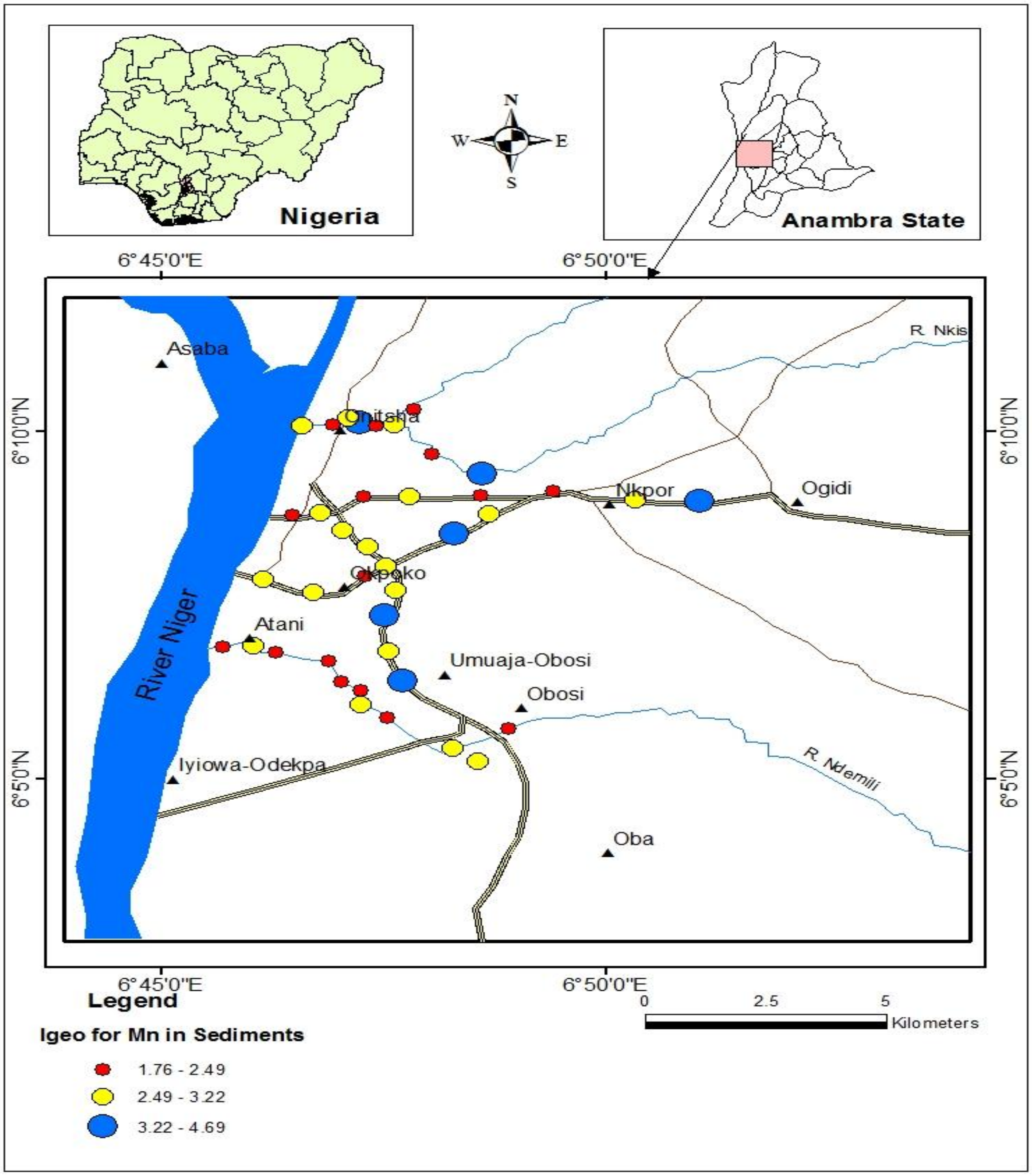


Fig. 4.79: Geo-accumulation index plot for Mn in Sediments

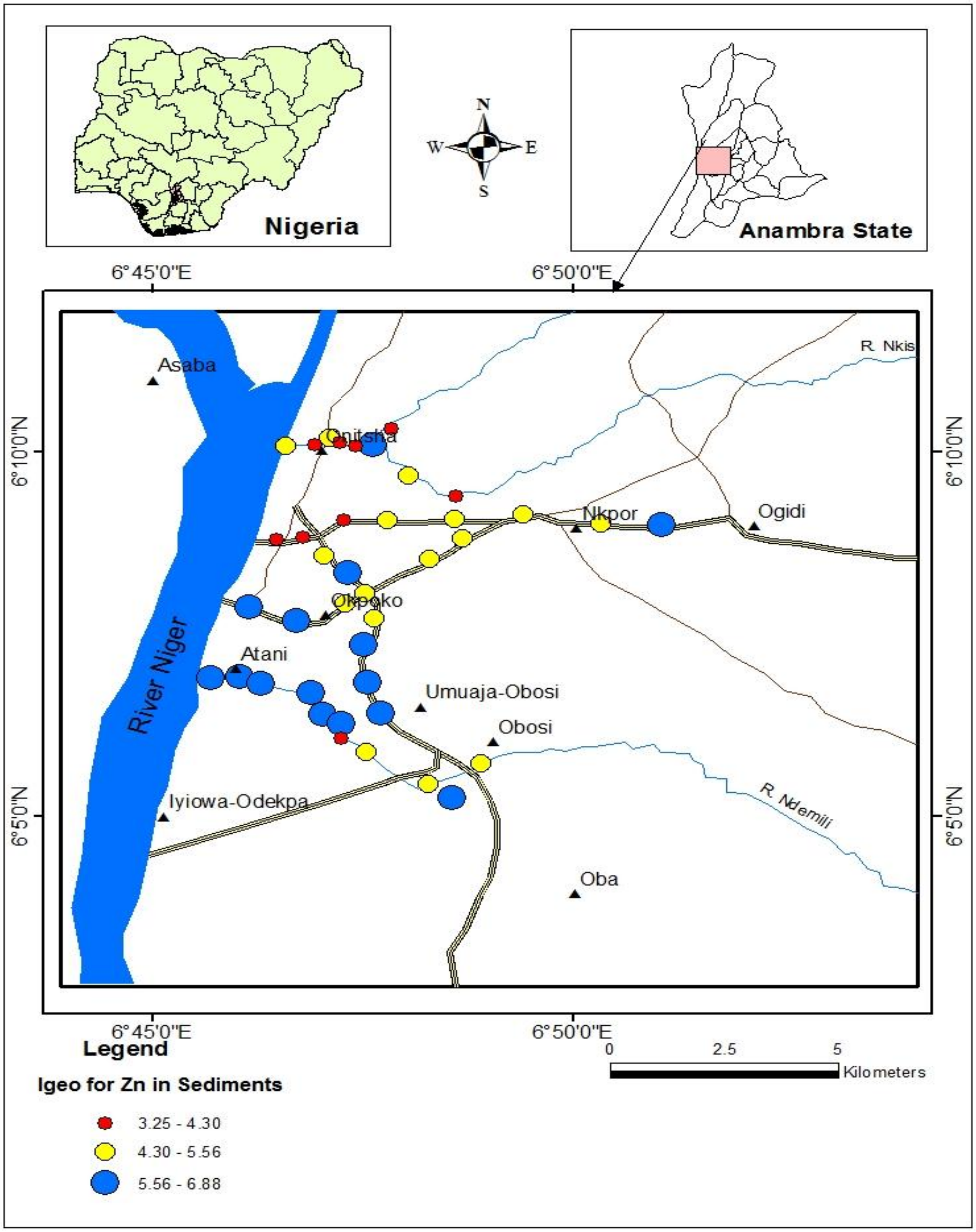


Fig. 4.80: Geo-accumulation index plot for Zn in Sediments

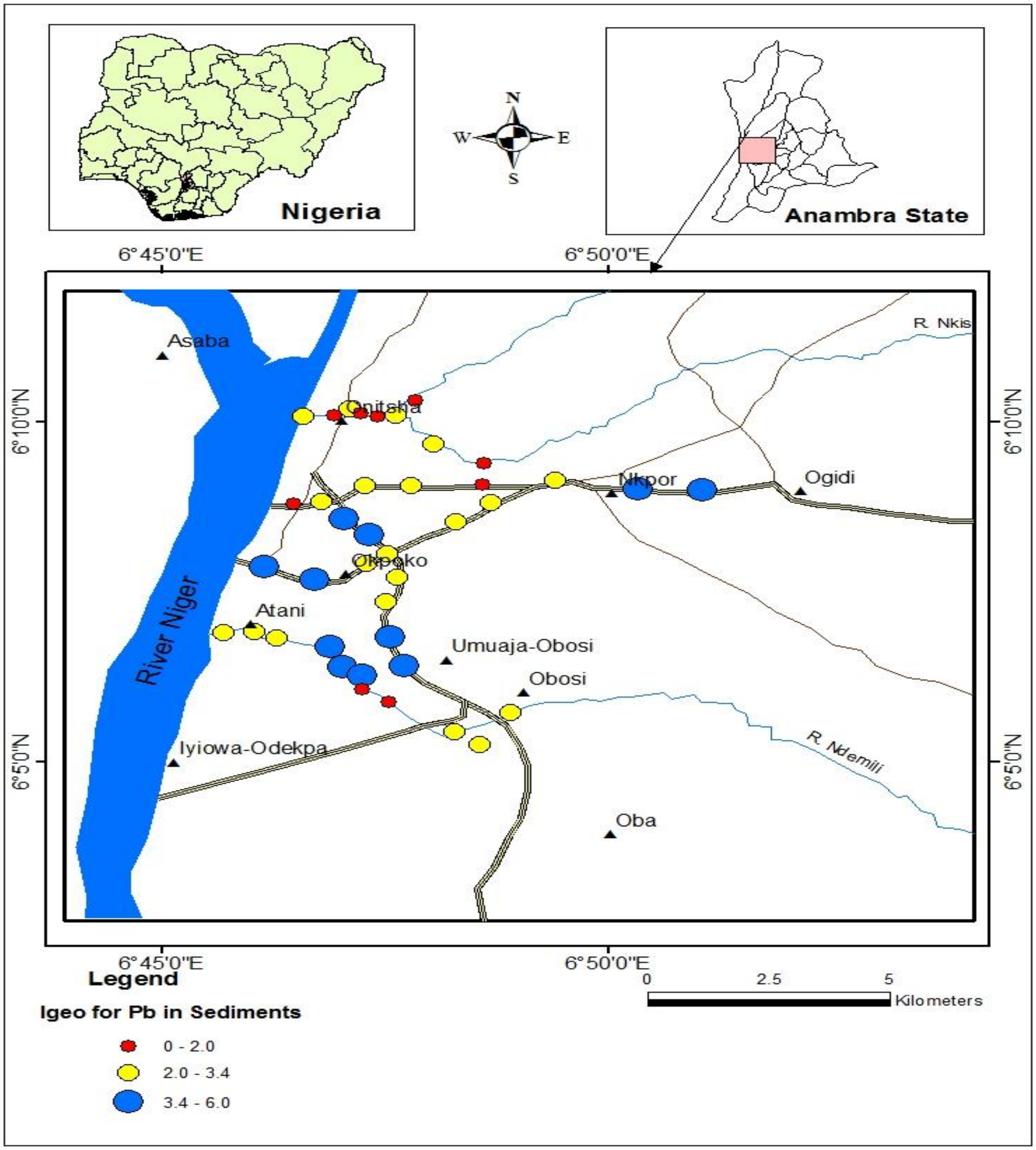


Fig. 4.81: Geo-accumulation index plot for Pb in Sediments

### 4.10.2 Contamination Factor for soils and sediment

The summary and detailed results of the calculated contamination factor values from selected metals in the Onitsha metropolis for soils and sediments are presented in Table 4.13 and Appendix 5(a and b). and Table 4.14 and Appendix 6 (a and b) respectively. The mean value for the control samples were used as background value for the calculation of the contamination factor for both soils and sediment. Several locations with relatively higher contamination factors were found with such locations influenced by landuse activities. The large variation between the minimum and maximum contamination factor for both soils and sediments Table 4.13 and Table 4.14, showed that the enrichment of most of the metals may have been influenced by anthrogenic effect.

Table 4.13: Summary of Calculated Contamination Factor for Soils in the study area

| Statistics | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Minimum | 0.3 | 0.4 | 0 | 0.1 | 0.3 | 0 | 0.0 | 0.0 | 0 | 0 |
| Maximum | 158.2 | 111.3 | 563 | 107.5 | 195.0 | 26 | 6.5 | 20.6 | 2 | 13 |
| Mean | 9.9 | 8.0 | 45 | 7.4 | 10.0 | 6 | 1.3 | 1.7 | 1 | 2 |

Table 4.14: Summary of Calculated Contamination Factor for Sediments of the study area.

| | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Minimum | 1.9 | 1.1 | 6 | 3.0 | 3.7 | 2 | 0.1 | 0.0 | 0 | 0 |
| Minimum | 31.9 | 29.7 | 79 | 41.3 | 25.0 | 17 | 4.0 | 3.2 | 2 | 2 |
| Mean | 9.9 | 6.5 | 30 | 8.9 | 8.9 | 5 | 1.6 | 1.1 | 1 | 1 |

### 4.10.3 Metal Ratios for soils and sediments

The results for the calculated metal ratios for soils and sediments are presented in Table 4.15, Table 4.16 and Appendix 6 (a and b). Quantification of the metal ratios for these selected elements were carried out by comparing the determined concentration in soil and sediments with the values of the Average Shale Concentration, by Turekian and Wedepohl (1961) . From the results, some locations exhibits metal ratio value < 1.0 for almost all the selected trace elements which suggest that such locations have not attained pollution status that calls for concern(Table 4.15 and Table 4.16.) there are many other locations were the value of the metal ratio is with 1.0 values which sugest optimal value. Again there are many other locations that the metal ratio for both the soils and sediments are greater than 1 (>1.0) which suggest hotspots high pollution effect. Elements such as Pb, Zn, Mn show significant higher metal ratios in many locations > 1 for both soils and sediments which calls for concern while elements such as V and Cr have lower Metal ratios in many locations for soils and sediment Appedix 6 (a and b). locations with relatively higher metal ratios were observed to have been influenced by landuse. Areas such Mechanic and metal workshops, Active waste dumps sites, roadside drian sediments, Indemilli river among others which received huge volume of human related waste were found to exhibit higher metal ratio.

Table 4.15: Summary of Calculated Metal Ratio for Soils in the study area

| Stat | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| Min | 0.04 | 0.32 | 0.03 | 0.00 | 0.01 | 0.01 | 0 | 0.00 | 0.12 | 0.15 |
| Max | 22.46 | 101.32 | 93.28 | 2.96 | 6.83 | 2.50 | 2.73 | 34.33 | 0.95 | 4.43 |
| Mean | 1.40 | 7.31 | 7.40 | 0.20 | 0.35 | 0.58 | 0.54 | 2.87 | 0.59 | 0.59 |

Table 4.16: Summary of Calculated Metal Ratio for Sediments in the study area.

| Stat | Cu | Pb | Zn | Ni | Co | Mn | Cd | V | Cr | As |
|---|---|---|---|---|---|---|---|---|---|---|
| Min | 0.27 | 0.99 | 1.06 | 0.08 | 0.13 | 0.06 | 0.00 | 0.23 | 0.33 | 0.06 |
| Max | 4.53 | 27.01 | 13.03 | 1.14 | 0.88 | 1.69 | 5.33 | 0.93 | 1.23 | 1.69 |
| Mean | 1.40 | 5.87 | 4.93 | 0.24 | 0.31 | 0.66 | 1.80 | 0.59 | 0.58 | 0.66 |

## 4.11 Lead Isotope Geochemistry of lead(Pb) in soils and sediemts

The results of the ratios of lead isotope analysed from the soils and sediment in the study area as well as coal, ore galena, vehicle exhuast and cell battery samples are presented in Table 4.17. The ratios are $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, $^{208}$Pb/$^{204}$Pb and $^{206}$Pb/$^{207}$Pb. The results showed varying compositions from one land use area to another in their mean ratios, Table 4.13. The results of $^{206}$Pb/$^{204}$Pb ratio are similar for all the land use, (Table4.13 and Appendix 4.) The highest concentration ratio for $^{206}$Pb/$^{204}$Pb was recorded the lead ore (galena) (20.30) against the mean ratio of residential area (RA) (17.63), school and office complex (SOC) (17.56), active waste dump site (AWD) (17.40), market and abattoir (MAP) (17.56), among others. The ratio of mechanic and metal workshops (MWM) (16.73) was found to be low compare to the other land use area. The $^{206}$Pb/$^{204}$Pb isotope signature show close resemblace with most of the land use, except for the lead ore and vehicle exhuast. This implies that the lead in these soils and sediments may have be enriched by a combination of more that one anthrogenic effect hence the close resemblance with battery cell, coal and vehicle exhuast but different completely from the galena ore isotope ratio.

There is a varying signature in $^{207}$Pb/$^{204}$Pb in the various landuse samples, Appendic 7 and Table 4.17. One clear observation is that the ratio of lead ore is significantly higher (16.32) compare to the other land use ratio, while there is a close resemblace between the ratio of vehicle exhuast (15.21) compare to most of the other land use Pb ratio, suggesting that most of the Pb in the samples analysed may have been enriched from input of vehicular activities.

Similarly, the ratio of $^{208}$Pb/$^{204}$Pb exhibited relative variation in ratio signatures among the various land use. The mean ratio of $^{208}$Pb/$^{204}$Pb (33.93) in MWM is the lowest while the highest ratio was found in galena Ore (39.22). other land use showed close resembrance in their ratio, Table 4.17 and Appendix 7. This shows similar sources of Pb element in the soils and sediment which is likely going to be more than one source of Pb enrichment.

The mean ratios of $^{206}$Pb/$^{207}$Pb (1.15 ±0.01) showed identical signature for most of the land use, Table 4.13, compare to the ratios of Lead Ore and Coal which showed (1.24 and 1.22) respectively which are significantly higher that most of the mean ratios of the different land use.

This appenrently suggest that the lead(Pb) in the soils and sediments may have been derived from atleast two sources, hence the close resemblance among the various land use as against the mechanicanic and metal workshops (MWM), Galena Ore and Coal which may have less source of Pb in the media.

Table 4.17: Lead Isotope compositions of soils, sediments, coal, vehicle exhaust and Ore-galena in the study area

| Sample | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb | 206Pb/207Pb |
|---|---|---|---|---|
| RA | 17.63 | 15.25 | 35.70 | 1.15 |
| SOC | 17.56 | 15.18 | 36.40 | 1.15 |
| MAP | 17.56 | 15.32 | 36.09 | 1.15 |
| MWM | 16.73 | 14.58 | 33.93 | 1.15 |
| FLG | 18.46 | 15.85 | 38.03 | 1.16 |
| AWD | 17.40 | 15.09 | 35.30 | 1.15 |
| ID | 17.42 | 15.15 | 35.24 | 1.15 |
| NK | 18.07 | 15.62 | 36.44 | 1.15 |
| RSD | 17.58 | 15.38 | 35.82 | 1.14 |
| CT | 17.82 | 15.54 | 37.59 | 1.15 |
| Coal | 17.64 | 14.41 | 34.83 | 1.22 |
| Galena | 20.3 | 16.32 | 39.22 | 1.24 |
| Vehicle exhaust | 18.9 | 15.21 | 36.3 | 1.15 |
| Battery cell | 17.23 | 14.43 | 34.15 | 1.19 |

The ratios of $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}$ , $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$, $^{208}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ in the soils and sediment analysed in this research are plotted in Figure 4.82 – 4.85 this various ratios exhibitted relatively near linear relationship among the land use except with galena ore, coal ore and vehicle exhuast. This characteristics is found to be such that these media have relatively less source of Pb concent enrichment as against the other land use that have apperntly more sources and same sources of Pb content enrichment in the media, hence their near perfect linear correlation, (Fig. 4.82 - 4.85) The Pb isotope characteristics as exhibitted by the various media (soil and sediment) in the study area, indicate that the Pb content pollution in the study area may have been from not less that two sources, with industrial Pb from gasoline, paint materials and battery cells as major sources of Pb in the environment.

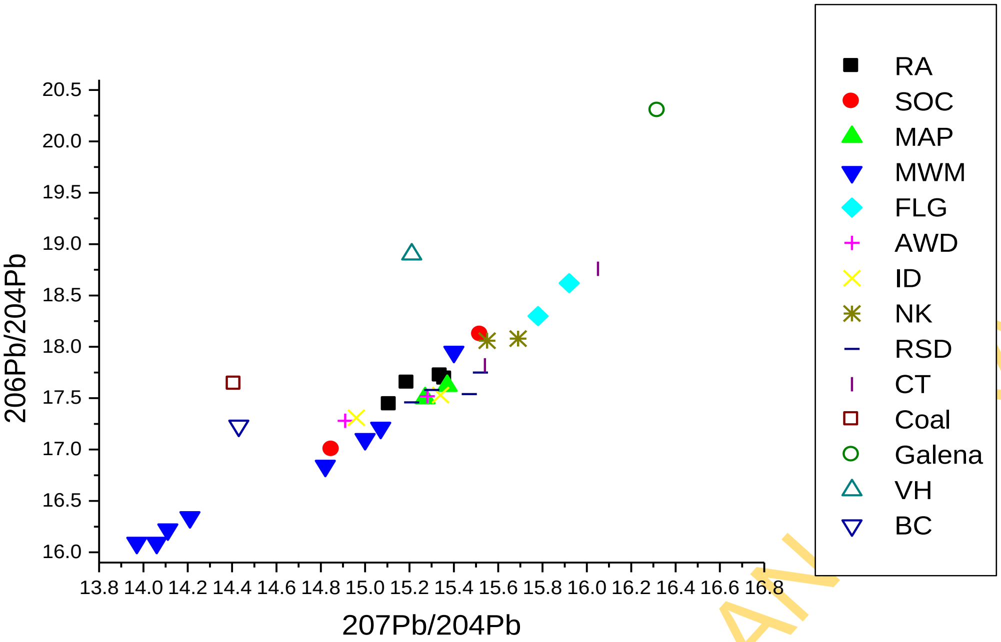


Fig. 4.82: $^{206}$Pb/$^{204}$Pb vs $^{207}$Pb/$^{204}$Pb correlation relationship for the sample media

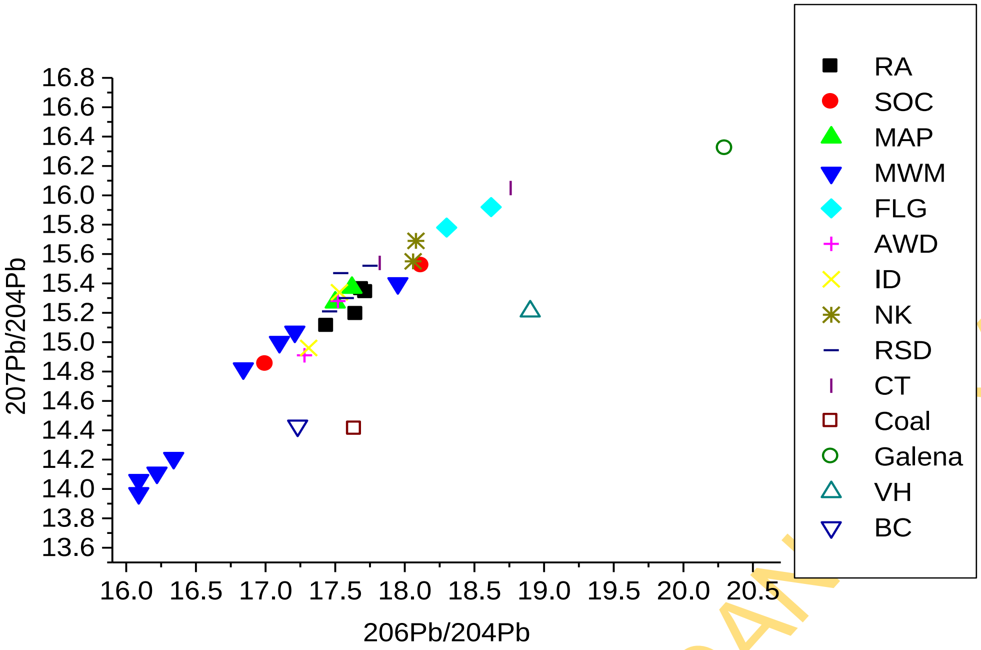


Fig. 4.83: $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ correlation relationship for the sample media

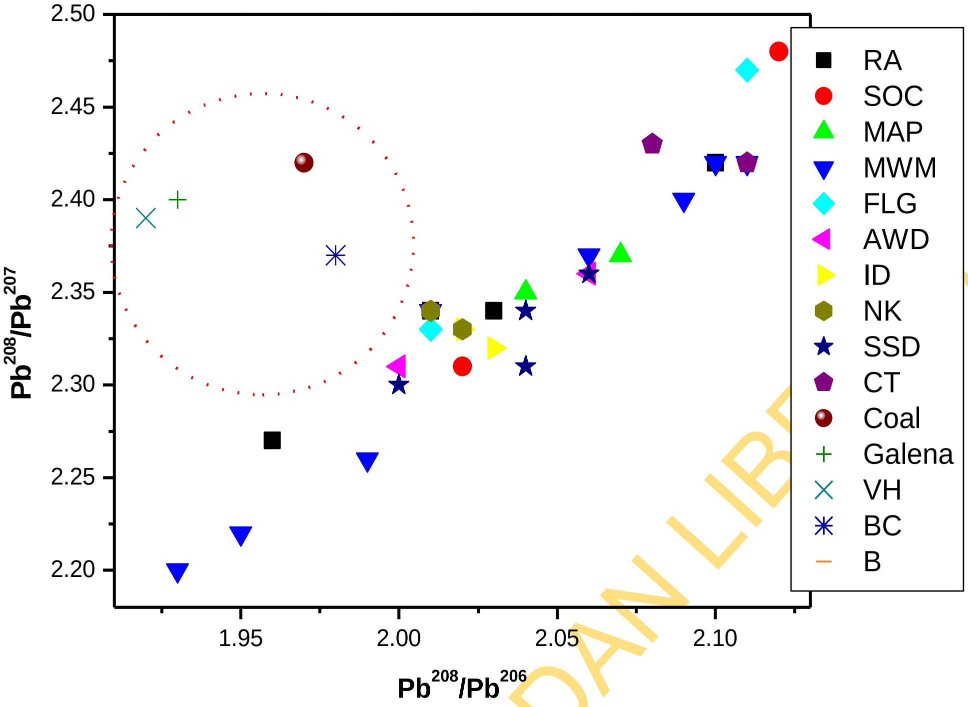


Fig. 4.84: $^{208}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ correlation relationship for the sample media

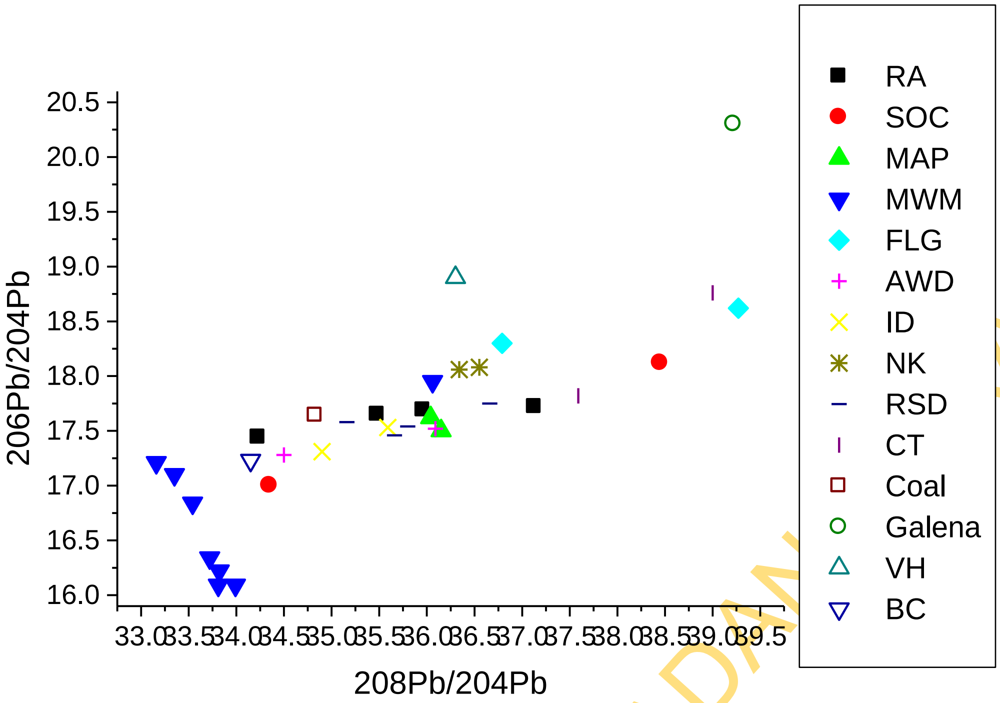


Fig. 4.85: $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$ correlation relationship for the sample media

## 4.12 Geochemical partitioning of trace elements: Result of sequential extraction

Chemical fractionation is a natural phenominor in trace elements within geologic environment, which are coursed by dissolution, precipitation, sorption and complexation (Abdel-Ghani and Elchaghaby, 2007; Abdel-Ghani et al. 2007). The use of sequential extraction method to evaluate phase characteristics within the geologic media is essential, which help to determine the bioavailability of the determined total elemental composition in the environment.

A five step sequential extraction methods fraction were used for both the soils and sediment in the study area. ten (10) samples that had relatively very high concentration of most of the potentially harmful elements were selected for the sequential extraction using LH1 (Demineralised $H_2O$), LH 2 (Carbonate fraction), LH 3 (Organic and Sulfide fraction), LH 4 (Reducible fraction), LH 5 (Residual fraction). The geochemical fractionation pattern of some potentially harmful elements , As, Ba, Cd, Co, Cu, Mn, Ni, Pb and Zn in the soils and sediments are shown in Figure 4.86 – Figure 4.94). the results are expressed in graphical form as leaching percentage, which shows the individual fraction that are removed relative to the sum of all fractions. The selected trace elements showned different chemical fractional availability, which suggest that at different chemical form, element varies relative to the total fractional composition. The chemical fraction of As (figure 4.86) is dominated by the organic and Sulfide fraction (LH 3), with average fractional composition of about 58% of the total As that were analysed and the Ammonium acetate fraction LH 2 average 18%, exhibitting that these two fractions are the most inportant fractions of consideration in terms of its ability to leach such quantity in both soils and sediments. It also become important to note that within the environment, any slit decrease in the pH of the water, it can react with the organic material and As can easily be available to any possible biologic (plants and animals) materials within the environment. The remaining chemical fraction of As are relatively negligable < 22% though of concern, especially that of the demineralise fraction, with < 7% can be said to be negligable to the biota.

The chemical fraction of Ba is dominated by the Reducible fraction (LH 4) and (Residual fraction) LH 5 fraction of mean fractional concentration of 50% and 27% respectively of the total Ba, fig. 4.89. This indicate that larger fraction of the total Ba can only leach to the environment at much lower pH. And that leaching can be effective for mobile Ba element. The remain fraction relatively did not show much enrichment in the demineralise water (LH 1) fraction <1%, Carbonate fraction (LH 2) < 21% and Organic and Sulfide fraction (LH 3) < 2% respectively.

Cd was identified to be bound to the LH2 fraction, Figure 4.88, with an average concentration of about 34% of the total mean Cd in the media. Others with relative fractional affinity are LH 4 33%, LH 5, 15% and LH 3, 11% of the total Cd respectively. Cd did not show much leach with the demineralissed fraction with <1% of total Cd in the media. Co was found to be mostly bound to the LH 4 fraction, accounting for 58% on an average of the total Co. while the other fractions, LH5, LH3, LH2 and LH1 accounted for 22%, 10%, 8% and 0.5% respectively. It shows that most of the Co are bound to the Reducible (LH 4) fraction is such that are of elements that are bound to the silicate phase, relative to the other fractions that has in total 40% of the Co concentration.

Cu was mainly bound to the organic (LH 3) fraction, Figure 4.97, accounting for on the average 52% of total Cu. While the residual (LH 5) fraction contained21% average of the remaining Cu concentration . LH2 8%, LH1 and LH4 each had 4% each respectively of the total Cu. This result shows that most of the Cu are bound to the Organic humic lattice (Fig. 4.90)

Mn exhibits a fractional pattern that shows that substantial fractions of the total Mn are bound to the LH 4 phase, with an average of 61% of the total Cu, while the remaining fraction has 39% of the total Mn in the samples. LH5 13%, LH 2 13%, LH3 11% and LH1, < 2% respectively. The relatively high proportion of Mn in the LH 4, fraction suggest that Mn is bounded more to the silicate lattice of the media analysed in the study area (Fig. 4.91)

The chemical fractionation of Ni shows that Ni has more potentially bioavailable element in the study media. A combination of LH 1, LH 2, and LH 3 fraction gives an average concentration of 30%. Though majority of Ni are bounded to the LH 5 fraction (34%) and LH 4 (38%) respectively, the relatively high proportion of LH 1, LH 2 and LH 3, suggest that under such favourable geochemical condition, it is possible for concederable proportion of total Ni to be bioavailable in the environment (Fig. 4.92).

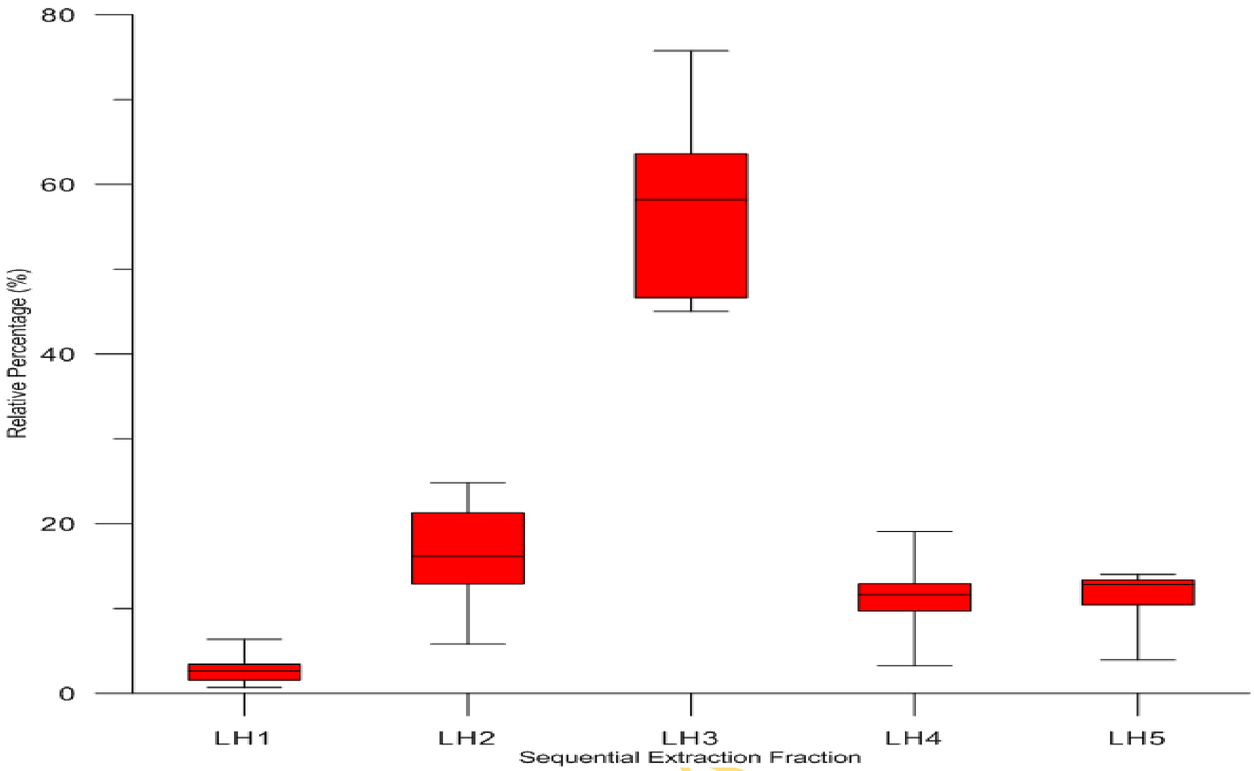
The geochemical phases exhibited by Pb shows that Pb is bounded more to the LH 5 fraction, accounting to an average of 66% of the total Pb in the study media. LH 4 accountted for 14%, LH 3, 13%, LH 2, 11% while LH 1 fraction is significantly less than 1% respective on the average of total Pb concentration in the study media. The relatively high proportion of Pb bound to LH 5 fraction shows that Ph in the study media Is bound to the silicate lattice, which suggest that it present does not show much bioavailability under normal environmental condition (Fig. 4.93)

The geochemical association of Zn in the study media is dominated by LH 2 (average 33%), and LH 4 (average 32%), Figure 4.94, of the total Zn concnetration respectively. LH 3 fraction accounted for (average 19%), LH 5 fraction (average 14% and LH 1 (average 1%). Zn concentration in the soils and sediment in many of the sample location had relatively high concentration, with the relatively high proportion of Zn in LH 2 accounting for (average 33%) of the total Zn, this calls for concern since any slight decrease in the pH in the environment of over 30% of total Zn will be released to the environment

### 4.13 Geochemical and Environmental impotance of solid phase partitioning

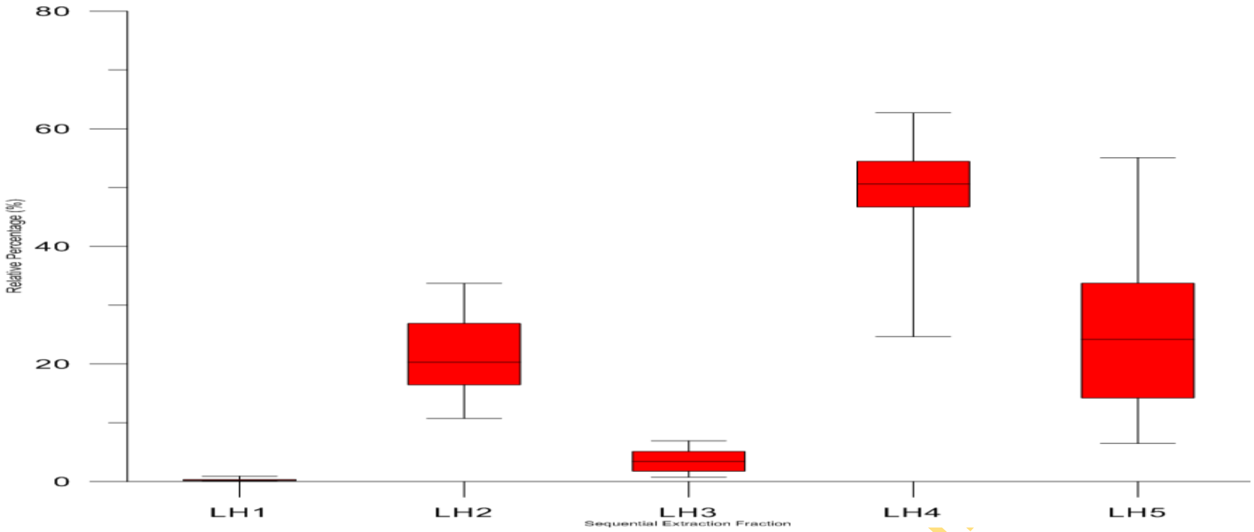
The results of the solid phase partitioning of the soil and sediment analysed suggest that comparative mibility and bioavailability of the metals in Onitsha metropolis tends to decrease in the following order Zn > Cd > Cu > AS > Ni > Co > Ba > Mn > Pb. From the results of metal partitionning in the soils and sediment from Onitsha indicates that any change in the pH in the environment changing toward weak acidic conditions may possibly remobilise substantial percentage of Zn (21 – 62%) for both LH1 +LH11, for Cd and Cu (> 56% and >40%) respectively. Hence acid rain (pH < 5.8) may appreciably dissolve substancial quantity of total Zn, Cd and Cu in the soil and sediment. This same chemical characteristics is been exhibited for As were as LH1 + LH2 apparently releases up to 30% of total As content in the soil and sediment. This cannot be said for Ba, Mn and Pb were much of the total concentration are leached at LH4 and LH5 respectively, which are more of higher strength of extraction reagent (cold and hot hydroxyamine HCl) respectively, of which such conditions though possible, are always very rear.

In terms of eco-toxicity, Zn, Cd, Cu and As are much of great concern, hence need frequent environmental monitoring for possible potential hazard. This is because of the quantum of the fractions of these elements release from weaker reagent which can possibly be exhibited by the soils and sediment as against the other element analyzed that are mainly leached in the reducible and residual fractions. Lead (Pb) was found to be mainly contained in the residual fraction, suggesting that the bioavailability health risk of Pb leaching is comparatively little, which suggests that Pb is of minor concern as it relate to eco-toxicity. Trace elements that are leached from soils and sediment eventually are drained through both the artificial and natural drains to the River Niger. Again, other pathways of metals such as the continuous cultivation of non-seasonal crops along the banks of the rivers, wet land in the area, rearing of animals that frequently feed on surface water, grasses in the streams and respiratory pathway from dust particles among other possible means are what should be considered.



As

Fig. 4.86: Result of five-step sequential extraction of As in soil and sediments of the study area



Ba

Fig. 4.87: Result of five-step sequential extraction of Ba in soil and sediments of the study area

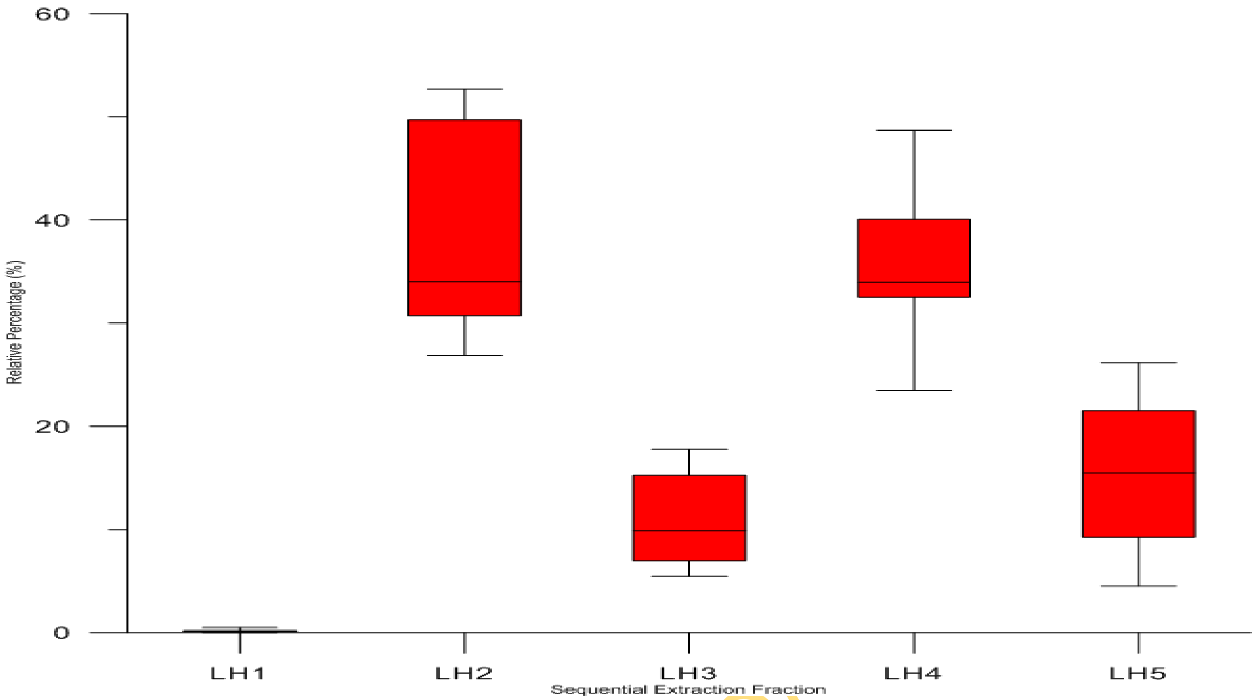


Fig. 4.88: Result of five-step sequential extraction of Cd in soil and sediments of the study area

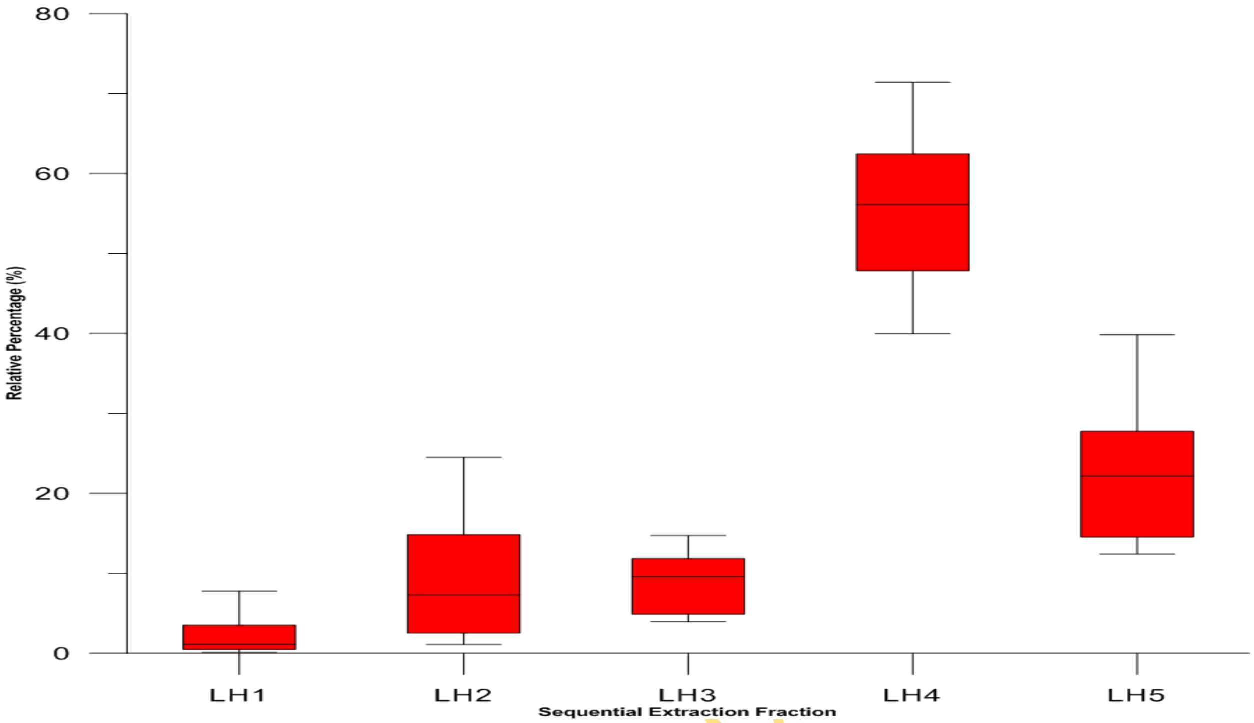


Fig. 4.89: Result of five-step sequential extraction of Co in soil and sediments of the study area

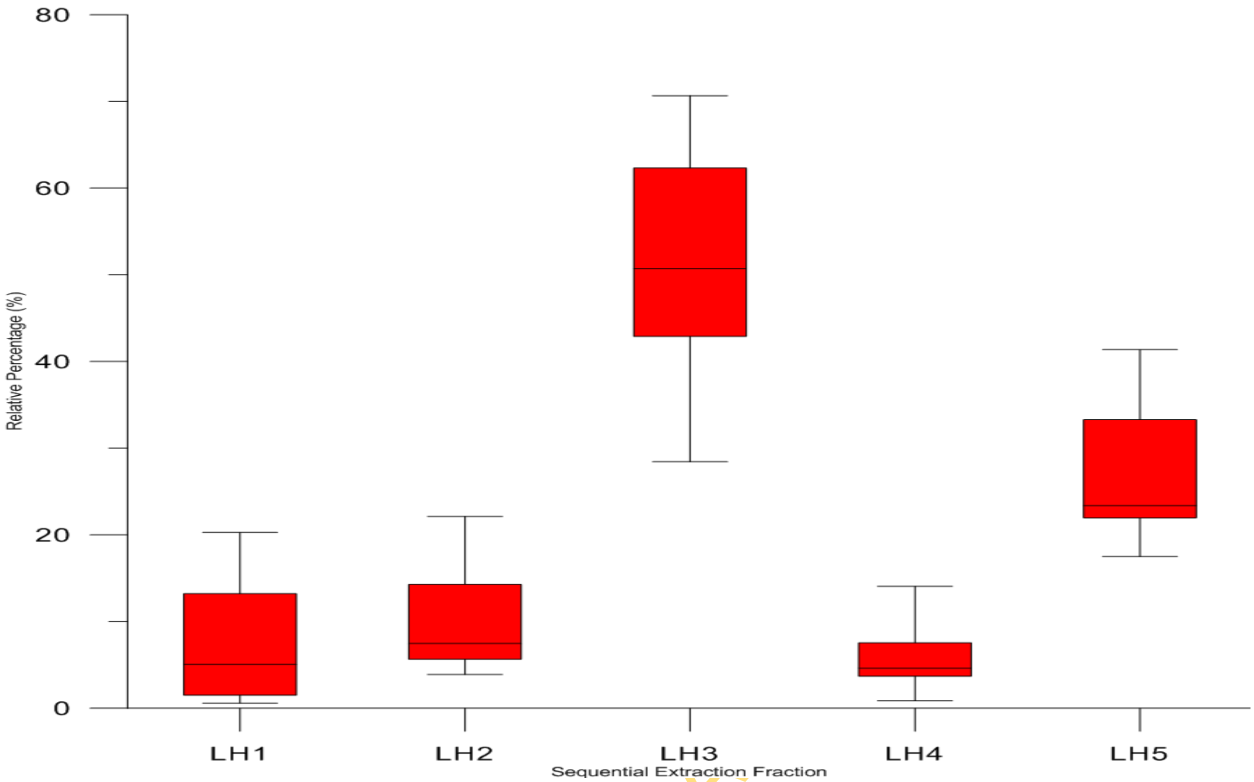


Fig. 4.90: Result of five-step sequential extraction of Cu in soil and sediments of the study area

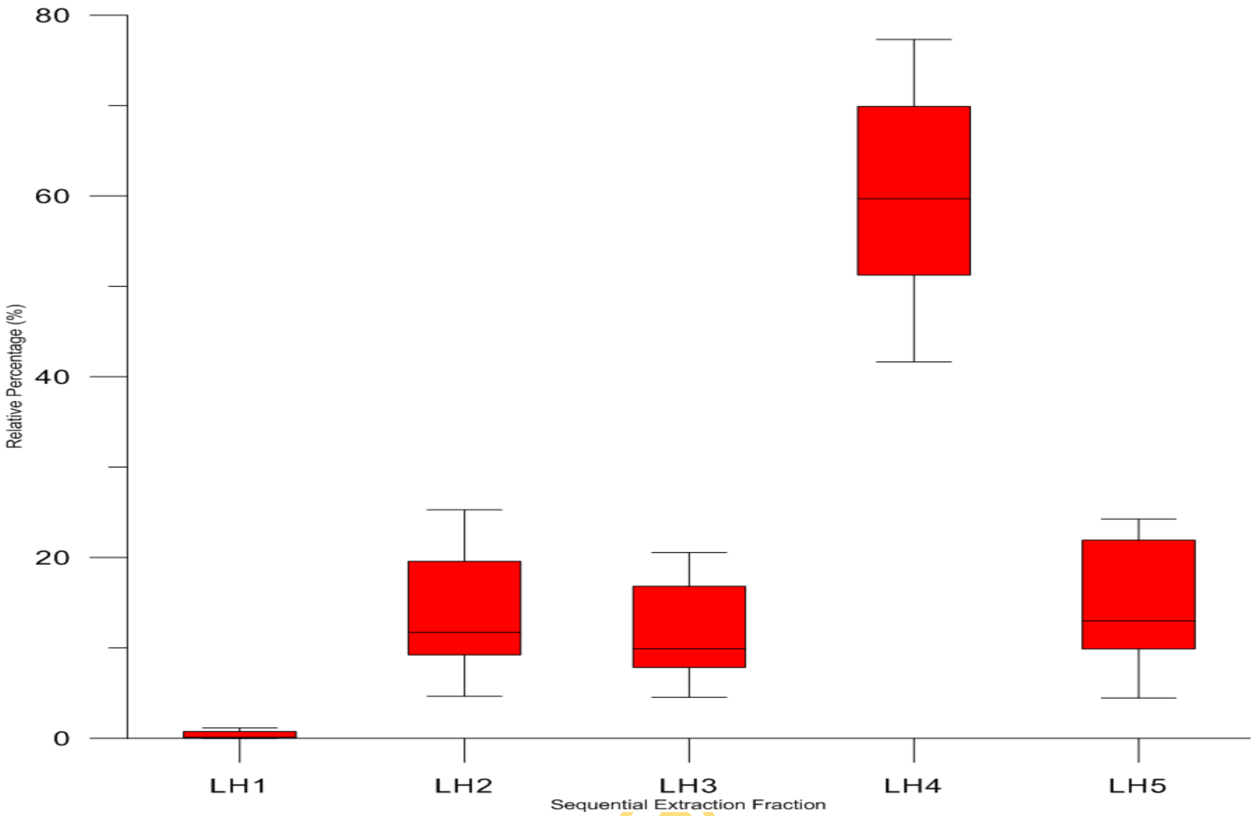


Fig. 4.91: Result of five-step sequential extraction of Mn in soil and sediments of the study area

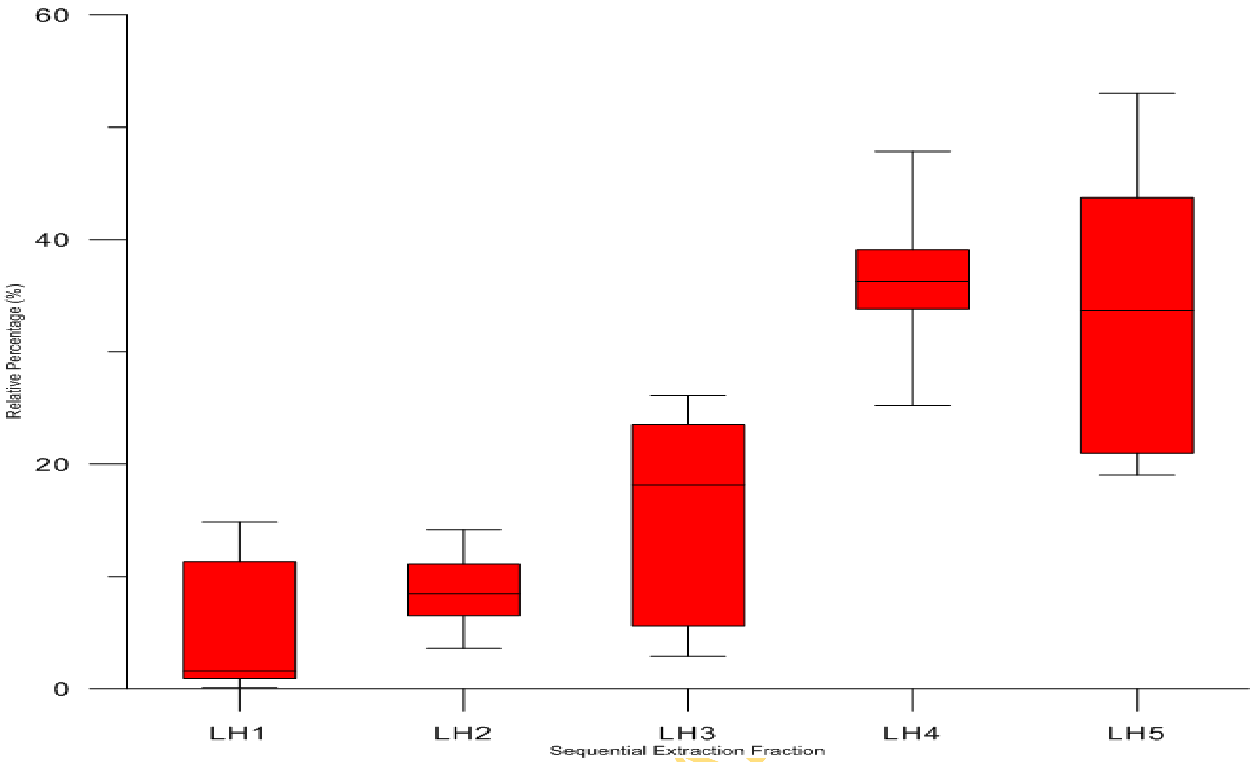


Fig. 4.92: Result of five-step sequential extraction of Ni in soil and sediments of the study area

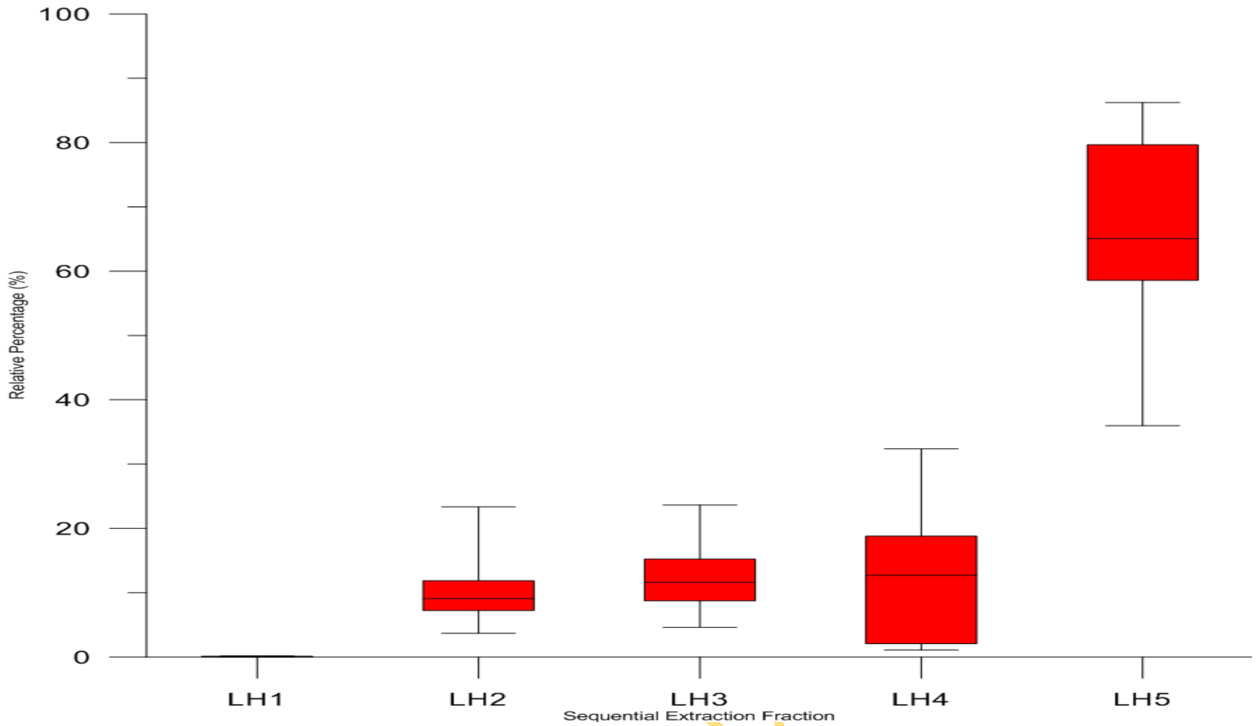


Fig. 4.93: Result of five-step sequential extraction of Pb in soil and sediments of the study area

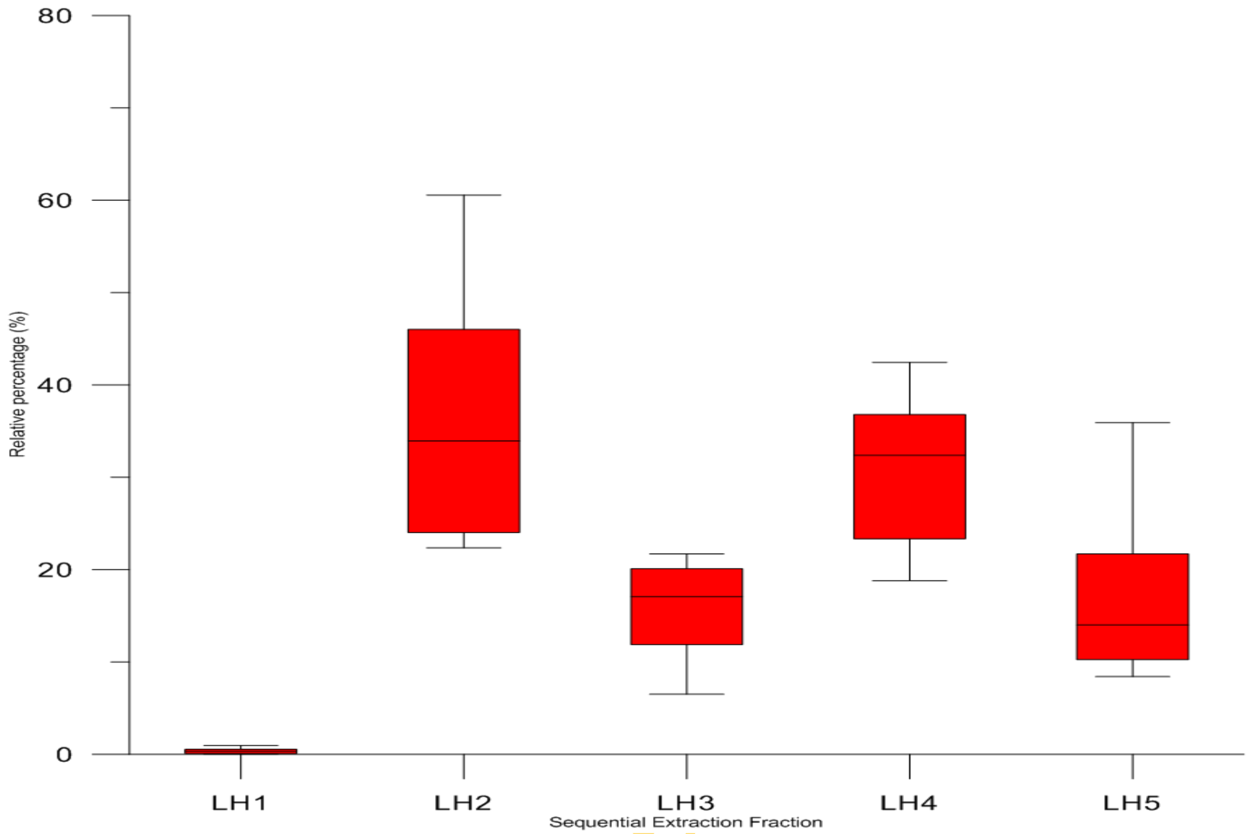


Fig. 4.94: Result of five-step sequential extraction of Zn in soil and sediments of the study area

## 4.14 Geochemistry of Polycyclic Aromatic Hydrocarbon (PAHs) in Soils and Sediments

The results of the concentrations of polycyclic aromatic hydrocarbon for soils and sediments in the study area are presented in Table 4.18, Table 4.19 and Appendix 8(a-d). Of the 16 PAHs, analysed for, 13 PAHs were detected in the soils and sediments with varying concentration from one location to the other. These PAHs include Fluorene, Anthracene, Phenanthrene, Fluoranthrene, Pyrene, Benzo[a]anthracene, Crysene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Indeno(1,2,3-cd)pyrene and Dibenzo[ah]anthracene. The other three PAHs that were not detected include Naphthalene, Acenaphthylene and Acenaphthene. The result of the concentration of Fluorene was found to be relatively high in soils collected from Mechanic and metal workshop vicinity with the highest concentration of Fluorene found in location MWM/11 (122.2 µg/kg). Other locations with relatively high concentration of Fluorene in (µg/kg) include MWM/9 (33.7), MWM/2A (16.9), ID/3 (20.1), ID/4 (31.1), ID/6 (20.2), ID/9 (12.9), AWD/3A (36.7) and MAP/2 (15.3), Appendix 8. Most of the samples in FLG, SOC and the control samples were found to be below detection limit. Summary result for Fluorene is contained in Table 4.18.

The content of Anthracene concentration showed varying concentration from one location to the other. The highest concentration was found in location MWM/11 (55.3µg/kg), location MWM/9 (41.8 µg/kg) also exhibited relatively high concentration of Anthracene relative to most other locations were low concentration were found, Appendix 8. Examples of such were locations FLG 3A, RK 20, SOC 5 among others with concentration (1, n.d and 1) in µg/kg respectively. Both the side drain sediments and the sediments from river Nkisi and NdeMilli exhibited relatively high concentration (µg/kg) of Anthracene; ID/3 (27.9), ID/4 (37.1), ID/5 (23.5), ID/6 (30.0), ID/9 (46.0), NK/14 (14.3) and NK/20 (16.2), Appendix 8.

The concentration of Phenanthrene also exhibited varying distribution in concentration in both the soils and sediment. The highest concentration of Phenanthrene was found in location MWM/11 (2045.8 µg/kg). Other locations with relatively high concentration of Phenenthrene were AWD/5A (245.3 µg/kg), MAP2 (229.9 µg/kg), RSD/20 (227.9 µg/kg), ID/3 (208.6 µg/kg), ID/4 (266.2 µg/kg) among others. Comparing these results with the control sample CT/4 (1.0 µg/kg) as well as other locations with relatively low concentration, appendix 8, it can be said there is considerable enrichment of Phenanthrene in those to over 2 to 10 fold.

Fluorathene concentration in soils sediments in the study area also exhibited spatial distribution as seen in the other compound earlier discussed. Relatively higher concentration of Fluorathene were found in locations RSD/20 (602.9 µg/kg), MWM/11 (463.5 µg/kg), AWD/5A (483.7 µg/kg), compare to other locations with relatively low concentration, such locations include CT/4 (1.0 µg/kg), SOC/2A (9.2 µg/kg), and FLG/3A (4.1 µg/kg) among others, Appendix 6

The concentration of Pyrene in the study area was found to vary from one location to the other. Relatively high concentration were found in locations MWM/3A (431.5 µg/kg), MWM/11 (533.4 µg/kg), ID/9 (531.8 µg/kg), compare to the control samples CT/4, and RK/1 which recorded NOT Detected (n.d) and some other locations with relatively lower concentration; FLG/3 (3.7 µg/kg), SOC/2A (7.1 µg/kg) among others. Other locations exhibited moderate to low concentration, appendix 6.

Benzo (a) anthracene compound concentration in the study area exhibited spatial variation in concentration in soils and sediments of the study area. Relatively high concentration were found in locations MWM/11 (127.8 µg/kg), RSD/20 (298.3 µg/kg), ID/9 (226.6 µg/kg) when compared with the control samples; CT/4 (n.d) and RK/2 (1.0 µg/kg). Other locations exhibited moderate to low concentration of Benzo (a) anthracene, Table 4.17, 4.19 and appendix 8.

Chrysene compound in the study area was observed to be present in the soils and sediments in varying concentration from one location to the other. Relatively high concentration were observed in location MWM/10 (426.4 µg/kg), MWW/11 (348.5 µg/kg), RSD/20 (336.8 µg/kg), MAP/2 (204.1 µg/kg) among others, compare to the concentration of the control samples; CT/4 (1.0 µg/kg), and RK/2 (3.9 µg/kg). Other locations with relatively low concentration of Chrysene include FLG/3A (1.3 µg/kg), RA/21 (8.1 µg/kg) among other locations of such, appendix 8.

Benzo[k] Fluoranthene compound exhibited varying concentrations in the soils and sediment that were analysed. Relatively moderate to low concentration were observed in virtually all the locations. Areas with relatively high concentration, include MWM/9 (166.5 µg/kg), SSD/20

(163.5 µg/kg), ID/9 (106.6 µg/kg), and MAP/2 (84.9 µg/kg) compare to the result from the central samples, such as CT/4 (n.d), RK/2 (1.0 µg/kg) as well as other locations with relatively very low concentration; FLG/3A (1.0 µg/kg), SOC/2A (2.4 µg/kg), MAP/1A (2.1 µg/kg) among other locations, appendix 8.

The concentration of Benz(a)Pyrene in the sample media showed spatial distribution from one location to the other. Relatively high concentration of Benzo (a)Pyrene were found in MWM/9 (525.9 µg/kg), RSD/20 (514. µg/kg), RA/18, (253.9 µg/kg), MAP/2 (259.7 µg/kg). The control samples recorded no detection (n.d) for CT and RK/2 (1.0 µg/kg), appendix 8.

The concentration of Benzo (b) Fluoranthene showed varying concentration in the soils and sediments analysed. It was observed that the highest concentration of Benzo (b) Fluoranthene was found in location MWM/9 (502.6 µg/kg). Other locations with relatively high concentration include RSD/20 (452.9 µg/kg), ID/4 (280.2 µg/kg) and RA/4 (247.2 µg/kg). When compared with the result of the control samples CT/4 (n.d), RK/2 (2.8 µg/kg) and other locations with relatively low concentration, such as FLG/3A (1.1 µg/kg) and SOC/2A (8.7 µg/kg). Moderate to low concentrations were recorded in most other locations, Appendix 8.

The result of the concentration of Benzo (ghi) Perylene in the soils and sediments also showed variation in the spatial distribution. The highest concentration was found in location MWM/16A(557.8 µg/kg), other locations with relatively high concentration of Benzo(ghi)Perylene include MWM/9 (500.9 µg/kg), MWM/18 (415.9 µg/kg), RSD 20 (329.3 µg/kg) ID/9 (326.6 µg/kg) among other locations when compared to the results of the control samples, CT/4 (n.d) and RK/2 (1.3) as well as some locations with relatively low concentration such as FLG/3A (1.0 µg/kg) and MAP/1A (8.5 µg/kg), Appendix 8.

Indeno (1,2,3-cd)pyrene compound showed spatial distribution from one location to the other. It was observed that the compound exhibited relatively high concentration in locations MWM/9 (412.2 µg/kg), MWM/16A (305.2 µg/kg), RSD/20 (300.2 µg/kg) and NK/14 (213.9 µg/kg) compare to the results from the control samples CT/4 (n.d) and RK/2 (1.1 µg/kg). Other locations such as FLG/3A (1.0 µg/kg), MAP/1A (6.2 µg/kg) and SOC/2A (5.2 µg/kg) that recorded relatively low concentration, appendix 8.

The concentration of Dibenz(ah)anthracene generally showed relatively moderately low to low concentration in distribution. The highest concentration was found in location SSD/20 (37.0 µg/kg). Other locations with moderately low concentrations of the compound include MWM/9 (33.4 µg/kg), RSD/14 (18.1 µg/kg), ID/9 (21.7 µg/kg) and RA/4 (22.8 µg/kg), compare to the results of the control samples CT/4 (n.d) and RK/2 (n.d). Relatively low concentration were found in RA/21 (1.0 µg/kg), SOC/5 (1.0 µg/kg) as well as many other locations, appendix 6.

The summary results for PAHs concentrations of soils and sediments analyzed are presented in Table 4.13 and Table 4,14. It was observed that there is relative enrichment of PAHs in the soils and sediments studied. This is shown from the spatial distribution of the concentration from location to location, appendix 8(a-d). Generally across the samples collected and analyzed, there were high rate of detection of PAHs in the soils and sediments compare to the control samples which were collected from relatively pristine areas which are at the outskirt of the metropolis. Again the result showed higher concentration in mechanic and metal workshops (MWM) areas, Public parks, waste dump site than residential and farm land/garden soils. Also, high concentrations of PAHs were detected in sediments samples analysed from the side drains and the rivers of Ndemili and Nkisi. These suggest that soils and sediment within the city center and its runoff are more susceptible to the deposition of PAHs from anthropogenic sources such as vehicular emissions, use of herbicides, domestic waste degradation and waste polymer rich materials.

Table 4.18: Summary Results for PAHs concentrations (µg/kg) of soils in Onitsha

| PAH | Min | Max | Mean | Stand dev | CV |
|---|---|---|---|---|---|
| Fluorene | 0 | 122.2 | 7.7 | 20.19 | 2.63 |
| Anthracene | 0 | 55.3 | 9.9 | 12.19 | 1.23 |
| Phenanthrene | 1 | 2045.8 | 137.2 | 324.64 | 2.37 |
| Fluoranthene | 1 | 483.7 | 104.2 | 123.91 | 1.19 |
| Pyrene | 3.7 | 533.4 | 125.1 | 134.36 | 1.07 |
| Benzo[a]anthracene | 1 | 222 | 43.0 | 45.49 | 1.06 |
| Chrysene | 1 | 426.4 | 87.1 | 95.78 | 1.10 |
| Benzo[k]fluoranthene | 1 | 166.5 | 31.0 | 32.73 | 1.05 |
| Benzo[a]pyrene | 1 | 525.9 | 87.3 | 102.56 | 1.18 |
| Benzo[b]fluoranthene | 1.1 | 502.6 | 106.5 | 102.43 | 0.96 |
| Benzo[ghi]perylene | 1 | 557.8 | 140.1 | 149.24 | 1.07 |
| Indeno(1,2,3-cd)pyrene | 1 | 412.2 | 88.9 | 89.86 | 1.01 |
| Dibenz[ah]anthracene | 1 | 33.4 | 6.8 | 7.00 | 1.03 |

Table 4.19: Summary Results for PAHs concentrations (µg/kg ) of sediments in Onitsha

| PAH | Min | Max | Mean | Stand dev | CV |
|---|---|---|---|---|---|
| Fluorene | 1.7 | 31.1 | 10.2 | 8.30 | 0.82 |
| Anthracene | 1.7 | 46 | 19.8 | 12.81 | 0.65 |
| Phenanthrene | 22.2 | 266.2 | 129.1 | 75.27 | 0.58 |
| Fluoranthene | 13.4 | 602.9 | 187.2 | 146.43 | 0.78 |
| Pyrene | 14.1 | 531.8 | 187.5 | 133.67 | 0.71 |
| Benzo[a]anthracene | 5.6 | 298.3 | 93.8 | 71.96 | 0.77 |
| Chrysene | 10 | 385.6 | 150.4 | 94.81 | 0.63 |
| Benzo[k]fluoranthene | 4 | 163.5 | 64.5 | 35.10 | 0.54 |
| Benzo[a]pyrene | 12.9 | 514.9 | 178.9 | 112.16 | 0.63 |
| Benzo[b]fluoranthene | 14.1 | 452.9 | 200.6 | 109.12 | 0.54 |
| Benzo[ghi]perylene | 25.5 | 449.8 | 209.9 | 104.48 | 0.50 |
| Indeno(1,2,3-cd)pyrene | 14.9 | 326 | 169.0 | 81.49 | 0.48 |
| Dibenz[ah]anthracene | 1 | 37 | 13.2 | 8.11 | 0.62 |

The relatively high presence of High Molecular Weight PAHs (HMW) as against the Low Molecular Weight (LMW) PAHs in the soils and sediments as observed suggests that the PAHs are as a result of pyrogenic processes as the dominant sources of PAHs. The HMW PAHs include; Fluoranthrene, Pyrene, Benzo[a]anthracene, Crysene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Indeno(1,2,3-cd)pyrene and Dibenzo[ah]anthracene. While the LMW PAHs include Fluorene, Anthracene and Phenanthrene, appendix 6, Table 4.18 and Table 4.19. It has been reported in many published works (Morillo et al., 2007; Wilcke, 2007 and Glennon et al. 2012) that pyrogenic contamination is characterized by high presence of HWM PAHs over LWMPAHs in soils and sediments.

Table 4.20: Comparative distribution of Polycyclic Aromatic Hydrocarbon of selected countries I the world and the results of this study.

| Location | No of PAHs | ∑PAHs (µg/kg) | Source type | Reference |
|---|---|---|---|---|
| Korea Peninsula | 13 | 109–178 | Industrial | (Hashmi et al. 2005) |
| Beijing, China | 16 | 467–5470 | Urban soil | (Li et al. 2006) |
| Beijing, China | 16 | 16–3884 | Surface soil | (Ma et al. 2005) |
| Canada | 17 | 1400 | Highway | (Wang and Meresz 1982 |
| United Kingdom | 7 | 2000 | Motorway | (Butler et al. 1984) |
| United Kingdom | 16 | 187 | Rural soils | (Wild and Jones 1995) |
| United States | 14 | 3000 | Highway | (Yang et al. 1991) |
| Japan | 8 | 1300800 | Urban soil | (Spitzer and Kuwatsuka 1993) |
| United Kingdom | 16 | 2700500 | Urban soil | (Meharg et al. 1998) |
| New Orleans, United States | 16 | 3731a | Urban soil | (Mielke et al. 2001) |
| West Macedonia, Greece | 16 | 55.2–495 | Lignite fire | (Stalikas, Chaidou, and Pilidis 1997) |
| Igbanko mangrove forest Lagos | 16 | 65.5–188.0 | Forest fire soil | Olatunbosun et al. 2011 |
| Valasske Mezirici, Czech Rep. | 16 | 861-3514 | Agric/urban soils | Daniela et al. 2009 |
| Onitsha | 13 | 20.0-4281.4 | soils and sediments | Current study |

Though scientific data on PAHs characteristics in urban areas are few, the soils and sediments that were investigated in this study was compared with results of published works from other countries, especially with respect to those countries that are relatively large with high industrial activities. It was observed that the soils and sediment analyzed are relatively high (Table 4.20). the 16 PAHs that were analyzed in the city of Beijing, China showed (467 – 5470 µg/kg) of surface soils, while Valasske Mezirici, Czech Republic showed (861-3514 µg/kg) among others in Table 4.20, as compared with our findings (20.0-4281.4 µg/kg) for 13 PAHs, this showed that the soils and sediments in the study area is of great concern, because there is considerably enrichment in the soils and sediment to pollution status.

The spatial values of the TOC in the soils and sediment samples are listed in appendix 8e. The TOC values ranges from 0.12% as found in location CT/4 to 10.5% TOC as found in location AWD/3A and a mean of 2.66%. Generally, the soils and sediment chosen for analyses contain relatively high percentage of TOC values for most locations compare to the control samples Appendix 8e. Activities such as burning of biomass in urban environment could increase the percentage of TOC. Also there was relatively non correlation relationship between the TOC and total PAH concentrations, which apparently suggest that the PAH in the soil are recent contamination and as established by different authors such as (Olatunbusun et al., 2011) yet to fully be partitioned into the organic matter in the soils. Olatunbusun et al. 2011, Baumard et al., 1999 and Simpson et al., 1996 have showed that relationship between TOC and total PAHs in the sediment was significant only if the area is highly contaminated to PAHs of >2000 µg/kg dw. This is further buttressed by the three component principal plot for the compounds with the TOC, fig 4.96, which shows clearly that the PAH occur almost together in cluster form suggesting similar sources of enrichment in the soil and sediment as against the TOC that exhibit non similar occurrence.

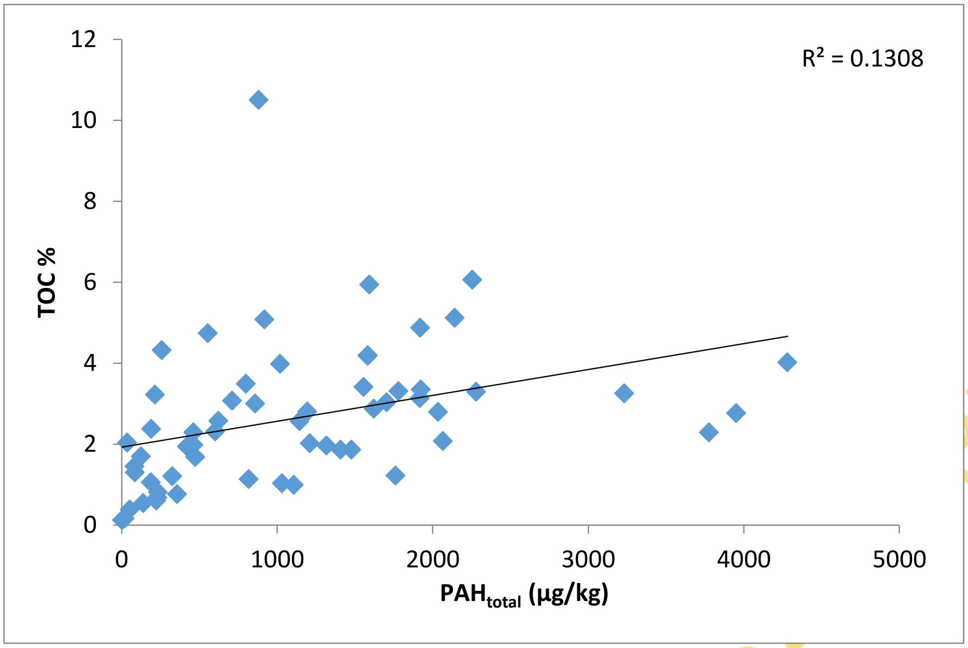


Fig. 4.95: Bivariate plot of between total PAHs and TOC (%) for soils and sediments in the study area.

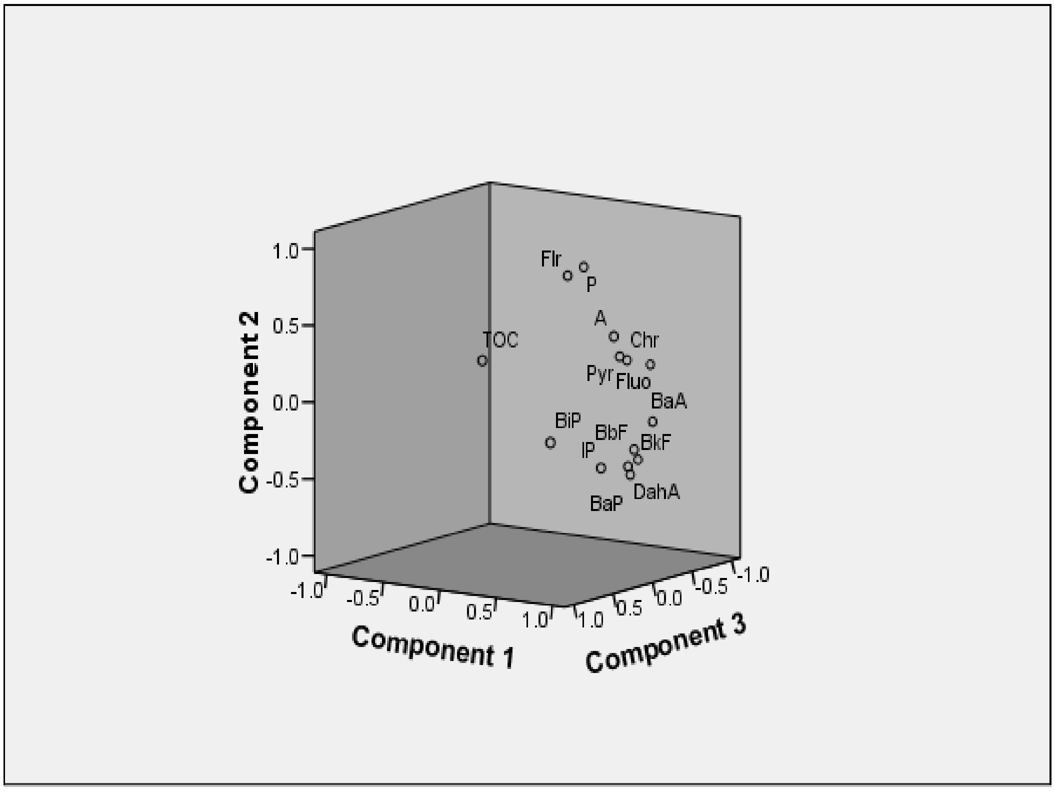


Fig. 4.96: Component plot for PAHs in the soils and sediments in the study area

## 4.15 Spatial distribution map of PAHs in soils and sediment in Onitsha metropolis

Spatial distribution map for Fluorene, Anthracene, Phenanthrene, Fluoranthrene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Indeno(1,2,3-cd)pyrene and Benzo[a]Pyrene were created to easily visualize the spatial distribution of the enrichment pattern of of the soils and sediment analysed in the study area, fig. 4.97 – fig.4.107. Generally, it is observed that the spatial distributions of the various compounds 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 in the study area. Most of these areas are soils collected within the vicinity of mechanic workshops, active waste dump site as well as soils collected close to high traffic highways, appendix 8d and fig4.97 – fig4.107.

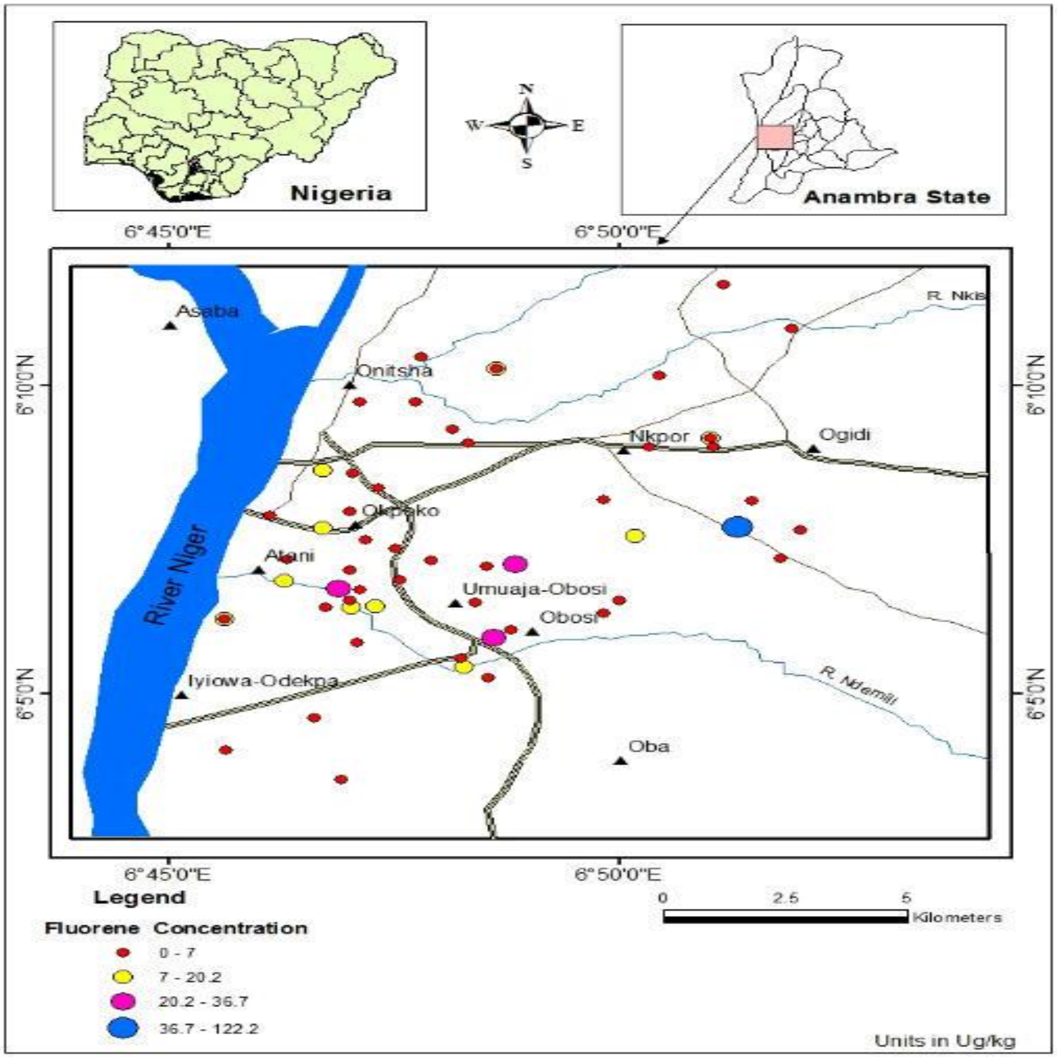


Fig. 4.97: Spatial distribution of Fluorene in soils and sediments of the study area

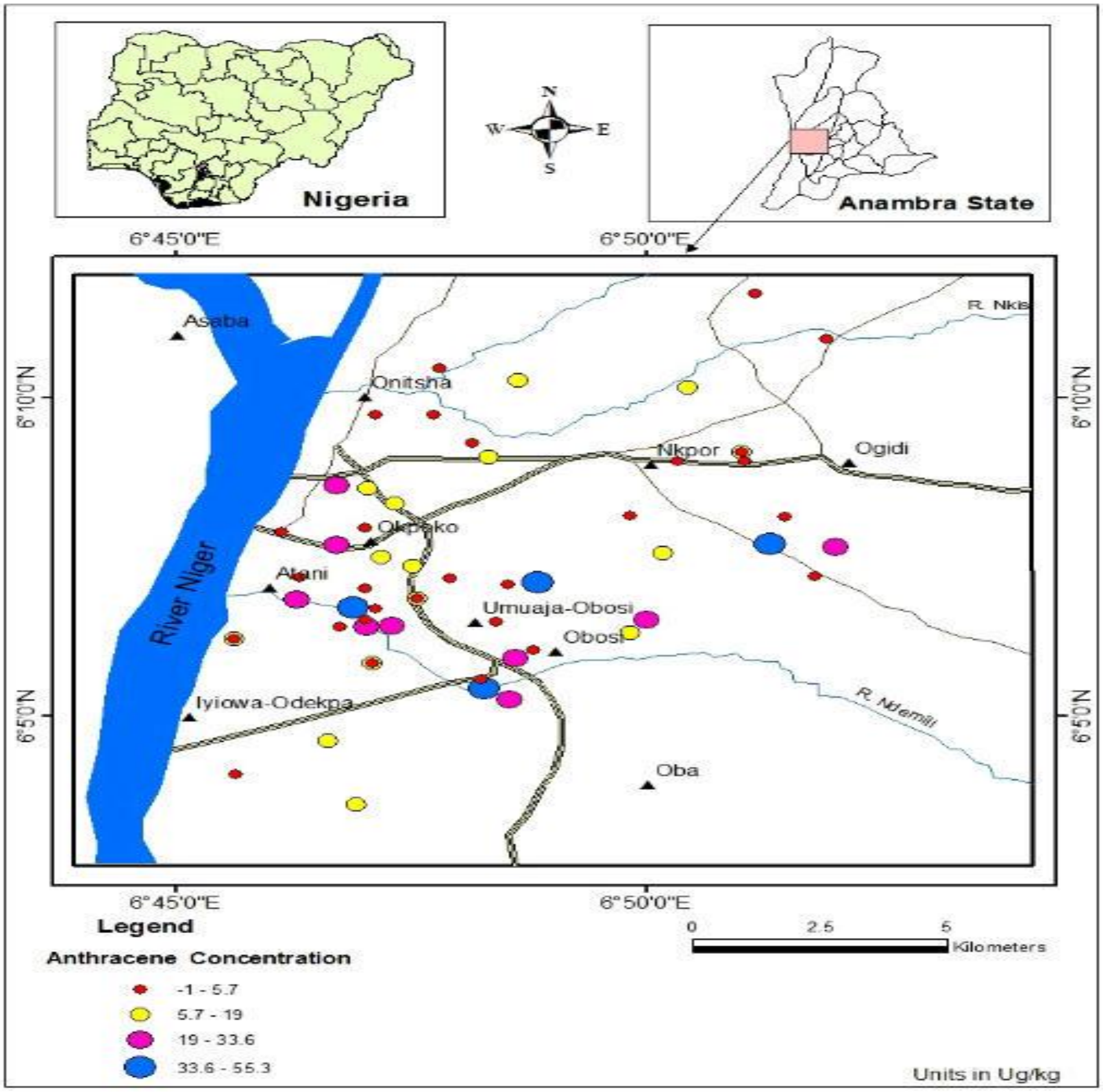


Fig. 4.98: Spatial distribution of Anthracene in soils and sediments of the study area

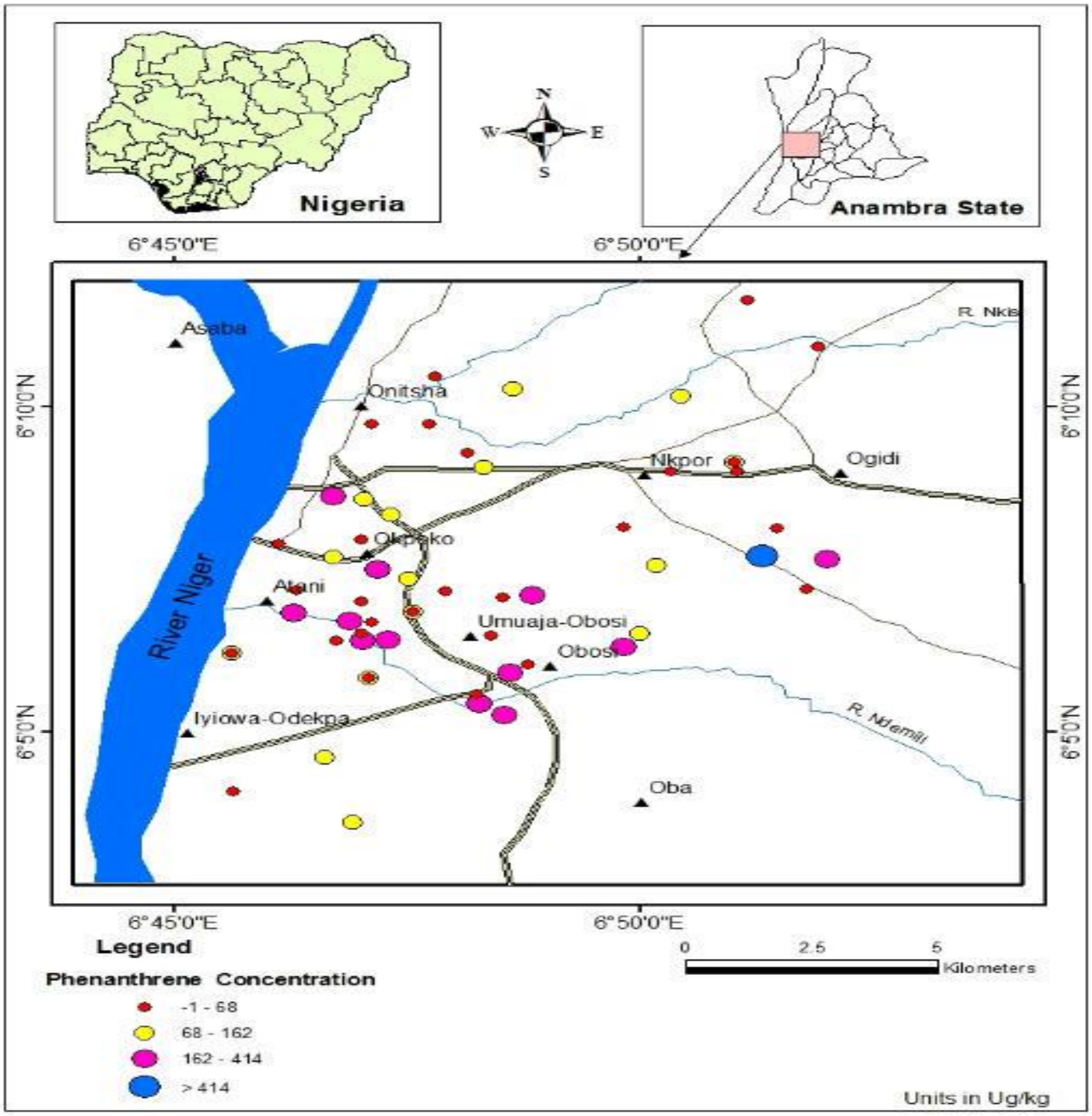


Fig. 4.99: Spatial distribution of Phenanthrene in soils and Sediments of the study area

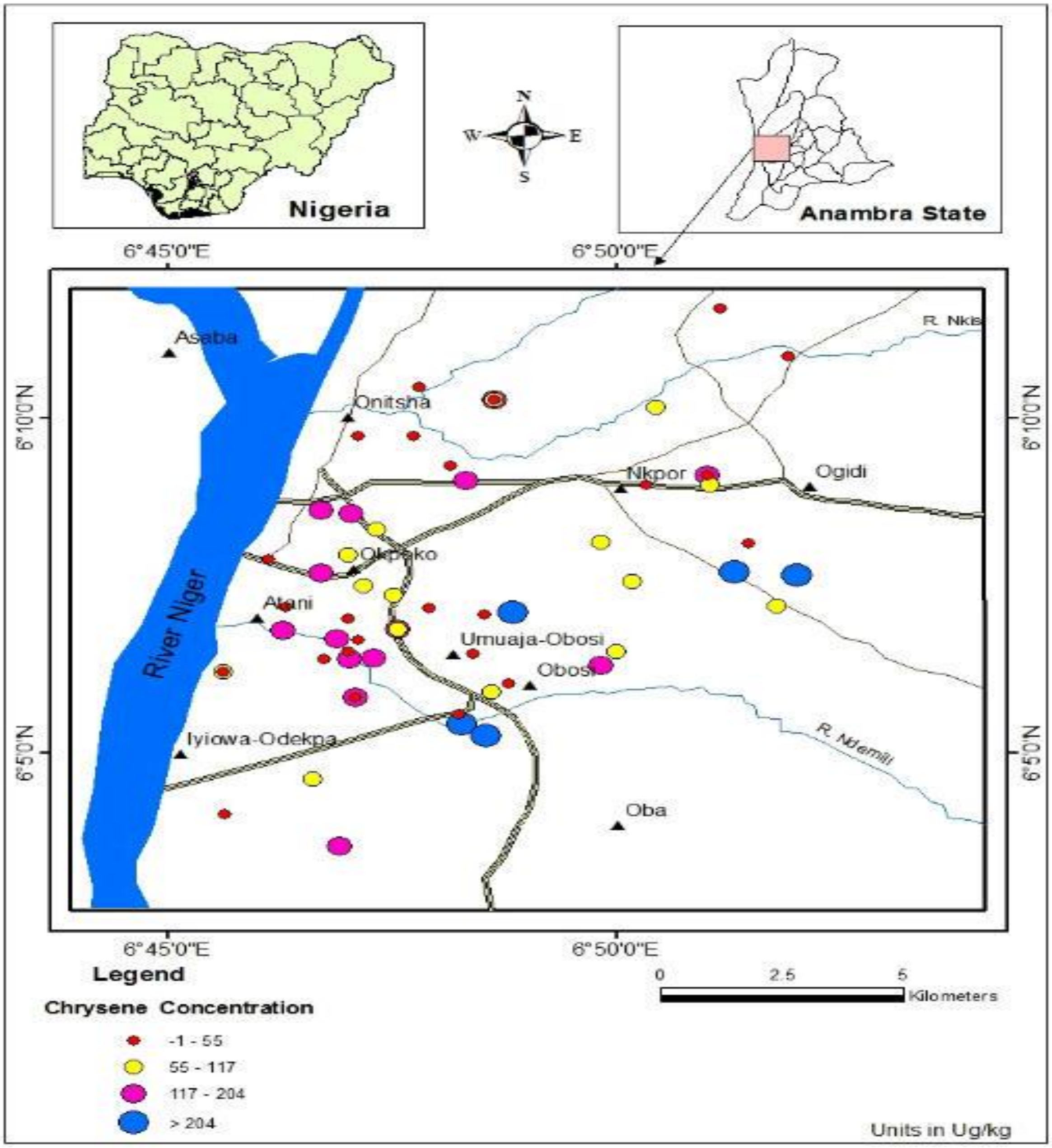


Fig. 4.100: Spatial distribution of Chrysene in soils and sediments of the study area

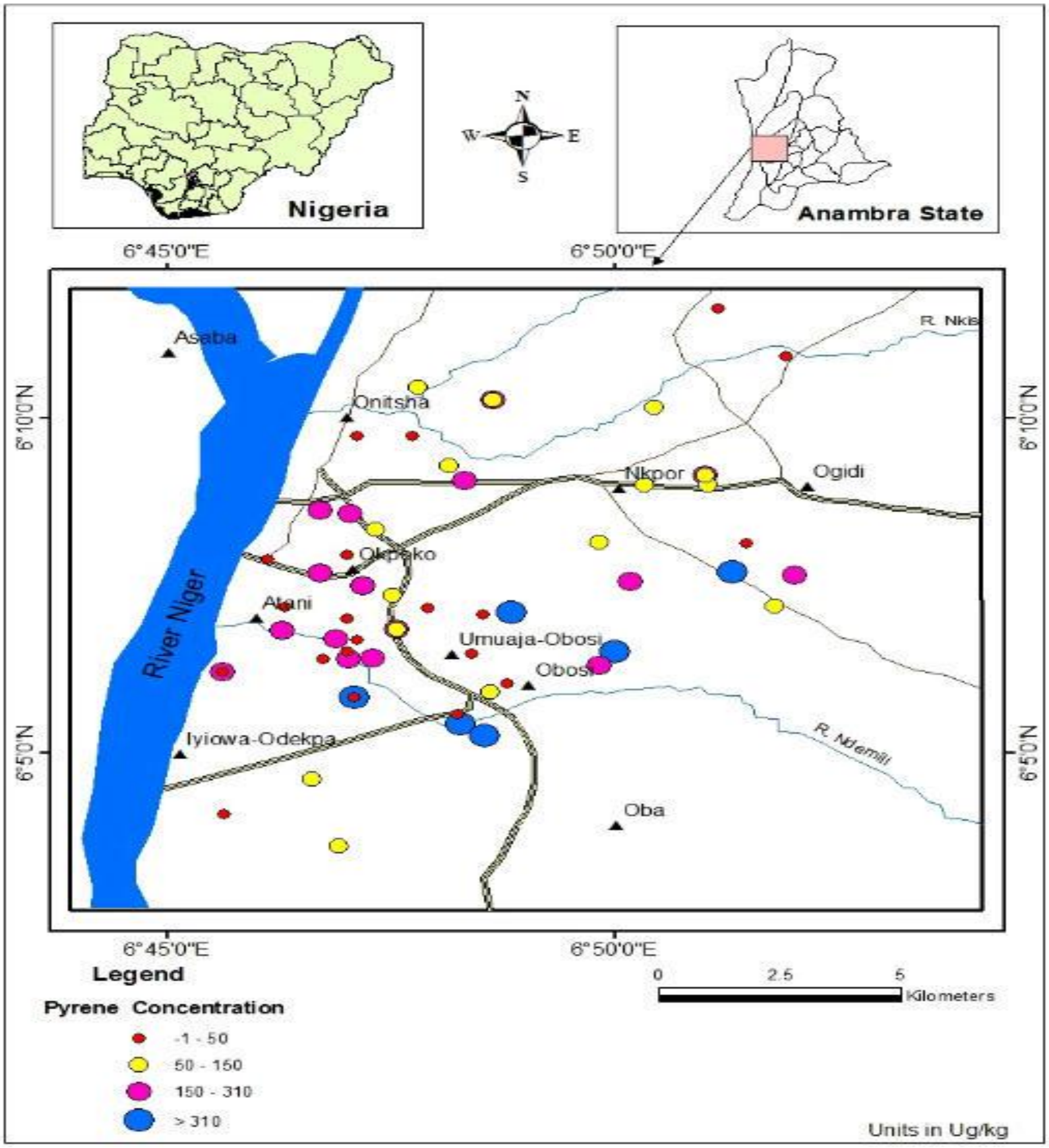


Fig. 4.101: Spatial distribution of Pyrene in soils and Sediments of the study area

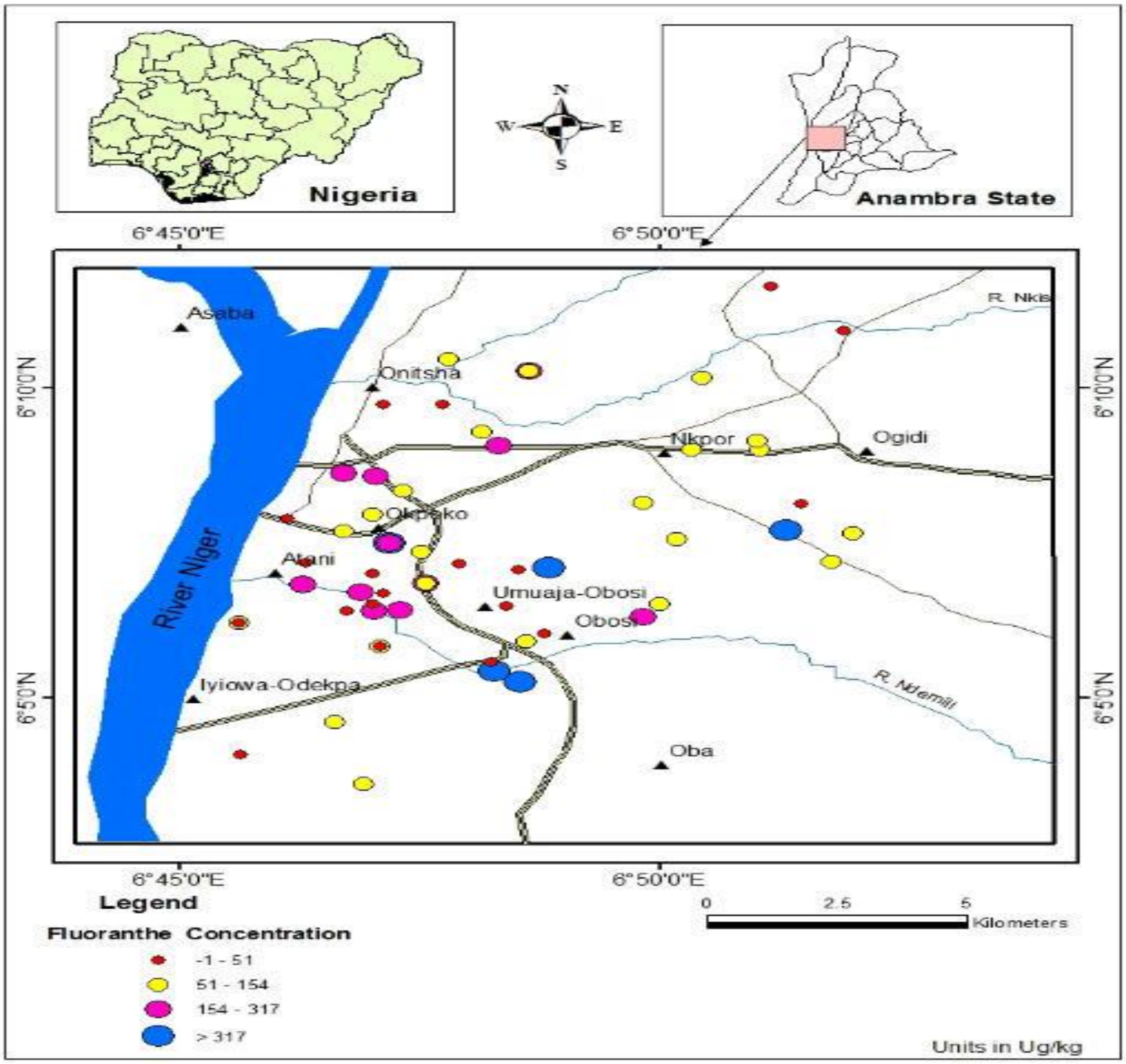


Fig. 4.102: Spatial distribution of Fluoranthene in soils and sediments of the study area

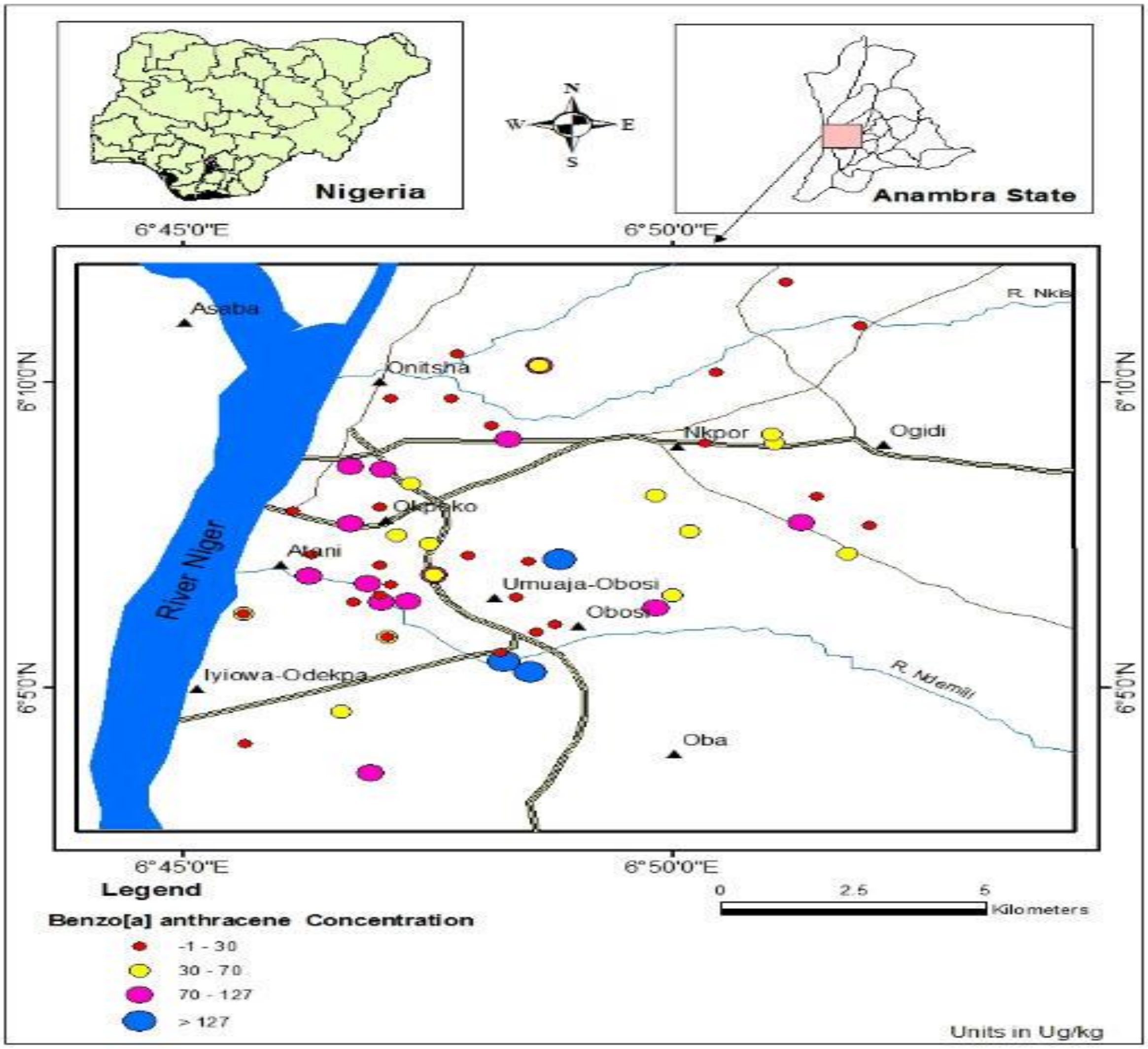


Fig. 4.103: Spatial distribution of Benzo[a]anthracene in soils and sediments of thestudy area

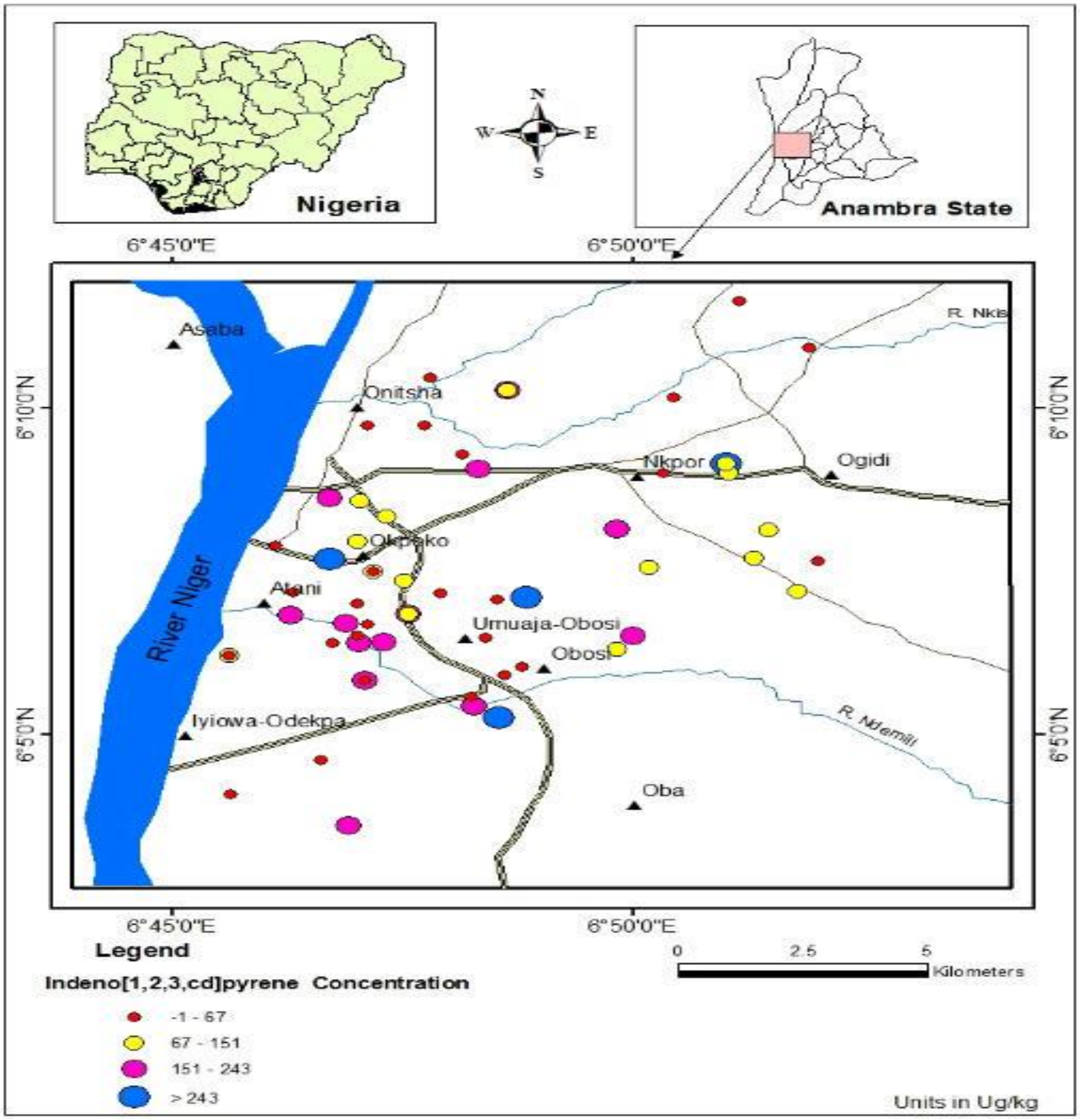


Fig. 4.104: Spatial distribution of indeno [1, 2, 3, cd] pyrene in soils and sediments of the study area

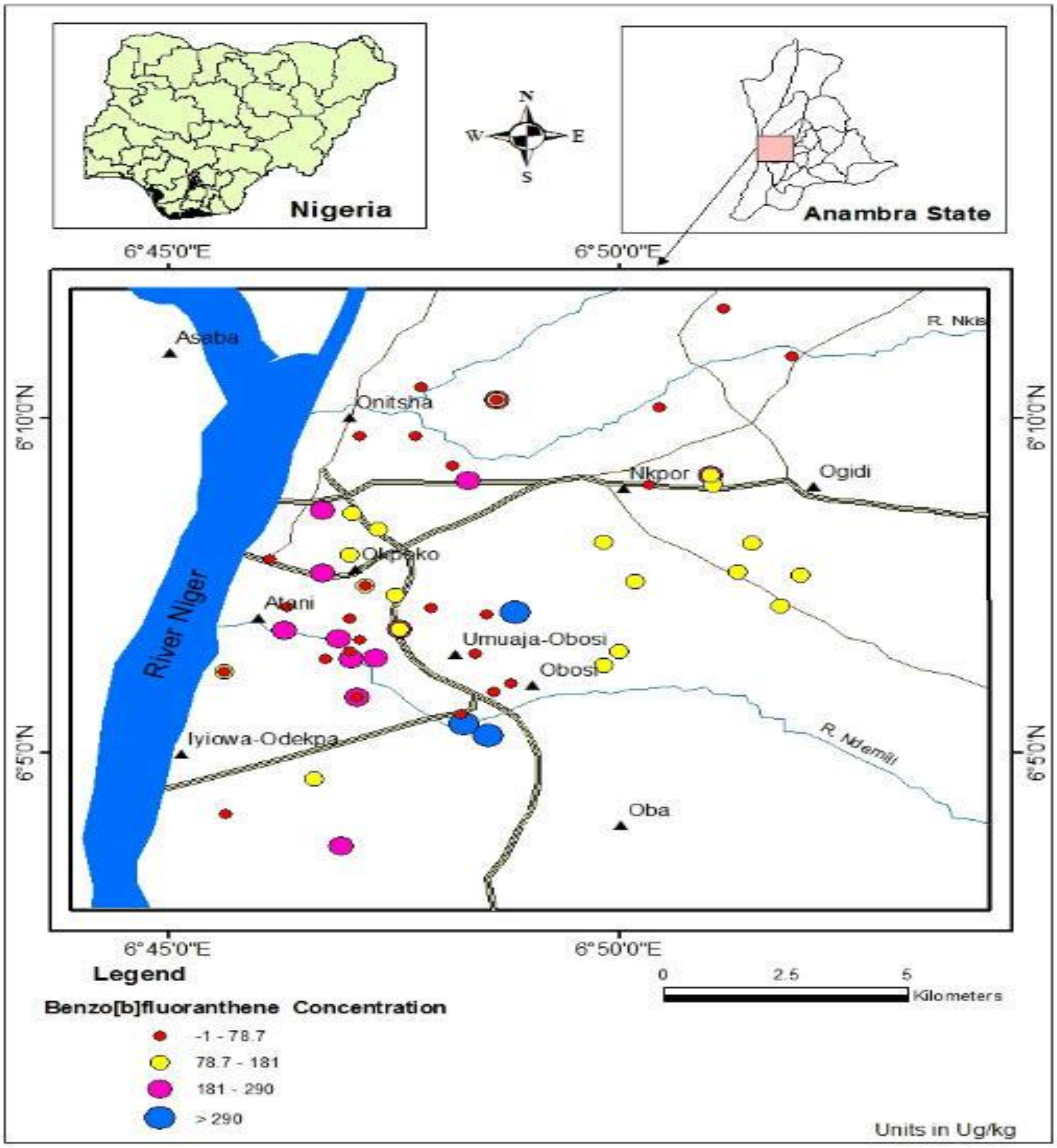


Fig. 4.105: Spatial distribution of benzo[b]fluoranthene in soils and sediments of the study area

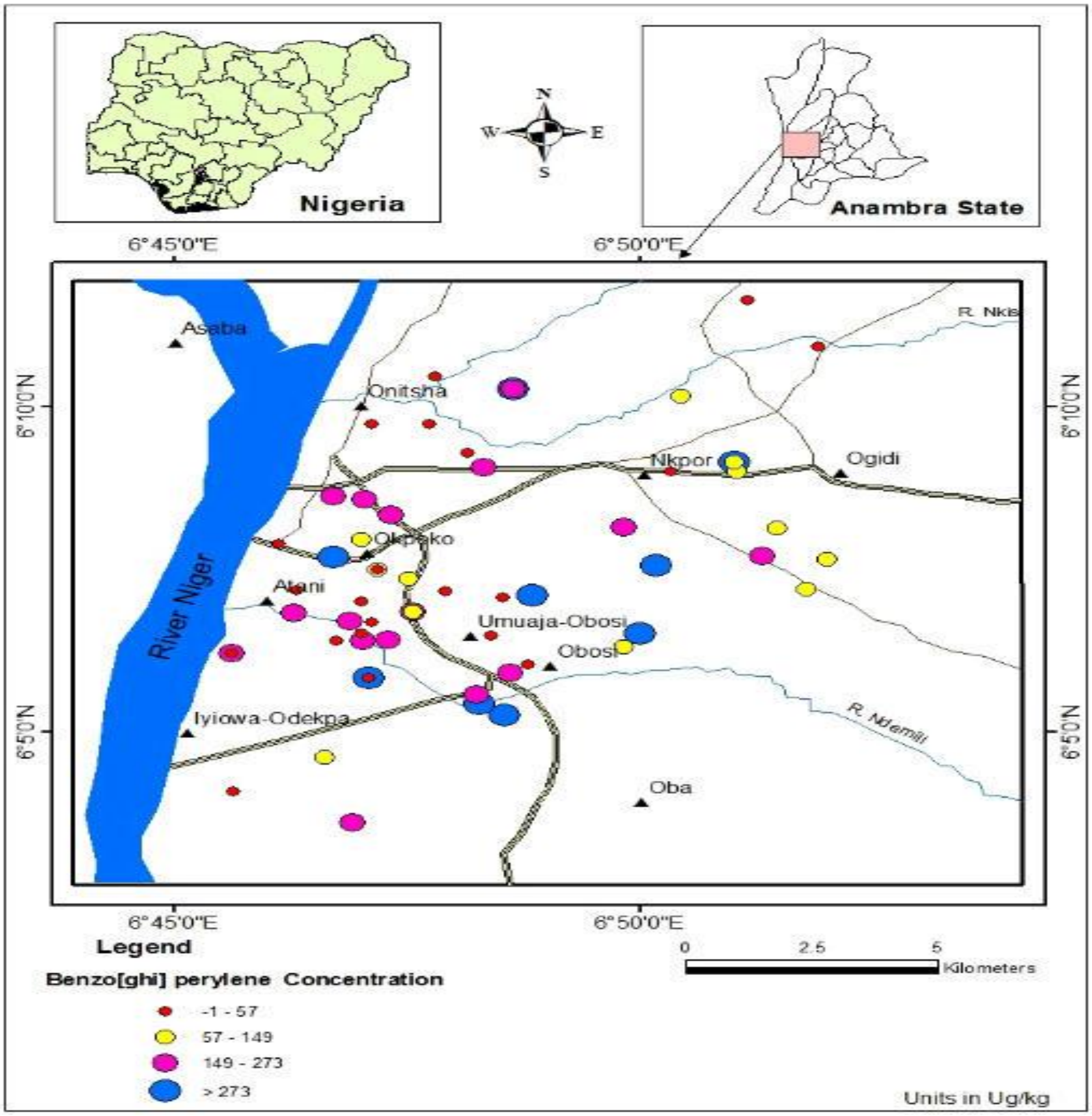


Fig. 4.106: Spatial distribution of Benzo [ghl] perylene in soils and sediments of the study area

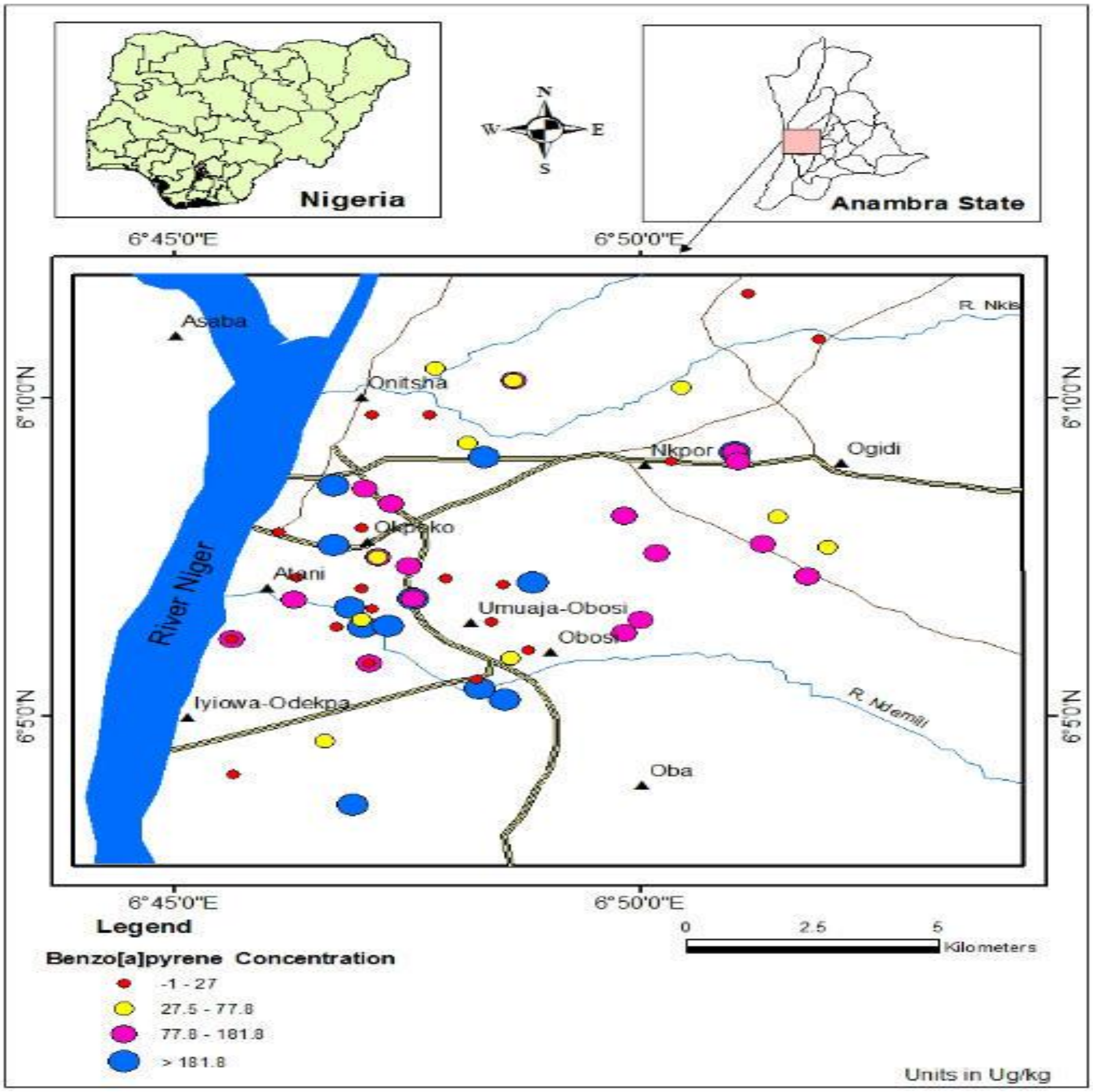


Fig. 4.107: Spatial distribution of Benzo[a]pyrene in soils and sediments of the area

## 4.16 Identification of sources of PAHs in soils and sediment of the study area.

The potential sources of PAH in the soils and sediments were carried out using PAH isomer ratio in other to identify the possible sources of these harmful compound. This is a method that have been used by published works , such as (Baumard et al.; 1998, Ma et al. 2005, Liu et al. 2008and Glennon et al., 2012) to ascertain weather it is from pyrolytic i.e (Combustion processes of organic rich matereials or through petrogenic input i.e (through petroleum product discharch like oil spillage). When the ratio of Flu/(Flu + Pry) is <0.4, it suggest petroleum source enrichment while Flu/(Flu + Pyr) is >0.5 it indicates PAH in the geo media is from combustion of grass, wood and coal and when (Flu/(Flu + pyr) is between 0.4 < and >0.5, it is from combustion of petroleum product (Li et al. 2006)

In similar vain, the ratio of Ant/(Ant + Pyr) < 0.1 are such enriched by petroleum product contamination, while the ratio of Ant/(Ant + Pyr) ratio > 0.1 are mainly from combustion related sources such as vehicle related activities (Li et al 2006). The ratio of IcdP/(Icdp + BiP) < 0.2, shows petroleum sources while value >0.5, indicate pyrolytic sources (Yunker et al, 2002). The same apply to the ratio of BaA/(BaA + Chr). When BaA/(BaA + Chr) ratio is < 0.2, it indicate petroleum input while when it is > 0.35, it indicate pyrolytic sources (Yinker et al. 2002). From the result of this work, it is observed that for the ratio of Flu/Flu + Pry), is between < 0.4 and >0.5 for most of the locations which suggest combustion source enrichment for most of the locations except for the control (0.00) in the ratio reading. The locations that recorded >0.6 suggest combustion of organic rich waste matrerials as in location AWD/5B which soil collected within the vicinity of active waste dump site.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## 5.1 CONCLUSION

A total of 162 soil and sediment samples were analyzed for Mo, Zn, Pb, Mn, Cr, Cu, Ni, As and Cd. Generally, it was found that most of the elements have relatively high concentrations of these metals that indicate potential environmental hazard. The result exhibit much more high concentration of these harmful element being influenced by human, industrial and commercial activities as against samples used as control which were collected at the outskirt of the city . The concentration of Pb and Zn in soils collected from mechanic and metal workshops, active waste dump, farmland and garden, market and Abattoir up to between 8 to10 fold higher than the control area which were sampled at relatively pristine locations of the study area. Manganese, Cu, Cr, Ni, Cd, content are high in the soils and sediment from MWM, AWD, FLG compare to the control samples. Similarly, the metal content of the element analysed are 2 to 4 fold higher in the top soils compare to the subsoil samples. The implication of these results suggests that the soils and sediment have received considerable imputs of anthropogenic enrichment of these metals, primarily from vehicular activities, industrial waste and commercial activities. This poses great threat health wise to the inhabitant and pedestrians in the metropolis.

Pb isotopes signature in the soils and sediments compare to the signature for galena ore, coal, soot of vehicle exhaust and battery cells in their ratio for example The mean ratio of $^{206}$Pb/$^{207}$Pb for RA (1.15) similar to the other land use such as SOC (1.15), MAP (1.15), MWM (1.15), NK (1.15), ID (1.15) among other landuse, compare to $^{206}$Pb/$^{207}$Pb ratio for galena (1.24) and coal (1.22) suggesting that the Pb content in the soils and sediments in the study area is not traced to have been enriched by these two possible natural suorces of Pb. But its closed similarity to the ratio of Pb in soot of vehicle exhuast suggest that anthropogenic activities may have contributed to enrichment of Pb in the soils and sediments. Other ratios such as $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb also showed slight similarities with each other for various landuse, but different from the ratios gotten from galena and coal but with similar signature with battery cells and vehicle exhuast. The significant correlation exhibitted by these Pb isotope ratios $^{206}$Pb/$^{204}$Pb vs $^{207}$Pb/$^{204}$ , $^{207}$Pb/$^{204}$Pb vs $^{206}$Pb/$^{204}$Pb, $^{208}$Pb/$^{207}$Pb vs $^{208}$Pb/$^{206}$Pb and $^{206}$Pb/$^{204}$Pb vs $^{208}$Pb/$^{204}$Pb showed that there is the possibility that the enrichment of Pb in both the soils and sediments in the study area may have been enriched by similar anthropogenic sources of not less that two, hence the sharp variaton exhibited by Pb isotope signature for the geogenic sources of Pb.

Results of the sequential extraction show that most of the metals selected for this research have varying potential mobility and bioavailability characteristics. From the result, significant quantities of most of the metals did not occur in the dimineralized fraction. But significant quantity were found in the organic fraction (LH2) making a combination of LH1 and LH2 to be significant as exhibited by Zn and Cd (21% - 62%) and (>56%) respectively of their total metal concentration. Other elements such as Cu (> 40%), As (>58%) and Ni (> 43%) are possibly leached at the organic and sulfide fraction (LH3), thus suggesting that when ever there is a relative decrease of the pH to the acidic value, will bring about metal remobilization of such percentage stated above.

Pb, Mn, Co and Ba exhibited limited metal mobility characteristics except under a very low pH conditions because larger percentage of the total metal content cound only be leached by the reducible (LH4) and residual (LH2) fractions respectively which suggest that they are mostly bound to the silicate lattice. Base on environmental significance, Zn, Cd, As, Cu and Ni can possibly be mobile and bioavailable under slight acidic environmental conditions, because they can be removed by a combination of (LH1, LH2 and LH3) with more than 50% of the total metals. While Pb, Mn, Co and Ba have relatively low potential to remobilize except under strong (acidic), very low pH conditions

The result of the Polycyclic Aromatic Hydrocarbon in the soils and sediments that were selected from locations initially found to be of relatively enrichment in potentially harmful element also have high content of 13 PAHs and 16PAHs that are of environmental concern. These PAHs include Fluorene, Anthracene, Phenanthrene, Fluoranthrene, Pyrene, Benzo[a]anthracene, Crysene, Benzo[b]fluoranthene, Benzo[ghi]perylene, Indeno(1,2,3-cd)pyrene and Dibenzo[ah]anthracene. The other three PAHs that were not detected include Naphthalene, Acenaphthylene and Acenaphthene. From the results, varying concentration of these PAHs were found from one location to the other for both soils and sediments. It was observed that land use activities was a major factor that influence the varying concentration of these organic compound, were areas such as MWM/11 (127.8 µg/kg), RSD/20 (298.3 µg/kg), ID/9 (226.6 µg/kg), of Benzo (a) anthracene compound that were found to be relatively high compare to their content in the control samples which Is below the detection limit of the analytical facility employed in their analysis

Similarly the varying concentrations other PAHs that suggest influence of high urban activities, for example, Benzo[k] Fluoranthene compound, MWM/9 (166.5 µg/kg), SSD/20 (163.5 µg/kg), ID/9 (106.6 µg/kg), and MAP/2 (84.9 µg/kg) compare to the result from the control samples, such as CT/4 (n.d), RK/2 (1.0 µg/kg). such pattern of PAHs enrichment in soils and sediment were found in Benz(a)Pyrene, Benzo(b) Fluoranthene, Benzo(ghi)Perylene, Indeno (1,2,3-cd)pyrene among other PAHs detected. The identification characterization of the possible sources of PAHs that were interpreted showed that most of the PAHs found in the soils and sediments of the study are related to pyrogenic sources which may have been influenced by combustion related activities within the urban environment. The main concern about PAHs presence to such level of concentration in some vital locations within the soils and sediments analysed is the fact that the PAHs detected are carcinogenic and mutagenic when it comes in contact with human beings most expecially through pathways such as dust inhalation, surface water intake by plants and animals that depend on such, among other possible pathways.

## 5.2 RECOMMENDATIONS

From the research works that have been carried out though largely successful, further work is recommended on the itemized area

I. Detailed geochemistry of the ferrogenised (iron stone) sand stone

II. Bioaccessbility of the soils, particulate (dust), sediment and surface water.

III. More samples for Pb and Zn isotope geochemistry

IV. Biogeochemistry of edible crops planted along Ndimili and Nkisi rivers

V. Regional geochemical mapping for statutary guidelines data aquisition

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APPENDIX 1: A: Physico-Chemical Analyses for soils

| LAND USE | pH | EC (µS/cm) | TDS (mg/l) |
|---|---|---|---|
| RA/01 | 7.1 | 83 | 53.3 |
| RA/02 | 7.2 | 92 | 67.2 |
| RA/3 | 6.9 | 37 | 26.7 |
| RA/3$^{B}$ | 7.6 | 53 | 34 |
| RA/04 | 7 | 133.4 | 85.4 |
| RA/05 | 6.8 | 23.5 | 15.01 |
| RA/5$^{B}$ | 6.7 | 16.84 | 10.79 |
| Ra/06 | 6.6 | 21.2 | 13.9 |
| RA/07 | 6.4 | 118.9 | 70.4 |
| RA/08 | 6.8 | 37.9 | 22.3 |
| RA/09 | 6.2 | 99.6 | 53.4 |
| RA/010 | 6.9 | 72 | 38.6 |
| RA/011 | 7.1 | 125.2 | 80.1 |
| RA/012 | 6.7 | 79.1 | 47.9 |
| RA/013 | 7.2 | 42.6 | 26.8 |
| RA/13$^{B}$ | 6.4 | 43.9 | 28.5 |
| RA/014 | 6.4 | 128.2 | 82.2 |
| RA/015 | 6.8 | 157.5 | 101.5 |
| RA/15$^{B}$ | 7.3 | 35 | 22.4 |
| RA/016 | 7 | 30.2 | 19.35 |
| RA/017 | 6.7 | 17.61 | 11.27 |
| RA/17$^{B}$ | 6.7 | 113.96 | 89.2 |
| RA/018 | 7.2 | 77.4 | 49.6 |
| RA/019 | 6.5 | 97.2 | 58.9 |
| RA/020 | 7.2 | 76 | 48.8 |

B: Physico-Chemical Analyses for soils, cont.

| | | | |
|---|---|---|---|
| RA//20$^{B}$ | 7.1 | 60.9 | 38.9 |
| RA/21 | 6.9 | 63.7 | 40.8 |
| RA/025 | 7.1 | 98.5 | 62.9 |
| FLG/01 | 4.8 | 142.9 | 91.4 |
| FLG/02 | 6.3 | 12.91 | 8.21 |
| FLG/03 | 6.2 | 17.1 | 11.33 |
| FLG/04 | 5.1 | 14.51 | 9.29 |
| FLG/05 | 6.2 | 32.4 | 20.8 |
| FLG/5$^{B}$ | 5.2 | 13.75 | 8.82 |
| FLG/06 | 6.7 | 66.4 | 42.5 |
| FLG/6$^{B}$ | 6.8 | 18.32 | 11.7 |
| FLG/07 | 5.4 | 41.6 | 26.6 |
| FLG/7$^{B}$ | 5 | 15.31 | 9.79 |
| FLG/08 | 5 | 15.3 | 9.83 |
| FLG/09 | 7.4 | 69.1 | 44.1 |
| FLG/9$^{B}$ | 7 | 65.3 | 41.8 |
| FLG/010 | 5.3 | 9.94 | 6.36 |
| FLG/011 | 6.2 | 25.4 | 16.29 |
| MAP/ 01 | 6.2 | 183.6 | 115.6 |
| MAP/1$^{B}$ | 6.7 | 121.9 | 77.7 |
| MAP/ 02 | 6.7 | 198.9 | 127.9 |
| MAP/03 | 6.6 | 209.0 | 132.7 |
| MAP/3$^{B}$ | 6.4 | 113.9 | 73 |
| CT/01 | 6.8 | 16.5 | 10.64 |
| Rk/1 | 6.9 | 21.3 | 15.7 |
| CT/05 | 5.9 | 9.7 | 5.9 |
| CT/02 | 4.8 | 6.41 | 4.05 |

|  |  |  |  |
|---|---|---|---|
| CT/03 | 5 | 23 | 14.79 |

C: Physico-Chemical Analyses for soils, cont.

|  |  |  |  |
|---|---|---|---|
| SOC/O1 | 6.3 | 108.8 | 69.7 |
| SOC/02 | 6.9 | 24.9 | 15.96 |
| SOC/3 | 6.3 | 19.35 | 12.14 |
| SOC/O4 | 6.8 | 18.65 | 11.97 |
| SOC/05 | 6.8 | 38.7 | 24.2 |
| SOC/06 | 6.9 | 54.9 | 35.3 |
| SOC/07 | 7.2 | 41.5 | 26.6 |
| SOC/7$^{B}$ | 7.4 | 35.6 | 22.8 |
| SOC/08 | 6.4 | 40.7 | 27.1 |
| SOC/09 | 6.7 | 32.1 | 20.6 |
| SOC/010 | 6.7 | 54.9 | 35.3 |
| SOC/10$^{B}$ | 7 | 8.48 | 5.44 |
| SOC/011 | 6.5 | 97.8 | 61.9 |
| SOC/012 | 7.2 | 138.8 | 88.8 |
| SOC/12$^{B}$ | 6.9 | 25.2 | 16.1 |
| SOC/13 | 7 | 63.4 | 40.6 |
| SOC/014 | 6.6 | 47.6 | 30.5 |
| SOC/14$^{B}$ | 5.2 | 26.2 | 16.63 |
| SOC/015 | 7.2 | 62.8 | 40.2 |
| AWD/01 | 6.8 | 79.8 | 51.1 |
| AWD/02 | 6.4 | 227 | 144.1 |
| AWD/03 | 7.1 | 92.5 | 59.2 |
| AWD/3$^{B}$ | 7.4 | 38.4 | 24.6 |
| AWD/04 | 6.4 | 794 | 508 |
| AWD/05 | 6.9 | 95.1 | 59.7 |
| AWD/5$^{B}$ | 7.2 | 184.4 | 118 |

|  |  |  |  |
|---|---|---|---|
| AWD/06 | 6.6 | 298 | 198.7 |
| AWD/7 | 6.5 | 694.0 | 444 |

D: Physico-Chemical Analyses for soils, cont.

|  |  |  |  |
|---|---|---|---|
| MWM/01 | 6.9 | 84.4 | 54 |
| MWM/02 | 7.3 | 134.4 | 86 |
| MWM/2$^B$ | 7.2 | 78.7 | 49.4 |
| MWM/03 | 6.8 | 111.6 | 70.3 |
| MWM/3$^B$ | 7.7 | 54.2 | 34.7 |
| MWM/4 | 7.1 | 162.6 | 104.1 |
| MWM/05 | 6.8 | 198.8 | 124 |
| MWM/07 | 7.1 | 60.7 | 38.9 |
| MWM/7$^B$ | 6 | 19.21 | 12.7 |
| MWM/08 | 6.8 | 91.8 | 58.7 |
| MWM/9 | 7.2 | 157.1 | 101.9 |
| MWM/010 | 7.1 | 117.4 | 75.8 |
| MWM/011 | 6.9 | 412 | 264 |
| MWM 12 | 6.8 | 332.0 | 207.2 |
| MWM/12$^B$ | 6.9 | 50.3 | 32.4 |
| MWM/013 | 7 | 52.9 | 33.6 |
| MWM/014 | 7 | 113.4 | 72.6 |
| MWM/015 | 7.1 | 58.8 | 37.9 |
| MWM/15$^B$ | 7 | 23.7 | 15.17 |
| MWM/016 | 6.7 | 143.6 | 91.9 |
| MWM/17$^A$ | 6.8 | 66.4 | 42.6 |
| MWM/17$^B$ | 6.2 | 21.8 | 13.97 |

E: Physico-Chemical Analyses for stream sediment

| LAND USE | pH | EC (µS/cm) | TDS (mg/l) |
|---|---|---|---|
| ID/01 | 6.4 | 163.4 | 109.7 |
| ID/02 | 6.6 | 127 | 81.9 |
| ID/03 | 6.6 | 98.2 | 62.4 |
| ID/04 | 6.9 | 87.7 | 51.7 |
| ID/05 | 7.2 | 118 | 76.2 |
| ID/06 | 6.4 | 98.7 | 61.6 |
| ID/07 | 6.9 | 109.7 | 68.9 |
| ID/08 | 6.9 | 103 | 64.8 |
| ID/09 | 6.7 | 121.5 | 82.1 |
| ID/010 | 6.8 | 92.7 | 58.3 |
| NK/011 | 6.4 | 71.8 | 48.6 |
| NK/012 | 6.7 | 69.2 | 44.7 |
| NK/013 | 6.8 | 76.2 | 49.7 |
| NK/014 | 6.6 | 57.9 | 36.2 |
| NK/015 | 7.1 | 59 | 37.7 |
| NK/016 | 6.9 | 74.3 | 47.6 |
| NK/017 | 6.8 | 82.7 | 57.1 |
| NK/018 | 6.8 | 50.1 | 31.4 |
| NK/019 | 6.7 | 55.7 | 34.2 |
| NK/020 | 6.7 | 48.2 | 30.9 |

F: Physico-Chemical Analyses for Roadside Drain Sediments.

| LAND USE | pH | EC (µS/cm) | TDS (mg/l) |
|---|---|---|---|
| RSD/01 | 7.3 | 54.1 | 34.6 |
| RSD/02 | 6.7 | 236 | 151.3 |
| RSD/3 | 6.4 | 209.7 | 132.5 |
| RSD/04 | 6.1 | 77.8 | 49.8 |
| RSD/05 | 6.8 | 101.9 | 65.2 |
| RSD/06 | 7.1 | 76.9 | 49 |
| RSD/07 | 6.5 | 96.5 | 61.5 |
| RSD/08 | 7.1 | 113.1 | 78.4 |
| RSD/09 | 6.9 | 94.1 | 60.2 |
| RSD/010 | 6.9 | 31.6 | 20.2 |
| RSD/011 | 6.81 | 553 | 354 |
| RSD/012 | 7 | 1059 | 668 |
| RSD/013 | 7.2 | 146.4 | 94.9 |
| RSD/014 | 7 | 409 | 262 |
| RSD/015 | 6.8 | 320 | 205 |
| RSD/016 | 6.5 | 334 | 214 |
| RSD/017 | 6.2 | 187.7 | 139.9 |
| RSD/018 | 6.5 | 218 | 130.9 |
| RSD/19 | 7 | 235 | 149.5 |
| RSD/20 | 6.7 | 349 | 224 |
| RSD/21 | 6.7 | 349 | 224 |
| RSD/22 | 6.8 | 264 | 169.1 |
| RSD/23 | 6.6 | 376 | 241 |

|  |  |  |  |
|---|---|---|---|
| RSD/024 | 7 | 309 | 197.4 |
| RSD/025 | 7.1 | 219 | 128.9 |

APPENDIX 2 A: Geochemical Composition of soil Samples from the study area (Major Oxides)

| Sample No | **Type** | $SiO_{2(calculated)}$ | $Fe_2O_3$ | CaO | $P_2O_5$ | MgO | $TiO_2$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/1 | Soil Pulp | 89.4112 | 8.19 | 1.35 | 0.05 | 0.10 | 0.023 | 0.86 | 0.014 | 0.0018 |
| RA/2 | Soil Pulp | 95.6227 | 2.97 | 0.46 | 0.04 | 0.09 | 0.019 | 0.78 | 0.016 | 0.0021 |
| RA/3 | Soil Pulp | 92.6352 | 3.67 | 2.24 | 0.06 | 0.07 | 0.020 | 1.30 | 0.008 | 0.0006 |
| RA/4 | Soil Pulp | 94.3408 | 3.54 | 1.00 | 0.12 | 0.06 | 0.017 | 0.90 | 0.027 | 0.0016 |
| RA/5$^A$ | Soil Pulp | 97.5524 | 1.77 | 0.21 | 0.03 | 0.01 | 0.014 | 0.41 | 0.002 | 0.0000 |
| RA/5$^B$ | Soil Pulp | 95.2044 | 3.50 | 0.21 | 0.03 | 0.02 | 0.018 | 1.01 | 0.002 | 0.0001 |
| RA/6 | Soil Pulp | 93.2229 | 4.33 | 1.31 | 0.04 | 0.05 | 0.018 | 1.01 | 0.020 | 0.0016 |
| RA/7 | Soil Pulp | 94.7673 | 3.72 | 0.19 | 0.04 | 0.02 | 0.016 | 1.22 | 0.024 | 0.0012 |
| RA/10 | Soil Pulp | 94.6227 | 3.57 | 0.45 | 0.06 | 0.04 | 0.017 | 1.20 | 0.045 | 0.0040 |
| RA/11$^A$ | Soil Pulp | 94.8145 | 3.60 | 1.00 | 0.02 | 0.05 | 0.016 | 0.50 | 0.002 | 0.0000 |
| RA/11$^B$ | Soil Pulp | 94.4872 | 3.77 | 0.71 | 0.02 | 0.03 | 0.018 | 0.96 | 0.001 | 0.0000 |
| RA/12 | Soil Pulp | 95.3146 | 3.41 | 0.31 | 0.03 | 0.02 | 0.015 | 0.88 | 0.004 | 0.0001 |
| RA/13$^A$ | Soil Pulp | 95.5934 | 3.08 | 0.33 | 0.03 | 0.02 | 0.017 | 0.93 | 0.004 | 0.0002 |
| RA/13$^B$ | Soil Pulp | 95.7793 | 2.91 | 0.39 | 0.03 | 0.02 | 0.017 | 0.84 | 0.004 | 0.0002 |
| RA/14 | Soil Pulp | 91.8983 | 5.61 | 1.44 | 0.25 | 0.11 | 0.007 | 0.65 | 0.036 | 0.0029 |
| RA/15$^A$ | Soil Pulp | 93.9839 | 4.09 | 1.04 | 0.04 | 0.07 | 0.015 | 0.75 | 0.013 | 0.0007 |
| RA/15$^B$ | Soil Pulp | 95.5473 | 3.26 | 0.13 | 0.01 | 0.01 | 0.008 | 1.02 | 0.008 | 0.0003 |
| RA/16$^A$ | Soil Pulp | 95.5225 | 3.32 | 0.24 | 0.03 | 0.02 | 0.016 | 0.85 | 0.003 | 0.0001 |
| RA/16$^B$ | Soil Pulp | 94.8968 | 3.68 | 0.22 | 0.02 | 0.02 | 0.017 | 1.14 | 0.002 | 0.0001 |
| RA/17 | Soil Pulp | 93.8097 | 4.97 | 0.21 | 0.02 | 0.03 | 0.016 | 0.94 | 0.001 | 0.0000 |
| RA/17$^B$ | Soil Pulp | 95.4459 | 3.33 | 0.18 | 0.02 | 0.02 | 0.014 | 0.99 | 0.001 | 0.0000 |
| RA/18 | Soil Pulp | 92.4389 | 2.64 | 3.84 | 0.12 | 0.19 | 0.017 | 0.55 | 0.181 | 0.0272 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/19 | Soil Pulp | 98.3475 | 1.24 | 0.01 | 0.00 | 0.00 | 0.017 | 0.38 | 0.001 | 0.0000 |
| RA/20$^A$ | Soil Pulp | 93.7365 | 4.26 | 0.73 | 0.04 | 0.04 | 0.020 | 1.16 | 0.011 | 0.0006 |
| RA/20$^B$ | Soil Pulp | 93.6595 | 4.71 | 0.16 | 0.01 | 0.02 | 0.021 | 1.41 | 0.006 | 0.0002 |
| RA/21 | Soil Pulp | 95.4956 | 3.12 | 0.26 | 0.04 | 0.02 | 0.012 | 1.03 | 0.016 | 0.0007 |

B: Geochemical Composition of soil Samples from the study area (Major Oxides)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| SOC/1$^A$ | Soil Pulp | 97.6280 | 1.35 | 0.14 | 0.04 | 0.11 | 0.017 | 0.70 | 0.006 | 0.0008 |
| SOC/1$^B$ | Soil Pulp | 97.7826 | 1.36 | 0.04 | 0.01 | 0.11 | 0.027 | 0.66 | 0.007 | 0.0011 |
| SOC/2$^A$ | Soil Pulp | 96.5726 | 2.52 | 0.19 | 0.04 | 0.02 | 0.016 | 0.64 | 0.003 | 0.0001 |
| SOC/2$^B$ | Soil Pulp | 99.3850 | 0.44 | 0.02 | 0.00 | 0.00 | 0.011 | 0.14 | 0.000 | 0.0000 |
| SOC/3 | Soil Pulp | 95.5439 | 3.16 | 0.16 | 0.02 | 0.02 | 0.014 | 1.09 | 0.001 | 0.0000 |
| SOC/4 | Soil Pulp | 95.4439 | 3.26 | 0.24 | 0.03 | 0.02 | 0.016 | 1.00 | 0.002 | 0.0000 |
| SOC/5 | Soil Pulp | 95.4979 | 3.18 | 0.33 | 0.04 | 0.02 | 0.016 | 0.92 | 0.003 | 0.0001 |
| SOC/6 | Soil Pulp | 91.5106 | 6.95 | 0.51 | 0.05 | 0.06 | 0.015 | 0.90 | 0.003 | 0.0001 |
| SOC/7$^A$ | Soil Pulp | 93.6915 | 4.63 | 0.67 | 0.05 | 0.05 | 0.017 | 0.88 | 0.006 | 0.0002 |
| SOC/7$^B$ | Soil Pulp | 94.4791 | 3.58 | 0.81 | 0.10 | 0.03 | 0.017 | 0.98 | 0.007 | 0.0002 |
| SOC/8$^A$ | Soil Pulp | 96.5529 | 2.66 | 0.23 | 0.03 | 0.02 | 0.014 | 0.49 | 0.004 | 0.0001 |
| SOC/8$^B$ | Soil Pulp | 94.7396 | 3.94 | 0.19 | 0.03 | 0.01 | 0.018 | 1.06 | 0.003 | 0.0001 |
| SOC/9 | Soil Pulp | 95.5020 | 3.21 | 0.35 | 0.02 | 0.02 | 0.014 | 0.88 | 0.001 | 0.0000 |
| SOC/10$^A$ | Soil Pulp | 96.6688 | 2.56 | 0.10 | 0.02 | 0.01 | 0.014 | 0.63 | 0.001 | 0.0000 |
| SOC/10$^B$ | Soil Pulp | 96.2655 | 2.77 | 0.08 | 0.01 | 0.01 | 0.016 | 0.85 | 0.001 | 0.0000 |
| SOC/11 | Soil Pulp | 94.5819 | 4.24 | 0.06 | 0.01 | 0.02 | 0.022 | 1.05 | 0.004 | 0.0003 |
| SOC/12$^A$ | Soil Pulp | 93.5508 | 2.57 | 2.87 | 0.02 | 0.11 | 0.020 | 0.85 | 0.009 | 0.0004 |
| SOC/12$^B$ | Soil Pulp | 96.0611 | 2.88 | 0.09 | 0.01 | 0.01 | 0.012 | 0.93 | 0.000 | 0.0000 |
| SOC/13 | Soil Pulp | 96.5482 | 2.18 | 0.60 | 0.03 | 0.07 | 0.014 | 0.54 | 0.013 | 0.0004 |
| SOC/14$^A$ | Soil Pulp | 94.7232 | 3.72 | 0.16 | 0.02 | 0.02 | 0.017 | 1.33 | 0.003 | 0.0001 |
| SOC/14$^B$ | Soil Pulp | 94.7062 | 4.00 | 0.03 | 0.01 | 0.01 | 0.018 | 1.22 | 0.001 | 0.0000 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| SOC/15^A | Soil Pulp | 93.7167 | 4.84 | 0.27 | 0.03 | 0.02 | 0.028 | 1.07 | 0.008 | 0.0002 |
| SOC/15^B | Soil Pulp | 92.9771 | 5.53 | 0.10 | 0.03 | 0.01 | 0.023 | 1.32 | 0.006 | 0.0001 |

C: Geochemical Composition of soil Samples from the study area (Major Oxides)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| CT/2 | Soil Pulp | 95.6213 | 3.49 | 0.00 | 0.01 | 0.01 | 0.024 | 0.85 | 0.000 | 0.0000 |
| CT/3 | Soil Pulp | 96.8847 | 2.28 | 0.01 | 0.01 | 0.01 | 0.011 | 0.80 | 0.000 | 0.0000 |
| CT/4 | Soil Pulp | 95.8504 | 3.40 | 0.00 | 0.01 | 0.00 | 0.014 | 0.73 | 0.001 | 0.0000 |
| CT/5 | Soil Pulp | 96.0036 | 3.30 | 0.00 | 0.01 | 0.00 | 0.014 | 0.68 | 0.002 | 0.0000 |
| CT/6 | Soil Pulp | 99.5853 | 0.32 | 0.00 | 0.00 | 0.00 | 0.014 | 0.08 | 0.000 | 0.0000 |
| RK/1 | Soil Pulp | 68.3591 | 31.09 | 0.00 | 0.01 | 0.00 | 0.028 | 0.51 | 0.004 | 0.0000 |
| RK2 | Soil Pulp | 89.6197 | 9.90 | 0.00 | 0.01 | 0.00 | 0.012 | 0.47 | 0.000 | 0.0000 |
| RK/3 | Soil Pulp | 96.3344 | 2.92 | 0.01 | 0.01 | 0.00 | 0.007 | 0.71 | 0.000 | 0.0000 |
| FLG/1 | Soil Pulp | 96.7710 | 1.98 | 0.09 | 0.04 | 0.16 | 0.024 | 0.92 | 0.010 | 0.0022 |
| FLG/2 | Soil Pulp | 97.4084 | 1.62 | 0.08 | 0.01 | 0.11 | 0.025 | 0.75 | 0.003 | 0.0004 |
| FLG/3^A | Soil Pulp | 93.8770 | 5.08 | 0.14 | 0.06 | 0.02 | 0.011 | 0.81 | 0.001 | 0.0000 |
| FLG/3^B | Soil Pulp | 94.8641 | 3.42 | 0.08 | 0.02 | 0.01 | 0.014 | 1.59 | 0.000 | 0.0000 |
| FLG/4 | Soil Pulp | 94.0927 | 4.73 | 0.01 | 0.02 | 0.01 | 0.013 | 1.12 | 0.000 | 0.0000 |
| FLG/5^A | Soil Pulp | 96.1823 | 2.89 | 0.20 | 0.04 | 0.03 | 0.015 | 0.61 | 0.023 | 0.0011 |
| FLG/5^B | Soil Pulp | 94.0094 | 4.60 | 0.06 | 0.02 | 0.02 | 0.013 | 1.28 | 0.000 | 0.0000 |
| FLG/6^A | Soil Pulp | 95.4363 | 3.19 | 0.32 | 0.04 | 0.03 | 0.014 | 0.96 | 0.004 | 0.0001 |
| FLG/6^B | Soil Pulp | 95.4989 | 3.37 | 0.07 | 0.01 | 0.01 | 0.018 | 1.02 | 0.001 | 0.0000 |
| FLG/7^A | Soil Pulp | 95.7624 | 3.02 | 0.09 | 0.03 | 0.02 | 0.014 | 1.07 | 0.001 | 0.0001 |
| FLG/7^B | Soil Pulp | 94.5849 | 4.06 | 0.02 | 0.02 | 0.01 | 0.017 | 1.29 | 0.000 | 0.0000 |
| FLG/8 | Soil Pulp | 95.0916 | 3.59 | 0.01 | 0.02 | 0.01 | 0.016 | 1.26 | 0.000 | 0.0000 |
| FLG/9^A | Soil Pulp | 93.8896 | 3.18 | 1.63 | 0.03 | 0.06 | 0.017 | 1.19 | 0.006 | 0.0004 |
| FLG/9^B | Soil Pulp | 95.1847 | 3.13 | 0.46 | 0.02 | 0.03 | 0.015 | 1.15 | 0.002 | 0.0001 |
| FLG/10^A | Soil Pulp | 95.0429 | 3.73 | 0.01 | 0.02 | 0.02 | 0.012 | 1.16 | 0.001 | 0.0000 |
| FLG/10^B | Soil Pulp | 93.9596 | 4.38 | 0.01 | 0.02 | 0.02 | 0.012 | 1.60 | 0.000 | 0.0000 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| FLG/11 | Soil Pulp | 93.6870 | 4.81 | 0.39 | 0.07 | 0.04 | 0.025 | 0.99 | 0.000 | 0.0000 |
| MAP/1$^A$ | Soil Pulp | 96.5344 | 2.13 | 0.50 | 0.06 | 0.07 | 0.011 | 0.64 | 0.043 | 0.0198 |
| MAP/1$^B$ | Soil Pulp | 96.6945 | 2.10 | 0.09 | 0.04 | 0.02 | 0.007 | 1.03 | 0.011 | 0.0022 |
| MAP/2 | Soil Pulp | 93.6061 | 3.27 | 2.05 | 0.15 | 0.15 | 0.018 | 0.73 | 0.024 | 0.0047 |
| MAP/3$^A$ | Soil Pulp | 91.7791 | 6.02 | 1.18 | 0.14 | 0.05 | 0.020 | 0.73 | 0.084 | 0.0109 |
| MAP/3$^B$ | Soil Pulp | 91.9751 | 6.51 | 0.30 | 0.10 | 0.02 | 0.019 | 1.02 | 0.044 | 0.0035 |

D : Geochemical Composition of soil Samples from the study area (Major Oxides)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| AWD/2 | Soil Pulp | 95.5725 | 3.06 | 0.16 | 0.01 | 0.10 | 0.026 | 1.07 | 0.004 | 0.0004 |
| AWD/3$^A$ | Soil Pulp | 93.8635 | 3.93 | 0.99 | 0.05 | 0.04 | 0.019 | 1.09 | 0.020 | 0.0012 |
| AWD/3$^B$ | Soil Pulp | 93.7327 | 4.56 | 0.21 | 0.02 | 0.04 | 0.022 | 1.40 | 0.021 | 0.0015 |
| AWD/4$^A$ | Soil Pulp | 93.6180 | 3.60 | 1.39 | 0.09 | 0.07 | 0.020 | 1.08 | 0.119 | 0.0155 |
| AWD/4$^B$ | Soil Pulp | 94.3318 | 4.12 | 0.25 | 0.03 | 0.02 | 0.019 | 1.21 | 0.015 | 0.0009 |
| AWD/5$^A$ | Soil Pulp | 92.3366 | 4.09 | 2.25 | 0.09 | 0.15 | 0.020 | 1.00 | 0.057 | 0.0069 |
| AWD/5$^B$ | Soil Pulp | 91.9985 | 5.13 | 1.48 | 0.07 | 0.09 | 0.022 | 1.19 | 0.021 | 0.0015 |
| AWD/6$^A$ | Soil Pulp | 91.8259 | 4.02 | 2.37 | 0.29 | 0.12 | 0.029 | 1.31 | 0.024 | 0.0029 |
| AWD/6$^B$ | Soil Pulp | 93.8923 | 4.48 | 0.26 | 0.06 | 0.02 | 0.027 | 1.25 | 0.007 | 0.0003 |
| AWD/7 | Soil Pulp | 94.3020 | 3.62 | 0.54 | 0.10 | 0.06 | 0.022 | 1.14 | 0.185 | 0.0388 |
| AWD/8 | Soil Pulp | 91.7195 | 3.96 | 2.25 | 0.12 | 0.20 | 0.021 | 1.66 | 0.056 | 0.0158 |
| MWM/1 | Soil Pulp | 95.0259 | 3.71 | 0.30 | 0.03 | 0.11 | 0.026 | 0.78 | 0.011 | 0.0011 |
| MWM/2$^A$ | Soil Pulp | 91.5060 | 4.31 | 3.22 | 0.04 | 0.12 | 0.029 | 0.75 | 0.017 | 0.0026 |
| MWM/2$^B$ | Soil Pulp | 96.2405 | 2.33 | 0.84 | 0.03 | 0.12 | 0.035 | 0.40 | 0.006 | 0.0012 |
| MWM/2$^A$ | Soil Pulp | 93.3489 | 5.04 | 0.31 | 0.04 | 0.04 | 0.017 | 1.19 | 0.007 | 0.0002 |
| MWM/3$^A$ | Soil Pulp | 97.0100 | 2.33 | 0.32 | 0.02 | 0.04 | 0.011 | 0.26 | 0.010 | 0.0003 |
| MWM/3$^B$ | Soil Pulp | 95.0823 | 3.93 | 0.21 | 0.02 | 0.04 | 0.019 | 0.70 | 0.012 | 0.0004 |
| MWM/4$^A$ | Soil Pulp | 94.3855 | 3.42 | 1.44 | 0.07 | 0.07 | 0.013 | 0.57 | 0.027 | 0.0027 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/4$^B$ | Soil Pulp | 95.1802 | 3.99 | 0.31 | 0.04 | 0.03 | 0.014 | 0.43 | 0.010 | 0.0002 |
| MWM/5 | Soil Pulp | 91.0748 | 5.87 | 2.19 | 0.07 | 0.21 | 0.016 | 0.52 | 0.041 | 0.0041 |
| MWM/6$^A$ | Soil Pulp | 94.5556 | 3.67 | 1.02 | 0.07 | 0.05 | 0.017 | 0.59 | 0.015 | 0.0006 |
| MWM/6$^B$ | Soil Pulp | 96.2115 | 2.66 | 0.21 | 0.02 | 0.02 | 0.018 | 0.85 | 0.008 | 0.0002 |
| MWM/7$^A$ | Soil Pulp | 97.8959 | 1.77 | 0.11 | 0.02 | 0.01 | 0.009 | 0.17 | 0.005 | 0.0000 |
| MWM/7$^B$ | Soil Pulp | 94.1826 | 4.52 | 0.14 | 0.01 | 0.01 | 0.019 | 1.11 | 0.006 | 0.0001 |

F: Geochemical Composition of soil Samples from the study area (Major Oxides)

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/8 | Soil Pulp | 94.4145 | 4.02 | 0.18 | 0.02 | 0.02 | 0.019 | 1.32 | 0.008 | 0.0003 |
| MWM/9 | Soil Pulp | 80.2587 | 15.83 | 2.64 | 0.10 | 0.17 | 0.022 | 0.93 | 0.029 | 0.0023 |
| MWM/10 | Soil Pulp | 93.9436 | 4.43 | 0.56 | 0.05 | 0.10 | 0.018 | 0.88 | 0.017 | 0.0010 |
| MWM/11 | Soil Pulp | 81.1450 | 16.76 | 1.24 | 0.05 | 0.10 | 0.019 | 0.51 | 0.157 | 0.0125 |
| MWM/12$^A$ | Soil Pulp | 93.8077 | 4.01 | 0.66 | 0.04 | 0.04 | 0.026 | 1.42 | 0.005 | 0.0002 |
| MWM/12$^B$ | Soil Pulp | 92.7383 | 4.55 | 1.05 | 0.03 | 0.04 | 0.030 | 1.56 | 0.007 | 0.0002 |
| MWM/13$^A$ | Soil Pulp | 94.2665 | 4.31 | 0.23 | 0.03 | 0.02 | 0.024 | 1.11 | 0.005 | 0.0002 |
| MWM/13$^B$ | Soil Pulp | 94.7517 | 3.94 | 0.03 | 0.02 | 0.02 | 0.025 | 1.21 | 0.002 | 0.0000 |
| MWM/14 | Soil Pulp | 93.2209 | 3.72 | 2.12 | 0.05 | 0.24 | 0.019 | 0.62 | 0.010 | 0.0004 |
| MWM/15$^A$ | Soil Pulp | 96.2911 | 2.60 | 0.49 | 0.02 | 0.03 | 0.014 | 0.54 | 0.006 | 0.0001 |
| MWM/15$^B$ | Soil Pulp | 94.7210 | 3.69 | 0.32 | 0.02 | 0.02 | 0.017 | 1.20 | 0.007 | 0.0001 |
| MWM/16$^A$ | Soil Pulp | 92.8094 | 5.37 | 0.84 | 0.07 | 0.09 | 0.019 | 0.78 | 0.016 | 0.0007 |
| MWM/16$^B$ | Soil Pulp | 94.2384 | 4.11 | 0.48 | 0.05 | 0.04 | 0.020 | 1.05 | 0.012 | 0.0004 |
| MWM/17$^A$ | Soil Pulp | 93.9510 | 4.48 | 0.59 | 0.04 | 0.17 | 0.020 | 0.73 | 0.010 | 0.0007 |
| MWM/17$^B$ | Soil Pulp | 95.4168 | 3.38 | 0.12 | 0.02 | 0.02 | 0.020 | 1.01 | 0.004 | 0.0001 |
| MWM/18 | Soil Pulp | 93.4866 | 4.11 | 1.34 | 0.05 | 0.17 | 0.047 | 0.78 | 0.010 | 0.0027 |

G: Geochemical Composition of Stream Sediment Samples from the study area (Major Oxides)

| S/N | **Type** | $SiO_{2(calculated)}$ | $Fe_2O_3$ | CaO | $P_2O_5$ | MgO | $TiO_2$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ID/1 | Sediment Pulp | 95.29 | 3.20 | 0.21 | 0.064 | 0.13 | 0.020 | 0.97 | 0.047 | 0.066 |
| ID/2 | Sediment Pulp | 94.78 | 3.44 | 0.31 | 0.073 | 0.14 | 0.023 | 1.09 | 0.054 | 0.091 |
| ID/3 | Sediment Pulp | 94.77 | 3.49 | 0.28 | 0.074 | 0.14 | 0.023 | 1.09 | 0.055 | 0.083 |
| ID/4 | Sediment Pulp | 94.76 | 3.64 | 0.21 | 0.070 | 0.11 | 0.023 | 1.07 | 0.052 | 0.050 |
| ID/5 | Sediment Pulp | 94.61 | 3.59 | 0.37 | 0.086 | 0.13 | 0.021 | 1.06 | 0.064 | 0.066 |
| ID/6 | Sediment Pulp | 94.85 | 3.57 | 0.21 | 0.068 | 0.11 | 0.020 | 1.07 | 0.051 | 0.050 |
| ID/7 | Sediment Pulp | 96.80 | 1.74 | 0.08 | 0.025 | 0.15 | 0.029 | 1.00 | 0.018 | 0.158 |
| ID/8 | Sediment Pulp | 92.93 | 5.88 | 0.09 | 0.026 | 0.02 | 0.022 | 1.00 | 0.019 | 0.008 |
| ID/9 | Sediment Pulp | 93.81 | 4.17 | 0.86 | 0.075 | 0.30 | 0.029 | 0.68 | 0.055 | 0.025 |
| ID/10 | Sediment Pulp | 93.53 | 5.08 | 0.16 | 0.042 | 0.04 | 0.030 | 1.07 | 0.031 | 0.017 |
| NK/11 | Sediment Pulp | 93.16 | 5.33 | 0.26 | 0.048 | 0.06 | 0.031 | 1.05 | 0.036 | 0.025 |
| NK/12 | Sediment Pulp | 90.87 | 7.81 | 0.10 | 0.027 | 0.02 | 0.023 | 1.12 | 0.020 | 0.017 |
| NK/13 | Sediment Pulp | 94.09 | 4.76 | 0.10 | 0.027 | 0.02 | 0.020 | 0.95 | 0.020 | 0.017 |
| NK/14 | Sediment Pulp | 92.20 | 5.90 | 0.56 | 0.087 | 0.10 | 0.020 | 1.04 | 0.064 | 0.033 |
| NK/15 | Sediment Pulp | 94.09 | 4.74 | 0.12 | 0.033 | 0.04 | 0.014 | 0.91 | 0.025 | 0.025 |
| NK/17 | Sediment Pulp | 93.44 | 5.28 | 0.15 | 0.044 | 0.04 | 0.021 | 0.97 | 0.033 | 0.017 |
| NK/18 | Sediment Pulp | 90.20 | 8.54 | 0.11 | 0.027 | 0.02 | 0.016 | 1.05 | 0.020 | 0.017 |
| NK/19 | Sediment Pulp | 94.07 | 4.80 | 0.10 | 0.026 | 0.02 | 0.018 | 0.93 | 0.019 | 0.017 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| NK/20 | Sediment Pulp | 92.78 | 5.49 | 0.39 | 0.055 | 0.11 | 0.022 | 1.08 | 0.040 | 0.033 |

H: Geochemical Composition of Roadside drain Sediment Samples from the study area (Major Oxides)

| S/N | Type | $SiO_2$(calculated) | $Fe_2O_3$ | CaO | $P_2O_5$ | MgO | $TiO_2$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/1 | Sediment Pulp | 95.67 | 3.20 | 0.42 | 0.022 | 0.16 | 0.020 | 0.48 | 0.016 | 0.017 |
| RSD/2 | Sediment Pulp | 94.03 | 4.06 | 0.76 | 0.025 | 0.07 | 0.021 | 0.99 | 0.018 | 0.033 |
| RSD/3 | Sediment Pulp | 95.59 | 2.88 | 0.71 | 0.031 | 0.14 | 0.018 | 0.58 | 0.023 | 0.033 |
| RSD/4 | Sediment Pulp | 92.38 | 5.50 | 1.24 | 0.047 | 0.16 | 0.020 | 0.59 | 0.035 | 0.042 |
| RSD/5 | Sediment Pulp | 95.48 | 3.27 | 0.69 | 0.038 | 0.11 | 0.019 | 0.32 | 0.028 | 0.042 |
| RSD/6 | Sediment Pulp | 94.85 | 3.62 | 0.79 | 0.043 | 0.15 | 0.023 | 0.43 | 0.032 | 0.058 |
| RSD/7 | Sediment Pulp | 93.57 | 3.28 | 1.90 | 0.072 | 0.44 | 0.022 | 0.61 | 0.053 | 0.050 |
| RSD/8 | Sediment Pulp | 93.37 | 3.97 | 1.58 | 0.084 | 0.18 | 0.021 | 0.66 | 0.062 | 0.066 |
| RSD/9 | Sediment Pulp | 94.79 | 3.09 | 0.94 | 0.065 | 0.30 | 0.018 | 0.71 | 0.048 | 0.042 |
| RSD/10 | Sediment Pulp | 95.20 | 3.31 | 0.43 | 0.045 | 0.05 | 0.019 | 0.88 | 0.034 | 0.033 |
| RSD/12 | Sediment Pulp | 94.02 | 2.87 | 1.39 | 0.266 | 0.25 | 0.017 | 0.54 | 0.197 | 0.448 |
| RSD/13 | Sediment Pulp | 95.22 | 3.01 | 1.06 | 0.055 | 0.17 | 0.019 | 0.40 | 0.041 | 0.033 |
| RSD/11 | Sediment Pulp | 93.62 | 4.34 | 0.66 | 0.079 | 0.13 | 0.025 | 1.00 | 0.059 | 0.100 |
| RSD/14 | Sediment Pulp | 92.19 | 3.99 | 2.03 | 0.120 | 0.52 | 0.029 | 0.92 | 0.089 | 0.108 |
| RSD/15 | Sediment Pulp | 95.12 | 3.26 | 0.61 | 0.076 | 0.11 | 0.020 | 0.59 | 0.056 | 0.149 |
| RSD/16 | Sediment Pulp | 94.83 | 3.58 | 0.56 | 0.062 | 0.10 | 0.023 | 0.76 | 0.046 | 0.050 |
| RSD/20 | Sediment Pulp | 92.88 | 4.92 | 1.36 | 0.051 | 0.16 | 0.019 | 0.46 | 0.038 | 0.125 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/21 | Sediment Pulp | 92.88 | 5.32 | 0.41 | 0.043 | 0.08 | 0.017 | 1.13 | 0.032 | 0.075 |
| RSD/22 | Sediment Pulp | 83.91 | 13.87 | 1.21 | 0.154 | 0.17 | 0.011 | 0.47 | 0.114 | 0.091 |
| RSD/23 | Sediment Pulp | 94.54 | 3.16 | 1.38 | 0.157 | 0.13 | 0.011 | 0.44 | 0.116 | 0.066 |
| RSD24 | Sediment Pulp | 90.69 | 6.01 | 2.17 | 0.216 | 0.18 | 0.026 | 0.47 | 0.160 | 0.083 |

I: Metallic Oxide Concentrations in Soils and Sediment in the study area (%)

| S/N | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $(SO_3)$ | LOI_SI | Sum_RF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RA/3 | 67.84 | 1.157 | 11.45 | 5.61 | 0.063 | 0.21 | 2.577 | 0.18 | 0.56 | 0.253 | 0.16 | 9.39 | 99.46 |
| RA/6 | 51.62 | 1.394 | 18.67 | 8.94 | 0.071 | 0.29 | 2.829 | 0.18 | 0.387 | 0.277 | 0.18 | 14.77 | 99.58 |
| RA/12A | 76.4 | 1.619 | 8.91 | 3.39 | 0.04 | 0.14 | 1.64 | 0.11 | 0.319 | 0.085 | 0.1 | 6.62 | 99.39 |
| RA/14 | 81.08 | 1.451 | 3.81 | 5.79 | 0.111 | 0.15 | 0.902 | 0.09 | 0.242 | 0.606 | 0.08 | 4.99 | 99.33 |
| RA/20 | 69.51 | 1.276 | 11.18 | 6.04 | 0.054 | 0.11 | 0.788 | 0.06 | 0.192 | 0.174 | 0.07 | 10.2 | 99.63 |
| MWM/3B | 85.08 | 0.706 | 5.82 | 3.35 | 0.022 | 0.11 | 0.343 | 0.29 | 0.77 | 0.066 | 0.02 | 3.16 | 99.73 |
| MWM/9 | 62.51 | 0.825 | 4.23 | 17.93 | 0.128 | 0.39 | 2.366 | 0.19 | 0.332 | 0.308 | 0.25 | 9.81 | 99.26 |
| MWM/17A | 90.34 | 1.102 | 3.49 | 1.92 | 0.031 | 0.04 | 0.129 | 0.04 | 0.149 | 0.076 | <0.01 | 2.31 | 99.66 |
| MWM/18 | 59.81 | 1.033 | 12.18 | 8.33 | 0.073 | 0.85 | 3.652 | 1.27 | 1.62 | 0.256 | 0.25 | 10.21 | 99.54 |
| MWM/29 | 64.13 | 1.107 | 8.96 | 8.38 | 0.072 | 0.26 | 1.136 | 0.13 | 0.263 | 0.257 | 0.2 | 14.54 | 99.43 |
| RK/1 | 23.68 | 0.649 | 8.08 | 59.95 | 0.009 | 0.02 | 0.018 | <0.01 | 0.037 | 0.077 | 0.09 | 7.24 | 99.85 |
| RK/2 | 89.99 | 0.173 | 2.47 | 5.33 | 0.003 | <0.01 | <0.005 | <0.01 | 0.013 | 0.021 | <0.01 | 1.92 | 99.93 |
| CT/4 | 64.69 | 1.623 | 18.76 | 5.73 | 0.018 | 0.06 | 0.008 | <0.01 | 0.055 | 0.084 | <0.01 | 8.59 | 99.59 |
| FLG/3A | 78.33 | 2.14 | 5.91 | 5.63 | 0.055 | 0.07 | 0.097 | <0.01 | 0.067 | 0.163 | <0.01 | 6.52 | 98.97 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FLG/5A | 53.26 | 1.439 | 19.11 | 8.68 | 0.039 | 0.15 | 0.352 | 0.02 | 0.175 | 0.243 | 0.01 | 16.12 | 99.57 |
| MAP/3A | 72.13 | 1.693 | 5.94 | 8.2 | 0.064 | 0.1 | 0.744 | 0.08 | 0.195 | 0.417 | 0.07 | 9.44 | 99.07 |
| MAP/48 | 83.04 | 1.068 | 5.04 | 3.52 | 0.07 | 0.14 | 0.508 | 0.12 | 0.534 | 0.195 | 0.04 | 5.28 | 99.56 |
| AWD/3A | 60.66 | 0.891 | 6.69 | 6.27 | 0.082 | 0.25 | 1.856 | 0.25 | 0.592 | 0.317 | 0.26 | 21.24 | 99.32 |
| AWD/5A | 79.39 | 1.302 | 5.33 | 4.73 | 0.07 | 0.23 | 1.195 | 0.13 | 0.276 | 0.218 | 0.1 | 6.48 | 99.45 |
| SOC/5 | 76.09 | 1.092 | 9.52 | 3.94 | 0.063 | 0.1 | 0.398 | 0.07 | 0.179 | 0.152 | 0.02 | 8.11 | 99.72 |
| SOC/6 | 74.2 | 1.169 | 7.66 | 8.42 | 0.039 | 0.13 | 0.545 | 0.09 | 0.223 | 0.19 | 0.05 | 6.86 | 99.58 |
| ID/6 | 52.69 | 1.588 | 19.61 | 7.69 | 0.041 | 0.49 | 0.54 | 0.37 | 0.82 | 0.421 | 0.04 | 15.29 | 99.6 |
| ID/47 | 54.65 | 1.565 | 18.63 | 7.46 | 0.041 | 0.47 | 0.555 | 0.39 | 0.883 | 0.408 | 0.04 | 14.49 | 99.58 |
| NK/14 | 45.85 | 1.483 | 19.85 | 11.33 | 0.057 | 0.39 | 1.158 | 0.18 | 0.311 | 0.51 | 0.19 | 18.33 | 99.65 |

I: Cont'

| S/N | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $(SO_3)$ | LOI_SI | Sum_RF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RSD/24 | 80.05 | 0.96 | 3.93 | 5.97 | 0.073 | 0.27 | 1.533 | 0.45 | 0.838 | 0.447 | 0.26 | 4.83 | 99.62 |
| RSD/35 | 70.12 | 0.905 | 3.25 | 19.63 | 0.144 | 0.21 | 0.877 | 0.3 | 0.462 | 0.311 | 0.15 | 3.25 | 99.61 |
| RSD/16 | 89.29 | 0.79 | 3.55 | 2.51 | 0.021 | 0.13 | 0.389 | 0.21 | 0.259 | 0.106 | 0.05 | 2.46 | 99.78 |

Appendix 3: A: Geochemical Composition of soil Samples from the study area (Trace Elements)

| | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **MDL** | 0.1 | 0.1 | 0.1 | 1 | 0.1 | 0.1 | 1 | 0.5 | 0.1 | 2 | 1 | 1 | 0.01 | 0.1 | 1 |
| RA/1 | Soil Pulp | 0.9 | 37.5 | 34.7 | 454 | 18.7 | 9.9 | 445 | 6.4 | 0.3 | 67 | 21 | 54 | 0.33 | 6.2 | 8 |
| RA/2 | Soil Pulp | 0.8 | 30 | 33.2 | 273 | 14.4 | 9.3 | 423 | 3.4 | 0.3 | 56 | 22 | 44 | 0.49 | 5 | 8 |
| RA/3 | Soil Pulp | 0.9 | 84.7 | 257.3 | 1509 | 18.5 | 7.4 | 589 | 6.6 | 1.7 | 85 | 24 | 63 | 0.55 | 7.8 | 14 |
| RA/4 | Soil Pulp | 0.92 | 77.29 | 213.5 | 1221.1 | 22.7 | 7.2 | 876 | 5.9 | 1.82 | 63 | 23 | 56.4 | 1415 | | |
| RA/5$^A$ | Soil Pulp | 0.6 | 27.4 | 39.1 | 99 | 7.3 | 4.1 | 1069 | 1.8 | 0.3 | 42 | 14 | 34 | 0.13 | 4.4 | 6 |
| RA/5$^B$ | Soil Pulp | 0.7 | 25.1 | 22.9 | 36 | 9.3 | 4.5 | 1148 | 4.2 | 0.1 | 102 | 20 | 52 | 0.11 | 10.3 | 15 |
| RA/6 | Soil Pulp | 1.2 | 56.6 | 139.8 | 440 | 14.9 | 4.2 | 443 | 6.7 | 0.6 | 92 | 13 | 63 | 0.23 | 8 | 13 |
| RA/7 | Soil Pulp | 1.4 | 23.1 | 44 | 117 | 9.3 | 3.4 | 422 | 8.1 | 0.2 | 116 | 11 | 52 | 0.23 | 9.7 | 17 |
| RA/10 | Soil Pulp | 1.2 | 36.7 | 54.3 | 592 | 12.3 | 3.1 | 678 | 6.3 | 0.5 | 103 | 9 | 57 | 0.41 | 8.8 | 15 |
| RA/11$^A$ | Soil Pulp | 0.7 | 16.4 | 17.1 | 137 | 6.3 | 2 | 160 | 5.5 | 0.1 | 62 | 8 | 54 | 0.17 | 4.4 | 6 |
| RA/11$^B$ | Soil Pulp | 0.9 | 14 | 23 | 72 | 7.1 | 2.1 | 232 | 6.2 | 0.1 | 90 | 10 | 56 | 0.14 | 7 | 12 |
| RA/12 | Soil Pulp | 1.2 | 25.8 | 28.5 | 181 | 7.9 | 2.4 | 238 | 5.7 | 0.3 | 90 | 10 | 58 | 0.21 | 7.6 | 13 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RA/13$^{A}$ | Soil Pulp | 0.9 | 24.8 | 17.8 | 39 | 7.9 | 3 | 739 | 4.7 | 0.1 | 88 | 15 | 49 | 0.09 | 9.1 | 13 |
| RA/13$^{B}$ | Soil Pulp | 1.5 | 25.2 | 23 | 92 | 8 | 3.4 | 969 | 4.5 | 0.1 | 81 | 15 | 60 | 0.12 | 8.4 | 13 |
| RA/14 | Soil Pulp | 1.73 | 145.67 | 160.8 | 2557 | 22.2 | 9.1 | 2127 | 9.1 | 2.2 | 57 | 12 | 83.5 | 0.00 | 6.3 | 8 |
| RA/15$^{A}$ | Soil Pulp | 0.84 | 54.41 | 75.5 | 464.7 | 12.1 | 3.1 | 362 | 6.9 | 0.52 | 73 | 20 | 67 | 0.00 | 7.1 | 9 |
| RA/15$^{B}$ | Soil Pulp | 0.6 | 8.1 | 26.4 | 35 | 3.6 | 1 | 99 | 5.7 | 0.1 | 78 | 34 | 41 | 0.07 | 14.8 | 15 |
| RA/16$^{A}$ | Soil Pulp | 1.2 | 27 | 82.8 | 253 | 10.4 | 3 | 440 | 5.8 | 0.7 | 78 | 10 | 125 | 0.29 | 6.6 | 12 |
| RA/16$^{B}$ | Soil Pulp | 1 | 17.1 | 31.1 | 92 | 9 | 3.9 | 520 | 5.5 | 0.4 | 97 | 14 | 69 | 0.23 | 9.1 | 16 |
| RA/17 | Soil Pulp | 1.6 | 39.8 | 51.2 | 363 | 14.4 | 6.3 | 875 | 6.3 | 0.7 | 85 | 14 | 68 | 0.13 | 7.6 | 13 |
| RA/17$^{B}$ | Soil Pulp | 1.2 | 27.6 | 32.9 | 96 | 10.1 | 4.4 | 849 | 4.5 | 0.3 | 88 | 14 | 47 | 0.1 | 7.5 | 13 |
| RA/18 | Soil Pulp | 1.4 | 85.32 | 158.2 | 1259.5 | 21.2 | 5.1 | 609 | 5.1 | 0.94 | 36 | 13 | 47.5 | 0.1 | 8. | 9 |
| RA/19 | Soil Pulp | 0.2 | 11.1 | 12.5 | 15 | 1.1 | 0.3 | 7 | 0.5 | 0.1 | 42 | 28 | 24 | 0.02 | 8.2 | 6 |
| RA/20$^{A}$ | Soil Pulp | 1.6 | 23.4 | 56.9 | 286 | 11.2 | 3.6 | 519 | 4 | 0.4 | 94 | 11 | 78 | 0.24 | 7.7 | 17 |

A Cont’

| | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **MDL** | 0.1 | 0.1 | 0.1 | 1 | 0.1 | 0.1 | 1 | 0.5 | 0.1 | 2 | 1 | 1 | 0.01 | 0.1 | 1 |
| RA/21 | Soil Pulp | 0.9 | 37 | 130 | 282 | 10 | 4.4 | 427 | 3.3 | 0.5 | 83 | 22 | 47 | 0.23 | 8.6 | 13 |

B:  Geochemical Composition of Soil Samples from the study area (Trace Elements) Contn.

|  | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | **MDL** | 0.1 | 0.1 | 0.1 | 1 | 0.1 | 0.1 | 1 | 0.5 | 0.1 | 2 | 1 | 1 | 0.01 | 0.1 | 1 |
| SOC/1$^{A}$ | Soil Pulp | 0.2 | 13.3 | 11.9 | 62 | 10.7 | 20.1 | 718 | 0.5 | 0.1 | 32 | 25 | 24 | 0.03 | 3.3 | 5 |
| SOC/1$^{B}$ | Soil Pulp | 0.2 | 9 | 9.9 | 37 | 10 | 6.1 | 123 | BDL | BDL | 32 | 26 | 26 | 0.03 | 3.8 | 5 |
| SOC/2$^{A}$ | Soil Pulp | 0.7 | 35 | 163 | 405 | 8.8 | 2.8 | 472 | 2.7 | 0.5 | 50 | 10 | 43 | 0.18 | 4.6 | 8 |
| SOC/2$^{B}$ | Soil Pulp | 0.2 | 1.8 | 6.4 | 11 | 1.3 | 0.6 | 98 | BDL | BDL | 15 | 2 | 15 | <0.01 | 1.4 | 2 |
| SOC/3 | Soil Pulp | 0.7 | 15.1 | 25.2 | 47 | 8.3 | 4.4 | 779 | 3.1 | BDL | 91 | 18 | 47 | 0.07 | 9.7 | 14 |
| SOC/4 | Soil Pulp | 1 | 18.7 | 32 | 123 | 8.2 | 2.4 | 408 | 7.1 | 0.2 | 102 | 13 | 45 | 0.16 | 8.9 | 15 |
| SOC/5 | Soil Pulp | 1 | 35.2 | 165.9 | 451 | 21.3 | 4.8 | 749 | 6.7 | 0.6 | 82 | 15 | 51 | 0.29 | 6.8 | 12 |
| SOC/6 | Soil Pulp | 1.3 | 47.4 | 253.1 | 395 | 16.4 | 3.7 | 339 | 12.8 | 0.4 | 98 | 15 | 76 | 0.27 | 8.9 | 12 |
| SOC/7$^{A}$ | Soil Pulp | 1 | 37.7 | 99.4 | 386 | 13 | 4 | 555 | 7 | 0.9 | 75 | 13 | 66 | 0.33 | 6.5 | 11 |
| SOC/7$^{B}$ | Soil Pulp | 1.2 | 20.2 | 43.2 | 127 | 8.6 | 2.6 | 531 | 5.9 | 0.3 | 90 | 11 | 59 | 0.17 | 7.3 | 14 |
| SOC/8$^{A}$ | Soil Pulp | 0.7 | 31.8 | 45.2 | 363 | 10 | 1.9 | 335 | 3 | 0.6 | 41 | 6 | 44 | 0.3 | 3.2 | 6 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SOC/8$^{B}$ | Soil Pulp | 1.1 | 18.2 | 35.7 | 111 | 7.5 | 1.9 | 253 | 7.9 | 0.2 | 104 | 10 | 56 | 0.31 | 9.8 | 17 |
| SOC/9 | Soil Pulp | 0.9 | 14.6 | 31.8 | 196 | 8.1 | 1.9 | 344 | 4.7 | 0.1 | 83 | 11 | 50 | 0.21 | 6.7 | 13 |
| SOC/10$^{A}$ | Soil Pulp | 0.6 | 13.1 | 33.6 | 76 | 5.8 | 1.9 | 294 | 3.3 | BDL | 53 | 10 | 37 | 0.07 | 4.7 | 8 |
| SOC/10$^{B}$ | Soil Pulp | 0.8 | 15.7 | 18.5 | 23 | 6.2 | 2.2 | 389 | 4.6 | BDL | 75 | 14 | 44 | 0.08 | 6.9 | 12 |
| SOC/11 | Soil Pulp | 1.1 | 31.6 | 60.3 | 62 | 6.8 | 1.4 | 151 | 3.9 | 0.1 | 99 | 26 | 45 | 0.07 | 10.5 | 17 |
| SOC/12$^{A}$ | Soil Pulp | 2.53 | 123.16 | 207 | 452.3 | 10.5 | 3.7 | 383 | 11 | 0.38 | 74 | 10.7 | 70 | 0.06 | 4.9 | 10 |
| SOC/12$^{B}$ | Soil Pulp | 1 | 11.9 | 15.8 | 40 | 4.9 | 1.7 | 298 | 13.2 | BDL | 98 | 9 | 41 | 0.14 | 8 | 15 |
| SOC/13 | Soil Pulp | 1.4 | 35 | 68.9 | 413 | 9 | 1.7 | 251 | 2.3 | 0.4 | 47 | 6 | 51 | 0.06 | 4.3 | 8 |
| SOC/14$^{A}$ | Soil Pulp | 1.3 | 18.1 | 19 | 39 | 9.5 | 3.9 | 706 | 2.8 | BDL | 99 | 21 | 78 | 0.08 | 10.6 | 18 |
| SOC/14$^{B}$ | Soil Pulp | 1.1 | 11.7 | 16.5 | 19 | 7.8 | 2.7 | 387 | 2.7 | BDL | 111 | 14 | 57 | 0.08 | 10.6 | 20 |
| SOC/15$^{A}$ | Soil Pulp | 0.96 | 18.68 | 24.1 | 125.3 | 8.9 | 2.6 | 388 | 3 | 0.08 | 105 | 7.1 | 72.2 | 0.09 | 11.1 | 21 |
| SOC/15$^{B}$ | Soil Pulp | 1.2 | 13.4 | 16.9 | 18 | 8.7 | 2.3 | 310 | 4 | BDL | 122 | 8 | 60 | 0.09 | 11 | 21 |

C: Geochemical Composition of Soil Samples from the study area (Trace Elements) Contn.

| | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **MDL** | 0.1 | 0.1 | 0.1 | 1 | 0.1 | 0.1 | 1 | 0.5 | 0.1 | 2 | 1 | 1 | 0.01 | 0.1 | 1 |
| Sample No | **Type** | | | | | | | | | | | | | | | |
| FLG/1 | Soil Pulp | 0.20 | 21.75 | 19.5 | 96.1 | 14.2 | 8.3 | 197 | 0.8 | 0.09 | 55 | 38.3 | 34.5 | 0.09 | 8.2 | 9 |
| FLG/2 | Soil Pulp | 0.2 | 10.3 | 10.9 | 37 | 11.8 | 8.4 | 152 | <0.5 | BDL | 38 | 28 | 28 | 0.02 | 4.7 | 6 |
| FLG/3$^{A}$ | Soil Pulp | 1.9 | 259.3 | 115.8 | 8395 | 20.9 | 136.5 | 579 | 9.8 | 1.0 | 71 | 11 | 47 | 0.22 | 5.3 | 10 |
| FLG/3$^{B}$ | Soil Pulp | 1.1 | 29.8 | 36.4 | 934 | 9.1 | 16.3 | 162 | 8.8 | 0.1 | 91 | 13 | 39 | 0.09 | 6.5 | 14 |
| FLG/4 | Soil Pulp | 0.9 | 5.3 | 18.3 | 27 | 6.6 | 1.5 | 109 | 8.0 | <0.1 | 90 | 10 | 38 | 0.06 | 8.6 | 14 |
| FLG/5$^{A}$ | Soil Pulp | 0.9 | 15.7 | 41.0 | 174 | 6.0 | 3.4 | 318 | 3.9 | 0.1 | 64 | 10 | 64 | 0.09 | 5.3 | 9 |
| FLG/5$^{B}$ | Soil Pulp | 1.0 | 8.6 | 18.3 | 221 | 8.0 | 5.8 | 131 | 10.3 | BDL | 106 | 9 | 42 | 0.11 | 9.4 | 15 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FLG/6$^{A}$ | Soil Pulp | 1.0 | 33.4 | 366.2 | 451 | 10.4 | 3.9 | 389 | 8.0 | 0.6 | 87 | 14 | 56 | 0.21 | 8.2 | 13 |
| FLG/6$^{B}$ | Soil Pulp | 0.9 | 8.7 | 28.1 | 35 | 6.4 | 2.7 | 256 | 6.5 | BDL | 107 | 19 | 47 | 0.11 | 10.4 | 16 |
| FLG/7$^{A}$ | Soil Pulp | 1.1 | 16.2 | 25.3 | 90 | 7.6 | 2.1 | 359 | 2.4 | 0.1 | 84 | 11 | 53 | 0.15 | 7.3 | 15 |
| FLG/7$^{B}$ | Soil Pulp | 1.1 | 8.5 | 22.2 | 37 | 7.6 | 2.0 | 271 | 2.8 | BDL | 115 | 12 | 58 | 0.11 | 11.4 | 21 |
| FLG/8 | Soil Pulp | 1.1 | 6.9 | 18.4 | 21 | 6.5 | 1.3 | 136 | 2.6 | BDL | 104 | 11 | 59 | 0.09 | 9.5 | 20 |
| FLG/9$^{A}$ | Soil Pulp | 1.3 | 36.2 | 36.0 | 118 | 10.9 | 4.8 | 786 | 3.6 | 0.3 | 87 | 16 | 59 | 0.09 | 7.6 | 14 |
| FLG/9$^{B}$ | Soil Pulp | 1.2 | 19.4 | 24.5 | 50 | 8.7 | 4.1 | 879 | 2.5 | BDL | 86 | 17 | 53 | 0.10 | 8.3 | 15 |
| FLG/10$^{A}$ | Soil Pulp | 0.7 | 12.8 | 18.4 | 17 | 7.6 | 4.1 | 699 | 2.2 | BDL | 75 | 17 | 37 | 0.06 | 8.6 | 13 |
| FLG/10$^{B}$ | Soil Pulp | 0.6 | 13.0 | 17.6 | 17 | 9.5 | 3.6 | 451 | 3.0 | BDL | 86 | 20 | 38 | 0.06 | 10.7 | 16 |
| FLG/11 | Soil Pulp | 0.98 | 70.34 | 57.5 | 414.1 | 13.3 | 6.3 | 1320 | 3.2 | 0.53 | 84 | 21.9 | 53.9 | 0.07 | 9.1 | 11 |
| MAP/1$^{A}$ | Soil Pulp | 1.22 | 45.66 | 124.7 | 1274.3 | 12.4 | 6.5 | 860 | 1.4 | 1.01 | 31 | 17.2 | 37.4 | 0.06 | 7.2 | 9 |
| MAP/1$^{B}$ | Soil Pulp | 0.5 | 27.3 | 16.3 | 249 | 8.8 | 7.3 | 947 | 0.8 | BDL | 60 | 28 | 37 | 0.05 | 6.7 | 12 |
| MAP/2 | Soil Pulp | 1.4 | 132.7 | 270.2 | 1214 | 22.1 | 6.1 | 526 | 6.4 | 2.0 | 48 | 18 | 51 | 0.51 | 4.1 | 7 |
| MAP/3$^{A}$ | Soil Pulp | 1.54 | 214.39 | 90.2 | 5169.0 | 47.9 | 43.3 | 593 | 7.2 | 0.81 | 52 | 9.2 | 57.1 | 0.29 | 5.2 | 8 |
| MAP/3$^{B}$ | Soil Pulp | 1.6 | 123.0 | 57.9 | 2899 | 35.0 | 22.0 | 470 | 7.0 | 0.5 | 82 | 11 | 75 | 0.43 | 7.7 | 14 |

D: Geochemical Composition of Soil Samples from the study area (Trace Elements) Contn.

|  | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | **MDL** | 0.1 | 0.1 | 0.1 | 1 | 0.1 | 0.1 | 1 | 0.5 | 0.1 | 2 | 1 | 1 | 0.01 | 0.1 | 1 |
| Sample | **Type** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

| No | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AWD/1 | Soil Pulp | 0.8 | 44.3 | 38.3 | 655 | 12.7 | 6.9 | 1128 | 1.1 | 0.5 | 61 | 31 | 39 | 0.18 | 7.2 | 12 |
| AWD/2 | Soil Pulp | 0.6 | 15 | 20.4 | 84 | 11.7 | 10.7 | 433 | 2.1 | BDL | 72 | 32 | 40 | 0.04 | 8 | 12 |
| AWD/3$^{A}$ | Soil Pulp | 1.6 | 22.9 | 135.7 | 584 | 10.3 | 3.8 | 416 | 4.1 | 1.7 | 91 | 12 | 78 | 0.3 | 7.4 | 16 |
| AWD/3$^{B}$ | Soil Pulp | 1.2 | 8.9 | 28.7 | 80 | 8.3 | 1.7 | 270 | 3.2 | 0.2 | 119 | 11 | 68 | 0.12 | 9.8 | 22 |
| AWD/4$^{A}$ | Soil Pulp | 2.22 | 32.81 | 153 | 388.5 | 9.8 | 8 | 405 | 5.5 | 0.33 | 91 | 11.7 | 74.1 | 0.27 | 6.8 | 15 |
| AWD/4$^{B}$ | Soil Pulp | 1.4 | 11.1 | 31.2 | 52 | 7 | 1.8 | 181 | 4.5 | BDL | 104 | 15 | 61 | 0.09 | 9.6 | 19 |
| AWD/5$^{A}$ | Soil Pulp | 1.8 | 206.2 | 267.5 | 1506 | 20.5 | 42.1 | 1073 | 5.6 | 4.5 | 60 | 13 | 75 | 0.24 | 5.4 | 9 |
| AWD/5$^{B}$ | Soil Pulp | 1.5 | 181.8 | 215.4 | 1337 | 18.7 | 10.1 | 610 | 7.2 | 2 | 92 | 19 | 78 | 0.51 | 8.1 | 15 |
| AWD/6$^{A}$ | Soil Pulp | 2.6 | 233.7 | 311.9 | 1855 | 33.1 | 11.6 | 974 | 7.2 | 4.8 | 95 | 17 | 118 | 0.95 | 7.5 | 16 |
| AWD/6$^{B}$ | Soil Pulp | 1.7 | 41.1 | 94.4 | 282 | 10.7 | 4.5 | 226 | 5.6 | 0.9 | 123 | 18 | 83 | 0.16 | 9.8 | 20 |
| AWD/7 | Soil Pulp | 1.26 | 35.4 | 44.7 | 352.4 | 10.2 | 3.2 | 429 | 5 | 0.45 | 93 | 9.6 | 50.9 | 0.34 | 6.3 | 9 |
| AWD/8 | Soil Pulp | 4.7 | 457 | 448.4 | 4298 | 31.1 | 34.6 | 631 | 9.6 | 5.6 | 82 | 22 | 85 | 0.34 | 7.2 | 14 |
| CT/2 | Soil Pulp | 0.69 | 9.83 | 15.7 | 35.5 | 5.2 | 1.5 | 241 | 3.8 | BDL | 95 | 12 | 43.9 | 0.06 | 5.7 | 7 |
| CT/3 | Soil Pulp | 0.7 | 5.6 | 7.2 | 10 | 3.6 | 1.1 | 104 | 6.9 | BDL | 81 | 11 | 27 | 0.07 | 7.4 | 11 |
| CT/4 | Soil Pulp | 0.6 | 5.3 | 22.1 | 9 | 2.6 | 0.8 | 66 | 6.2 | BDL | 83 | 24 | 35 | 0.04 | 9.7 | 14 |
| CT/5 | Soil Pulp | 0.5 | 7.1 | 18.6 | 15 | 2.4 | 0.7 | 101 | 3.5 | BDL | 83 | 23 | 33 | 0.03 | 7.7 | 13 |
| CT/6 | Soil Pulp | 0.3 | 5.5 | 16.1 | 3 | 0.3 | 0.2 | 10 | 0.5 | BDL | 55 | 24 | 24 | <0.01 | 2.8 | 3 |
| RK/1 | Soil Pulp | 0.48 | 5.42 | 28.1 | 21.9 | 0.7 | 0.3 | 30 | 12 | BDL | 44 | 5.4 | 44.5 | 0.01 | 3.0 | 5 |
| RK2 | Soil Pulp | 0.6 | 11.3 | 15.7 | 17 | 0.3 | 0.3 | 41 | 27.3 | BDL | 81 | 18 | 28 | 0.03 | 10.2 | 5 |
| RK/3 | Soil Pulp | 0.4 | 7 | 22 | 8 | 2.1 | 0.7 | 59 | 5.6 | BDL | 69 | 26 | 29 | 0.05 | 9.4 | 11 |

E: Geochemical Composition of Soil Samples from the study area (Trace Elements) Contn.

| Sample No | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MWM/1 | Soil Pulp | 0.8 | 31.2 | 34.9 | 197 | 12.7 | 7.8 | 340 | 3.3 | 0.2 | 69 | 26 | 58 | 0.05 | 6.5 | 8 |

E Cont'n

| Sample No | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MWM/2$^{A}$ | Soil Pulp | 2.1 | 81.4 | 314.6 | 687 | 24.7 | 7.5 | 417 | 4.4 | 0.7 | 50 | 21 | 59 | 0.07 | 4.7 | 7 |
| MWM/2$^{B}$ | Soil Pulp | 1.09 | 46.42 | 119 | 366.1 | 14.5 | 4.8 | 232 | 2.6 | 0.37 | 29 | 15.2 | 34.8 | 0.10 | 5.2 | 6 |
| MWM/2$^{A}$ | Soil Pulp | 2.2 | 101.9 | 182.7 | 433 | 17.3 | 4.7 | 286 | 10.8 | 0.6 | 86 | 13 | 67 | 0.11 | 7.2 | 12 |
| MWM/3$^{A}$ | Soil Pulp | 1.5 | 70.71 | 192 | 381.8 | 23.9 | 2.7 | 200 | 2.9 | 0.55 | 24 | 6.5 | 42.9 | 0.09 | 6.7 | 8 |
| MWM/3$^{B}$ | Soil Pulp | 1 | 48.4 | 310.5 | 357 | 12.1 | 4.7 | 214 | 4.1 | 0.3 | 61 | 17 | 59 | 0.07 | 5.9 | 8 |
| MWM/4$^{A}$ | Soil Pulp | 2.39 | 151.38 | 327 | 3477.4 | 19.4 | 22 | 615 | 5 | 3.39 | 34 | 14.5 | 47.9 | 0.21 | 7.5 | 5 |
| MWM/4$^{B}$ | Soil Pulp | 1.1 | 28.3 | 58.6 | 233 | 7.2 | 2 | 226 | 5.3 | 0.4 | 55 | 14 | 52 | 0.23 | 5.3 | 6 |
| MWM/5 | Soil Pulp | 6.01 | 219.97 | 580.6 | 2079.2 | 54 | 11 | 521 | 7.8 | 4.8 | 44 | 9.3 | 96.4 | 0.19 | 6.2 | 9 |
| MWM/6$^{A}$ | Soil Pulp | 2.9 | 166.2 | 1444.3 | 939 | 29.1 | 7.5 | 992 | 6.8 | 4.3 | 51 | 10 | 69 | 0.7 | 4.2 | 7 |
| MWM/6$^{B}$ | Soil Pulp | 0.7 | 17.3 | 41.1 | 50 | 7.9 | 2.7 | 763 | 4.2 | 0.1 | 82 | 11 | 43 | 0.13 | 6.7 | 12 |
| MWM/7$^{A}$ | Soil Pulp | 0.4 | 33.3 | 30.9 | 121 | 4.4 | 1 | 117 | 2 | 0.2 | 28 | 5 | 29 | 0.11 | 2.6 | 3 |
| MWM/7$^{B}$ | Soil Pulp | 0.8 | 12 | 22.7 | 24 | 7.5 | 3 | 509 | 5.3 | 0.1 | 118 | 23 | 55 | 0.07 | 11.4 | 17 |
| MWM/8 | Soil Pulp | 1 | 23.5 | 72.5 | 111 | 10.2 | 3.7 | 311 | 2.7 | 0.1 | 109 | 13 | 49 | 0.22 | 13 | 17 |
| MWM/9 | Soil Pulp | 10.1 | 1123.2 | 1067.5 | 5218 | 223.7 | 24.8 | 1698 | 12.5 | 10.3 | 59 | 12 | 157 | 0.91 | 4 | 8 |
| MWM/10 | Soil Pulp | 4.7 | 236.4 | 211.6 | 1228 | 27.9 | 6.2 | 284 | 5.9 | 1.4 | 69 | 25 | 70 | 0.12 | 6.3 | 10 |
| MWM/11 | Soil Pulp | 46.88 | 1048.9 | 429.5 | 2208.1 | 236.6 | 21.3 | 1920 | 19.8 | 5.3 | 51 | 9 | 443 | 0.21 | 7.1 | 6 |
| MWM/12$^{A}$ | Soil Pulp | 1.6 | 29.7 | 38 | 237 | 12.1 | 3.9 | 615 | 3.5 | 0.3 | 94 | 15 | 70 | 0.14 | 8.6 | 17 |
| MWM/12$^{B}$ | Soil Pulp | 1.2 | 14.7 | 24.8 | 77 | 14.3 | 3.8 | 483 | 7.2 | 0.1 | 121 | 15 | 78 | 0.14 | 11.6 | 20 |
| MWM/13$^{A}$ | Soil Pulp | 1.3 | 29.7 | 73.8 | 92 | 11.7 | 3.1 | 462 | 4.6 | 0.1 | 107 | 16 | 60 | 0.12 | 8.9 | 17 |
| MWM/13$^{B}$ | Soil Pulp | 1 | 17.1 | 22.4 | 28 | 9.2 | 2.9 | 511 | 3.1 | 0.1 | 102 | 15 | 54 | 0.1 | 10.1 | 18 |
| MWM/14 | Soil Pulp | 5.77 | 167.88 | 1048.1 | 1372.8 | 42.6 | 8.4 | 481 | 5.5 | 6 | 49 | 10.6 | 121 | 0.15 | 9.5 | 9 |
| MWM/15$^{A}$ | Soil Pulp | 1.9 | 62.6 | 81.9 | 300 | 19.4 | 2.8 | 220 | 5.4 | 0.7 | 42 | 8 | 58 | 0.07 | 3.1 | 6 |
| MWM/15$^{B}$ | Soil Pulp | 1.2 | 16.6 | 22.4 | 33 | 9.3 | 2.4 | 350 | 9.3 | 0.1 | 92 | 12 | 47 | 0.15 | 6.3 | 15 |
| MWM/16$^{A}$ | Soil Pulp | 4.89 | 232.61 | 1730.5 | 1570.5 | 32.5 | 9 | 758 | 8 | 2.87 | 69 | 14.3 | 118 | 0.19 | 7.1 | 12 |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MWM/16$^{B}$ | Soil Pulp | 3.1 | 126.7 | 2026.4 | 1018 | 19.5 | 6 | 998 | 4.5 | 2.4 | 80 | 16 | 67 | 0.26 | 7.4 | 13 |
| MWM/17$^{A}$ | Soil Pulp | 1.67 | 116.39 | 239.9 | 7568.1 | 26.8 | 8.3 | 577 | 3.2 | 10.19 | 58 | 14.1 | 67.1 | 0.14 | 9.1 | 12 |
| MWM/17$^{B}$ | Soil Pulp | 0.9 | 24.4 | 28.6 | 346 | 10.1 | 4.3 | 900 | 3.4 | 0.8 | 81 | 20 | 45 | 0.08 | 8.1 | 14 |
| MWM/18 | Soil Pulp | 2 | 83.7 | 217.2 | 612 | 24.1 | 7.6 | 402 | 4.2 | 0.6 | 54 | 35 | 54 | 0.08 | 5.2 | 7 |

F: Geochemical Composition of Stream sediment Samples from the study area (Trace Elements)

|  | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Th | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ID/1 | Sediment Pulp | 0.9 | 57.6 | 119.5 | 518 | 16.5 | 6.7 | 204 | 4.1 | 7.8 | 0.6 | 77 | 26 | 51 | 0.38 | 6.1 | 10 |
| ID/2 | Sediment Pulp | 1.3 | 71.9 | 119.9 | 599 | 18.5 | 10.1 | 348 | 4.6 | 9.2 | 0.6 | 83 | 30 | 54 | 0.42 | 7 | 11 |
| ID/3 | Sediment Pulp | 0.91 | 71.6 | 126.4 | 596.6 | 19.4 | 8.6 | 255 | 4.5 | 9.2 | 0.61 | 71 | 29.8 | 53.6 | 0.25 | 9.2 | 12 |
| ID/4 | Sediment Pulp | 0.96 | 82.55 | 150 | 686.9 | 18.7 | 6.2 | 234 | 5 | 9.2 | 0.76 | 82 | 25.7 | 60.6 | 0.17 | 5.2 | 9 |
| ID/5 | Sediment Pulp | 1.4 | 82 | 180.3 | 776 | 19.8 | 7 | 307 | 5.7 | 6.8 | 0.9 | 89 | 24 | 60 | 0.49 | 6.7 | 12 |
| ID/6 | Sediment Pulp | 1.3 | 79.4 | 147.8 | 693 | 18.6 | 6.1 | 242 | 5 | 8.7 | 0.8 | 92 | 25 | 60 | 0.48 | 7.2 | 12 |
| ID/7 | Sediment Pulp | 0.3 | 18.4 | 19.7 | 101 | 16.3 | 11.3 | 332 | 0.6 | 9.2 | 0.1 | 51 | 39 | 33 | 0.07 | 5.3 | 8 |
| ID/8 | Sediment Pulp | 1.6 | 32 | 25.2 | 239 | 6.7 | 3.6 | 253 | 7.3 | 18.4 | <0.1 | 117 | 11 | 58 | 0.07 | 8.5 | 17 |
| ID/9 | Sediment Pulp | 2.2 | 104.3 | 117.4 | 293 | 40.2 | 8.2 | 395 | 5.5 | 8.5 | 0.5 | 69 | 18 | 57 | 0.07 | 4.8 | 9 |
| ID/10 | Sediment Pulp | 1.3 | 44.4 | 63.3 | 319 | 12.6 | 4.1 | 252 | 7.9 | 13.2 | 0.3 | 115 | 17 | 59 | 0.22 | 9.6 | 14 |
| NK/11 | Sediment Pulp | 1.4 | 52.9 | 64.3 | 378 | 13.1 | 4.1 | 313 | 8.7 | 14.5 | 0.5 | 114 | 15 | 58 | 0.22 | 9.5 | 14 |
| NK/12 | Sediment Pulp | 1.6 | 21.6 | 25.7 | 154 | 7.9 | 3.8 | 837 | 13.6 | 17.2 | <0.1 | 121 | 12 | 51 | 0.09 | 10 | 15 |
| NK/13 | Sediment Pulp | 0.82 | 20.89 | 36.4 | 146 | 8.9 | 2.6 | 222 | 10.5 | 16.2 | 0.23 | 104 | 12.6 | 49.4 | 0.17 | 8.7 | 9 |
| NK/14 | Sediment Pulp | 1.43 | 77.67 | 83.7 | 555.9 | 16.4 | 6.3 | 380 | 10.9 | 10.3 | 0.75 | 93 | 20 | 58.3 | 0.29 | 7.9 | 11 |
| NK/15 | Sediment Pulp | 1.4 | 35.3 | 43.9 | 196 | 8.2 | 2.8 | 185 | 10.7 | 11.7 | 0.3 | 109 | 13 | 48 | 0.16 | 8.3 | 12 |
| NK/17 | Sediment Pulp | 1.4 | 45.9 | 64.6 | 325 | 12 | 4.2 | 263 | 8.4 | 14 | 0.2 | 117 | 17 | 61 | 0.26 | 10 | 14 |
| NK/18 | Sediment Pulp | 1.5 | 13.7 | 24.1 | 116 | 8.1 | 3.7 | 1178 | 16.9 | 15.8 | 0.1 | 117 | 12 | 46 | 0.09 | 10.1 | 14 |
| NK/19 | Sediment Pulp | 1.1 | 19.9 | 35 | 144 | 8.2 | 2.6 | 237 | 11.7 | 14.6 | 0.3 | 115 | 12 | 49 | 0.1 | 9.9 | 13 |
| NK/20 | Sediment Pulp | 1.6 | 50.9 | 72.3 | 357 | 13.6 | 5.2 | 377 | 11 | 13 | 0.4 | 116 | 19 | 62 | 0.22 | 9.5 | 13 |

G: Geochemical Composition of Roadside Drain sediment Samples from the study area (Trace Elements)

|  | **Analyte** | Mo | Cu | Pb | Zn | Ni | Co | Mn | As | Th | Cd | V | La | Cr | Hg | Sc | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RSD/1 | Sediment Pulp | 0.8 | 38.9 | 45.7 | 95 | 13.1 | 4.1 | 250 | 3.8 | 7.4 | 0.1 | 56 | 10 | 68 | 0.02 | 4.1 | 6 |
| RSD/2 | Sediment Pulp | 1.4 | 120.6 | 66.2 | 187 | 12.3 | 3.7 | 335 | 5 | 15.5 | 0.4 | 101 | 12 | 55 | 0.12 | 9.7 | 14 |
| RSD/3 | Sediment Pulp | 1.1 | 28.2 | 54.4 | 180 | 12.2 | 3.9 | 254 | 3.3 | 8.6 | 0.2 | 63 | 12 | 50 | 0.1 | 4.9 | 8 |
| RSD/4 | Sediment Pulp | 1.6 | 51 | 65 | 365 | 12.3 | 4.2 | 317 | 6.3 | 8.7 | 0.3 | 70 | 12 | 79 | 0.17 | 5.1 | 7 |
| RSD/5 | Sediment Pulp | 1.7 | 47.5 | 49.8 | 222 | 13.8 | 3.6 | 251 | 3.5 | 6.4 | 0.4 | 38 | 12 | 56 | 0.04 | 2.6 | 4 |
| RSD/6 | Sediment Pulp | 1.7 | 56 | 74.8 | 306 | 14.9 | 4.5 | 294 | 4.1 | 7.2 | 0.5 | 47 | 15 | 60 | 0.07 | 3.3 | 5 |
| RSD/7 | Sediment Pulp | 1.6 | 82.9 | 540.1 | 439 | 18.7 | 5.9 | 389 | 5.2 | 6.7 | 0.7 | 61 | 13 | 57 | 0.1 | 4.5 | 8 |
| RSD/8 | Sediment Pulp | 6.2 | 122.1 | 331.4 | 1045 | 45.6 | 10.7 | 613 | 5.5 | 4 | 1.6 | 56 | 12 | 82 | 0.31 | 3.7 | 7 |
| RSD/9 | Sediment Pulp | 1.4 | 55.1 | 89.9 | 354 | 24.5 | 7.6 | 470 | 4.1 | 5.3 | 0.5 | 67 | 13 | 58 | 0.21 | 4.8 | 8 |
| RSD/10 | Sediment Pulp | 1.3 | 38 | 81.1 | 293 | 14.1 | 4.3 | 623 | 6.4 | 7.9 | 0.5 | 89 | 14 | 51 | 0.22 | 7 | 12 |
| RSD/12 | Sediment Pulp | 2.3 | 120.3 | 320.5 | 469 | 15.8 | 6.1 | 365 | 5.9 | 3.3 | 0.6 | 48 | 12 | 42 | 0.14 | 2.8 | 6 |
| RSD/13 | Sediment Pulp | 1.1 | 46.4 | 90 | 277 | 11.2 | 5.2 | 350 | 2.6 | 2.9 | 0.3 | 35 | 10 | 33 | 0.04 | 2.2 | 4 |
| RSD/11 | Sediment Pulp | 1.8 | 104.45 | 151.2 | 582.3 | 26.9 | 6 | 405 | 7.9 | 9.1 | 1.01 | 87 | 17.2 | 63.9 | 0.06 | 4.1 | 6 |
| RSD/14 | Sediment Pulp | 2.11 | 129.35 | 140.9 | 519.3 | 23.5 | 8 | 411 | 6.8 | 7.1 | 0.65 | 68 | 18.6 | 55.9 | 0.07 | 5.0 | 8 |
| RSD/15 | Sediment Pulp | 1.3 | 61.3 | 70.5 | 390 | 12 | 3.7 | 298 | 4.5 | 8.5 | 0.3 | 56 | 14 | 49 | 0.1 | 4.7 | 7 |
| RSD/16 | Sediment Pulp | 1.16 | 65.62 | 145.9 | 715.3 | 15.3 | 10.7 | 407 | 5.2 | 8.9 | 0.54 | 65 | 17.2 | 56.5 | 0.03 | 2.8 | 8 |
| RSD/20 | Sediment Pulp | 3.1 | 69.7 | 124.9 | 1173 | 23.2 | 7.3 | 448 | 6.4 | 5.5 | 0.6 | 46 | 16 | 63 | 0.13 | 3.2 | 5 |
| RSD/21 | Sediment Pulp | 2.18 | 67.51 | 60.3 | 372.4 | 35.3 | 8.6 | 508 | 3.6 | 11.8 | 0.35 | 68 | 28.7 | 63.6 | 0.05 | 2.4 | 7 |
| RSD/22 | Sediment Pulp | 10.5 | 226.4 | 125.3 | 737 | 90.8 | 17.5 | 1410 | 8.6 | 3.9 | 1.6 | 35 | 12 | 123 | 1.06 | 2.8 | 6 |
| RSD/23 | Soil Pulp | 1.8 | 123.2 | 140.8 | 965 | 25.1 | 5.6 | 456 | 3.8 | 2 | 1.4 | 30 | 10 | 46 | 1.28 | 2.1 | 4 |
| RSD24 | Soil Pulp | 3 | 160.7 | 410.1 | 866 | 36.1 | 10.2 | 625 | 8.6 | 4.4 | 1.1 | 39 | 11 | 77 | 0.41 | 3 | 4 |

Appendix 4:

A: Results of the calculate Geo-accumulation Index (I-geo) for soil samples in Onitsha area.

| Sample No | Cu Igeo | PbIgeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo | Mo Igeo |
|---|---|---|---|---|---|---|---|---|
| RA/1 | 3 | 1.5 | 6 | 3.7 | 4.4 | 3 | 0.2 | 1.4 |
| RA/2 | 2.7 | 1.5 | 5 | 3.3 | 4.3 | 3 | -0.7 | 1.3 |
| RA/3 | 4.2 | 4.4 | 7 | 3.7 | 4 | 3 | 0.3 | 1.4 |
| RA/4 | 4 | 4.1 | 7 | 4 | 3.9 | 4 | 0.1 | 1.5 |
| RA/5$^{A}$ | 2.5 | 1.7 | 3 | 2.3 | 3.1 | 4 | -1.6 | 0.8 |
| RA/5$^{B}$ | 2.4 | 0.9 | 2 | 2.7 | 3.3 | 4 | -0.4 | 1.1 |
| RA/6 | 3.6 | 3.5 | 6 | 3.3 | 3.2 | 3 | 0.3 | 1.8 |
| RA/7 | 2.3 | 1.9 | 4 | 2.7 | 2.9 | 3 | 0.6 | 2.1 |
| RA/10 | 3 | 2.2 | 6 | 3.1 | 2.7 | 4 | 0.2 | 1.8 |
| RA/11$^{A}$ | 1.8 | 0.5 | 4 | 2.1 | 2.1 | 2 | 0 | 1.1 |
| RA/11$^{B}$ | 1.6 | 0.9 | 3 | 2.3 | 2.2 | 2 | 0.2 | 1.4 |
| RA/12 | 2.4 | 1.2 | 4 | 2.4 | 2.4 | 2 | 0.1 | 1.8 |
| RA/13$^{A}$ | 2.4 | 0.6 | 2 | 2.4 | 2.7 | 4 | -0.2 | 1.4 |
| RA/13$^{B}$ | 2.4 | 0.9 | 3 | 2.4 | 2.9 | 4 | -0.3 | 2.2 |
| RA/14 | 4.9 | 3.7 | 8 | 3.9 | 4.3 | 5 | 0.7 | 2.4 |
| RA/15$^{A}$ | 3.5 | 2.6 | 6 | 3 | 2.7 | 3 | 0.3 | 1.3 |
| RA/15$^{B}$ | 0.8 | 1.1 | 2 | 1.3 | 1.1 | 1 | 0.1 | 0.8 |
| RA/16$^{A}$ | 2.5 | 2.8 | 5 | 2.8 | 2.7 | 3 | 0.1 | 1.8 |
| RA/16$^{B}$ | 1.9 | 1.4 | 3 | 2.6 | 3.1 | 3 | 0 | 1.6 |
| RA/17 | 3.1 | 2.1 | 5 | 3.3 | 3.8 | 4 | 0.2 | 2.3 |
| RA/17$^{B}$ | 2.5 | 1.4 | 3 | 2.8 | 3.2 | 4 | -0.3 | 1.8 |
| RA/18 | 4.2 | 3.7 | 7 | 3.9 | 3.5 | 3 | -0.1 | 2.1 |
| RA/19 | 1.2 | 0 | 1 | -0.4 | -0.6 | -3 | -3.5 | -0.7 |
| RA/20$^{A}$ | 2.3 | 2.2 | 5 | 2.9 | 2.9 | 3 | -0.5 | 2.3 |
| RA/20$^{B}$ | 0.8 | 0.8 | 1 | 2.6 | 2 | 2 | -0.7 | 1.7 |
| RA/21 | 3 | 3.4 | 5 | 2.8 | 3.2 | 3 | -0.7 | 1.4 |
| SOC/1$^{A}$ | 1.5 | 0 | 3 | 2.9 | 5.4 | 4 | -3.5 | -0.7 |

A: Cont’

| Sample No | Cu Igeo | PbIgeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo | Mo Igeo |
|---|---|---|---|---|---|---|---|---|
| SOC/1$^B$ | 0.9 | -0.3 | 2 | 2.8 | 3.7 | 1 | 0 | -0.7 |
| SOC/2$^A$ | 2.9 | 3.7 | 5 | 2.6 | 2.6 | 3 | -1 | 1.1 |
| SOC/2$^B$ | -1.4 | -0.9 | 0 | -0.2 | 0.4 | 1 | 0 | -0.7 |
| SOC/3 | 1.7 | 1.1 | 2 | 2.5 | 3.2 | 4 | -0.8 | 1.1 |
| SOC/4 | 2 | 1.4 | 4 | 2.5 | 2.4 | 3 | 0.4 | 1.6 |
| SOC/5 | 2.9 | 3.8 | 6 | 3.9 | 3.4 | 4 | 0.3 | 1.6 |
| SOC/6 | 3.3 | 4.4 | 5 | 3.5 | 3 | 3 | 1.2 | 2 |
| SOC/7$^A$ | 3 | 3 | 5 | 3.1 | 3.1 | 3 | 0.4 | 1.6 |
| SOC/7$^B$ | 2.1 | 1.8 | 4 | 2.6 | 2.5 | 3 | 0.1 | 1.8 |
| SOC/8$^A$ | 2.7 | 1.9 | 5 | 2.8 | 2 | 3 | -0.9 | 1.1 |
| SOC/8$^B$ | 1.9 | 1.6 | 4 | 2.4 | 2 | 2 | 0.5 | 1.7 |
| SOC/9 | 1.6 | 1.4 | 4 | 2.5 | 2 | 3 | -0.2 | 1.4 |
| SOC/10$^A$ | 1.5 | 1.5 | 3 | 2 | 2 | 2 | -0.7 | 0.8 |
| SOC/10$^B$ | 1.7 | 0.6 | 1 | 2.1 | 2.2 | 3 | -0.2 | 1.3 |
| SOC/11 | 2.7 | 2.3 | 3 | 2.2 | 1.6 | 1 | -0.5 | 1.7 |
| SOC/12$^A$ | 4.7 | 4.1 | 6 | 2.8 | 3 | 3 | 1 | 2.9 |
| SOC/12$^B$ | 1.3 | 0.4 | 2 | 1.7 | 1.9 | 2 | 1.3 | 1.6 |
| SOC/13 | 2.9 | 2.5 | 5 | 2.6 | 1.9 | 2 | -1.2 | 2.1 |
| SOC/14$^A$ | 1.9 | 0.6 | 2 | 2.7 | 3.1 | 4 | -1 | 2 |
| SOC/14$^B$ | 1.3 | 0.4 | 1 | 2.4 | 2.5 | 3 | -1 | 1.7 |
| SOC/15$^A$ | 2 | 1 | 4 | 2.6 | 2.5 | 3 | -0.9 | 1.5 |
| SOC/15$^B$ | 1.5 | 0.5 | 1 | 2.6 | 2.3 | 3 | -0.5 | 1.8 |
| CT/2 | 1.1 | 0.4 | 2 | 1.8 | 1.7 | 2 | -0.5 | 1 |
| CT/3 | 0.2 | -0.8 | 0 | 1.3 | 1.2 | 1 | 0.3 | 1.1 |
| CT/4 | 0.2 | 0.9 | 0 | 0.8 | 0.8 | 0 | 0.2 | 0.8 |
| CT/5 | 0.6 | 0.6 | 1 | 0.7 | 0.6 | 1 | -0.6 | 0.6 |
| CT/6 | 0.2 | 0.4 | -2 | -2.3 | -1.2 | -2 | -3.5 | -0.2 |
| RK/1 | 0.2 | 1.2 | 1 | -1.1 | -0.6 | -1 | 1.1 | 0.5 |
| RK2 | 1.3 | 0.4 | 1 | -2.3 | -0.6 | 0 | 2.3 | 0.8 |
| RK/3 | 0.6 | 0.9 | 0 | 0.5 | 0.6 | 0 | 0 | 0.3 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| FLG/1 | 2.2 | 0.7 | 3 | 3.3 | 4.2 | 2 | -2.8 | -0.7 |

A: Cont’

| Sample No | Cu Igeo | PbIgeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo | Mo Igeo |
|---|---|---|---|---|---|---|---|---|
| FLG/2 | 1.1 | -0.2 | 2 | 3 | 4.2 | 1 | -3.8 | -0.7 |
| FLG/3$^{A}$ | 5.8 | 3.3 | 10 | 3.8 | 8.2 | 3 | 0.8 | 2.5 |
| FLG/3$^{B}$ | 2.7 | 1.6 | 7 | 2.6 | 5.1 | 2 | 0.7 | 1.7 |
| FLG/4 | 0.2 | 0.6 | 2 | 2.2 | 1.7 | 1 | 0.5 | 1.4 |
| FLG/5$^{A}$ | 1.7 | 1.8 | 4 | 2 | 2.9 | 3 | -0.5 | 1.4 |
| FLG/5$^{B}$ | 0.9 | 0.6 | 5 | 2.4 | 3.6 | 1 | 0.9 | 1.6 |
| FLG/6$^{A}$ | 2.8 | 4.9 | 6 | 2.8 | 3.1 | 3 | 0.5 | 1.6 |
| FLG/6$^{B}$ | 0.9 | 1.2 | 2 | 2.1 | 2.5 | 2 | 0.2 | 1.4 |
| FLG/7$^{A}$ | 1.8 | 1.1 | 3 | 2.4 | 2.2 | 3 | -1.2 | 1.7 |
| FLG/7$^{B}$ | 0.8 | 0.9 | 2 | 2.4 | 2.1 | 2 | -1 | 1.7 |
| FLG/8 | 0.5 | 0.6 | 1 | 2.1 | 1.5 | 1 | -1.1 | 1.7 |
| FLG/9$^{A}$ | 2.9 | 1.6 | 4 | 2.9 | 3.4 | 4 | -0.6 | 2 |
| FLG/9$^{B}$ | 2 | 1 | 2 | 2.6 | 3.1 | 4 | -1.1 | 1.8 |
| FLG/10$^{A}$ | 1.4 | 0.6 | 1 | 2.4 | 3.1 | 4 | -1.3 | 1.1 |
| FLG/10$^{B}$ | 1.5 | 0.5 | 1 | 2.7 | 2.9 | 3 | -0.9 | 0.8 |
| FLG/11 | 3.9 | 2.2 | 5 | 3.2 | 3.8 | 5 | -0.8 | 1.6 |
| MAP/1$^{A}$ | 3.3 | 3.4 | 7 | 3.1 | 3.8 | 4 | -2 | 1.9 |
| MAP/1$^{B}$ | 2.5 | 0.4 | 5 | 2.6 | 4 | 4 | -2.8 | 0.6 |
| MAP/2 | 4.8 | 4.5 | 7 | 3.9 | 3.7 | 3 | 0.2 | 2.1 |
| MAP/3$^{A}$ | 5.5 | 2.9 | 9 | 5 | 6.5 | 3 | 0.4 | 2.2 |
| MAP/3$^{B}$ | 4.7 | 2.3 | 8 | 4.6 | 5.6 | 3 | 0.4 | 2.3 |
| AWD/1 | 3.2 | 1.7 | 6 | 3.1 | 3.9 | 4 | -2.3 | 1.3 |
| AWD/2 | 1.7 | 0.7 | 3 | 3 | 4.5 | 3 | -1.4 | 0.8 |
| AWD/3$^{A}$ | 2.3 | 3.5 | 6 | 2.8 | 3 | 3 | -0.4 | 2.3 |
| AWD/3$^{B}$ | 0.9 | 1.2 | 3 | 2.5 | 1.9 | 2 | -0.8 | 1.8 |
| AWD/4$^{A}$ | 2.8 | 3.7 | 5 | 2.7 | 4.1 | 3 | 0 | 2.7 |
| AWD/4$^{B}$ | 1.2 | 1.4 | 2 | 2.3 | 1.9 | 2 | -0.3 | 2.1 |
| AWD/5$^{A}$ | 5.4 | 4.5 | 7 | 3.8 | 6.5 | 4 | 0 | 2.4 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| AWD/5$^{B}$ | 5.3 | 4.1 | 7 | 3.7 | 4.4 | 3 | 0.4 | 2.2 |
| AWD/6$^{A}$ | 5.6 | 4.7 | 8 | 4.5 | 4.6 | 4 | 0.4 | 3 |

A: Cont'

| Sample No | Cu Igeo | PbIgeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo | Mo Igeo |
|---|---|---|---|---|---|---|---|---|
| AWD/6$^{B}$ | 3.1 | 3 | 5 | 2.9 | 3.3 | 2 | 0 | 2.4 |
| AWD/7 | 2.9 | 1.9 | 5 | 2.8 | 2.8 | 3 | -0.1 | 1.9 |
| AWD/8 | 6.6 | 5.2 | 9 | 4.4 | 6.2 | 4 | 0.8 | 3.8 |
| MWM/1 | 2.7 | 1.5 | 4 | 3.1 | 4.1 | 3 | -0.7 | 1.3 |
| MWM/2$^{A}$ | 4.1 | 4.7 | 6 | 4.1 | 4 | 3 | -0.3 | 2.7 |
| MWM/2$^{B}$ | 3.3 | 3.3 | 5 | 3.3 | 3.4 | 2 | -1.1 | 1.7 |
| MWM/2$^{A}$ | 4.4 | 3.9 | 6 | 3.6 | 3.3 | 2 | 1 | 2.7 |
| MWM/3$^{A}$ | 3.9 | 4 | 5 | 4 | 2.5 | 2 | -0.9 | 2.2 |
| MWM/3$^{B}$ | 3.4 | 4.7 | 5 | 3 | 3.3 | 2 | -0.4 | 1.6 |
| MWM/4$^{A}$ | 5 | 4.8 | 9 | 3.7 | 5.6 | 4 | -0.1 | 2.8 |
| MWM/4$^{B}$ | 2.6 | 2.3 | 5 | 2.3 | 2.1 | 2 | 0 | 1.7 |
| MWM/5 | 5.5 | 5.6 | 8 | 5.2 | 4.6 | 3 | 0.5 | 4.2 |
| MWM/6$^{A}$ | 5.1 | 6.9 | 7 | 4.3 | 4 | 4 | 0.3 | 3.1 |
| MWM/6$^{B}$ | 1.9 | 1.8 | 2 | 2.4 | 2.5 | 4 | -0.4 | 1.1 |
| MWM/7$^{A}$ | 2.8 | 1.3 | 4 | 1.6 | 1.1 | 1 | -1.5 | 0.3 |
| MWM/7$^{B}$ | 1.3 | 0.9 | 1 | 2.4 | 2.7 | 3 | 0 | 1.3 |
| MWM/8 | 2.3 | 2.6 | 4 | 2.8 | 3 | 3 | -1 | 1.6 |
| MWM/9 | 7.9 | 6.5 | 9 | 7.3 | 5.7 | 5 | 1.2 | 4.9 |
| MWM/10 | 5.6 | 4.1 | 7 | 4.2 | 3.7 | 2 | 0.1 | 3.8 |
| MWM/11 | 7.8 | 5.1 | 8 | 7.3 | 5.5 | 5 | 1.9 | 7.1 |
| MWM/12$^{A}$ | 2.6 | 1.6 | 5 | 3 | 3.1 | 4 | -0.6 | 2.3 |
| MWM/12$^{B}$ | 1.6 | 1 | 3 | 3.3 | 3 | 3 | 0.4 | 1.8 |
| MWM/13$^{A}$ | 2.6 | 2.6 | 3 | 3 | 2.7 | 3 | -0.2 | 2 |
| MWM/13$^{B}$ | 1.9 | 0.9 | 2 | 2.6 | 2.6 | 3 | -0.8 | 1.6 |
| MWM/14 | 5.1 | 6.4 | 7 | 4.9 | 4.2 | 3 | 0 | 4.1 |
| MWM/15$^{A}$ | 3.7 | 2.8 | 5 | 3.7 | 2.6 | 2 | 0 | 2.5 |
| MWM/15$^{B}$ | 1.8 | 0.9 | 2 | 2.7 | 2.4 | 3 | 0.8 | 1.8 |
| MWM/16$^{A}$ | 5.6 | 7.2 | 7 | 4.5 | 4.3 | 4 | 0.5 | 3.9 |
| MWM/16$^{B}$ | 4.7 | 7.4 | 7 | 3.7 | 3.7 | 4 | -0.3 | 3.2 |
| MWM/17$^{A}$ | 4.6 | 4.3 | 10 | 4.2 | 4.2 | 3 | -0.8 | 2.3 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| MWM/17$^{B}$ | 2.4 | 1.2 | 5 | 2.8 | 3.2 | 4 | -0.7 | 1.4 |
| MWM/18 | 4.1 | 4.2 | 6 | 4 | 4 | 3 | -0.4 | 2.6 |

B: Results of the calculated Geoaccumulation Index (I-geo) for sediments samples in Onitsha area.

| Sample Numb | Cu Igeo | Pb Igeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo |
|---|---|---|---|---|---|---|---|
| ID/1 | 3.6 | 3.3 | 6 | 3.5 | 3.8 | 2 | -0.4 |
| ID/2 | 3.9 | 3.3 | 6 | 3.7 | 4.4 | 3 | -0.2 |
| ID/3 | 3.9 | 3.4 | 6 | 3.7 | 4.2 | 2 | -0.3 |
| ID/4 | 4.1 | 3.6 | 6 | 3.7 | 3.7 | 2 | -0.1 |
| ID/5 | 4.1 | 3.9 | 6 | 3.8 | 3.9 | 2 | 0.1 |
| ID/6 | 4.1 | 3.6 | 6 | 3.7 | 3.7 | 2 | -0.1 |
| ID/7 | 2 | 0.7 | 3 | 3.5 | 4.6 | 3 | -3.2 |
| ID/8 | 2.8 | 1.1 | 5 | 2.2 | 2.9 | 2 | 0.4 |
| ID/9 | 4.5 | 3.3 | 5 | 4.8 | 4.1 | 3 | 0 |
| ID/10 | 3.2 | 2.4 | 5 | 3.1 | 3.1 | 2 | 0.5 |
| NK/11 | 3.5 | 2.4 | 5 | 3.2 | 3.1 | 3 | 0.7 |
| NK/12 | 2.2 | 1.1 | 4 | 2.4 | 3 | 4 | 1.3 |
| NK/13 | 2.1 | 1.6 | 4 | 2.6 | 2.5 | 2 | 0.9 |
| NK/14 | 4 | 2.8 | 6 | 3.5 | 3.8 | 3 | 1 |
| NK/15 | 2.9 | 1.9 | 4 | 2.5 | 2.6 | 2 | 1 |
| NK/17 | 3.3 | 2.4 | 5 | 3 | 3.2 | 2 | 0.6 |
| NK/18 | 1.5 | 1 | 4 | 2.5 | 3 | 4 | 1.6 |
| NK/19 | 2.1 | 1.5 | 4 | 2.5 | 2.5 | 2 | 1.1 |
| NK/20 | 3.4 | 2.6 | 5 | 3.2 | 3.5 | 3 | 1 |
| RSD/1 | 3 | 1.9 | 3 | 3.2 | 3.1 | 2 | -0.5 |
| RSD/2 | 4.7 | 2.4 | 4 | 3.1 | 3 | 3 | -0.1 |
| RSD/3 | 2.6 | 2.2 | 4 | 3.1 | 3.1 | 2 | -0.7 |
| RSD/4 | 3.4 | 2.4 | 5 | 3.1 | 3.2 | 3 | 0.2 |
| RSD/5 | 3.3 | 2 | 4 | 3.2 | 2.9 | 2 | -0.6 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| RSD/6 | 3.6 | 2.6 | 5 | 3.3 | 3.3 | 2 | -0.4 |
| RSD/7 | 4.1 | 5.5 | 5 | 3.7 | 3.7 | 3 | -0.1 |
| RSD/8 | 4.7 | 4.8 | 7 | 5 | 4.5 | 3 | 0 |

B: Cont’

| Sample Numb | Cu Igeo | Pb Igeo | Zn Igeo | Ni Igeo | Co Igeo | Mn Igeo | As Igeo |
|---|---|---|---|---|---|---|---|
| RSD/9 | 3.5 | 2.9 | 5 | 4.1 | 4 | 3 | -0.4 |
| RSD/10 | 3 | 2.7 | 5 | 3.3 | 3.2 | 4 | 0.2 |
| RSD/12 | 4.7 | 4.7 | 6 | 3.4 | 3.7 | 3 | 0.1 |
| RSD/13 | 3.3 | 2.9 | 5 | 2.9 | 3.5 | 3 | -1.1 |
| RSD/11 | 4.5 | 3.6 | 6 | 4.2 | 3.7 | 3 | 0.5 |
| RSD/14 | 4.8 | 3.5 | 6 | 4 | 4.1 | 3 | 0.3 |
| RSD/15 | 3.7 | 2.5 | 5 | 3 | 3 | 2 | -0.3 |
| RSD/16 | 3.8 | 3.6 | 6 | 3.4 | 4.5 | 3 | -0.1 |
| RSD/20 | 3.9 | 3.4 | 7 | 4 | 4 | 3 | 0.2 |
| RSD/21 | 3.8 | 2.3 | 5 | 4.6 | 4.2 | 3 | -0.6 |
| RSD/22 | 5.6 | 3.4 | 6 | 6 | 5.2 | 5 | 0.7 |
| RSD/23 | 4.7 | 3.5 | 7 | 4.1 | 3.6 | 3 | -0.5 |
| RSD24 | 5.1 | 5.1 | 6 | 4.6 | 4.5 | 4 | 0.7 |

Appendix 5

A: Results of the calculated Contamination Factor for Soils of the study area

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/1 | 5.3 | 1.9 | 30 | 8.5 | 14.1 | 5 | 1.5 | 0.6 | 1 | 2 |
| RA/2 | 4.2 | 1.8 | 18 | 6.5 | 13.3 | 5 | 0.8 | 0.6 | 1 | 1 |
| RA/3 | 11.9 | 14.1 | 101 | 8.4 | 10.6 | 7 | 1.6 | 3.4 | 1 | 2 |
| RA/4 | 10.9 | 11.7 | 82 | 10.3 | 10.3 | 11 | 1.4 | 3.6 | 1 | 2 |
| RA/5$^{A}$ | 3.9 | 2.1 | 7 | 3.3 | 5.9 | 13 | 0.4 | 0.6 | 1 | 1 |
| RA/5$^{B}$ | 3.5 | 1.3 | 2 | 4.2 | 6.4 | 14 | 1.0 | 0.2 | 1 | 2 |
| RA/6 | 8.0 | 7.7 | 30 | 6.8 | 6.0 | 5 | 1.6 | 1.2 | 1 | 2 |
| RA/7 | 3.3 | 2.4 | 8 | 4.2 | 4.9 | 5 | 1.9 | 0.4 | 1 | 2 |
| RA/10 | 5.2 | 3.0 | 40 | 5.6 | 4.4 | 8 | 1.5 | 1.0 | 1 | 2 |
| RA/11$^{A}$ | 2.3 | 0.9 | 9 | 2.9 | 2.9 | 2 | 1.3 | 0.2 | 1 | 2 |
| RA/11$^{B}$ | 2.0 | 1.3 | 5 | 3.2 | 3.0 | 3 | 1.5 | 0.2 | 1 | 2 |
| RA/12 | 3.6 | 1.6 | 12 | 3.6 | 3.4 | 3 | 1.4 | 0.6 | 1 | 2 |
| RA/13$^{A}$ | 3.5 | 1.0 | 3 | 3.6 | 4.3 | 9 | 1.1 | 0.2 | 1 | 1 |
| RA/13$^{B}$ | 3.5 | 1.3 | 6 | 3.6 | 4.9 | 12 | 1.1 | 0.2 | 1 | 2 |
| RA/14 | 20.5 | 8.8 | 172 | 10.1 | 13.0 | 26 | 2.2 | 4.4 | 1 | 3 |
| RA/15$^{A}$ | 7.7 | 4.1 | 31 | 5.5 | 4.4 | 4 | 1.7 | 1.0 | 1 | 2 |
| RA/15$^{B}$ | 1.1 | 1.5 | 2 | 1.6 | 1.4 | 1 | 1.4 | 0.2 | 1 | 1 |
| RA/16$^{A}$ | 3.8 | 4.5 | 17 | 4.7 | 4.3 | 5 | 1.4 | 1.4 | 1 | 4 |
| RA/16$^{B}$ | 2.4 | 1.7 | 6 | 4.1 | 5.6 | 6 | 1.3 | 0.8 | 1 | 2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/17 | 5.6 | 2.8 | 24 | 6.5 | 9.0 | 11 | 1.5 | 1.4 | 1 | 2 |
| RA/17$^{B}$ | 3.9 | 1.8 | 6 | 4.6 | 6.3 | 10 | 1.1 | 0.6 | 1 | 1 |
| RA/18 | 12.0 | 8.7 | 85 | 9.6 | 7.3 | 7 | 1.2 | 1.9 | 0 | 1 |
| RA/19 | 1.6 | 0.7 | 1 | 0.5 | 0.4 | 0 | 0.1 | 0.2 | 1 | 1 |
| RA/20$^{A}$ | 3.3 | 3.1 | 19 | 5.1 | 5.1 | 6 | 1.0 | 0.8 | 1 | 2 |

A: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/20$^{B}$ | 1.2 | 1.1 | 2 | 4.0 | 2.7 | 3 | 0.8 | 0.2 | 2 | 2 |
| RA/21 | 5.2 | 7.1 | 19 | 4.5 | 6.3 | 5 | 0.8 | 1.0 | 1 | 1 |
| SOC/1$^{A}$ | 1.9 | 0.7 | 4 | 4.9 | 28.7 | 9 | 0.1 | 0.2 | 0 | 1 |
| SOC/1$^{B}$ | 1.3 | 0.5 | 2 | 4.5 | 8.7 | 2 | 0.0 | 0.0 | 0 | 1 |
| SOC/2$^{A}$ | 4.9 | 9.0 | 27 | 4.0 | 4.0 | 6 | 0.6 | 1.0 | 1 | 1 |
| SOC/2$^{B}$ | 0.3 | 0.4 | 1 | 0.6 | 0.9 | 1 | 0.0 | 0.0 | 0 | 0 |
| SOC/3 | 2.1 | 1.4 | 3 | 3.8 | 6.3 | 10 | 0.7 | 0.0 | 1 | 1 |
| SOC/4 | 2.6 | 1.8 | 8 | 3.7 | 3.4 | 5 | 1.7 | 0.4 | 1 | 1 |
| SOC/5 | 5.0 | 9.1 | 30 | 9.7 | 6.9 | 9 | 1.6 | 1.2 | 1 | 2 |
| SOC/6 | 6.7 | 13.9 | 27 | 7.5 | 5.3 | 4 | 3.1 | 0.8 | 1 | 2 |
| SOC/7$^{A}$ | 5.3 | 5.5 | 26 | 5.9 | 5.7 | 7 | 1.7 | 1.8 | 1 | 2 |
| SOC/7$^{B}$ | 2.8 | 2.4 | 9 | 3.9 | 3.7 | 7 | 1.4 | 0.6 | 1 | 2 |
| SOC/8$^{A}$ | 4.5 | 2.5 | 24 | 4.5 | 2.7 | 4 | 0.7 | 1.2 | 1 | 1 |
| SOC/8$^{B}$ | 2.6 | 2.0 | 7 | 3.4 | 2.7 | 3 | 1.9 | 0.4 | 1 | 2 |
| SOC/9 | 2.1 | 1.7 | 13 | 3.7 | 2.7 | 4 | 1.1 | 0.2 | 1 | 2 |
| SOC/10$^{A}$ | 1.8 | 1.8 | 5 | 2.6 | 2.7 | 4 | 0.8 | 0.0 | 1 | 1 |
| SOC/10$^{B}$ | 2.2 | 1.0 | 2 | 2.8 | 3.1 | 5 | 1.1 | 0.0 | 1 | 1 |
| SOC/11 | 4.5 | 3.3 | 4 | 3.1 | 2.0 | 2 | 0.9 | 0.2 | 1 | 1 |
| SOC/12$^{A}$ | 17.3 | 11.4 | 30 | 4.8 | 5.3 | 5 | 2.6 | 0.8 | 1 | 2 |
| SOC/12$^{B}$ | 1.7 | 0.9 | 3 | 2.2 | 2.4 | 4 | 3.2 | 0.0 | 1 | 1 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| SOC/13 | 4.9 | 3.8 | 28 | 4.1 | 2.4 | 3 | 0.6 | 0.0 | 1 | 2 |
| SOC/14$^{A}$ | 2.5 | 1.0 | 3 | 4.3 | 5.6 | 9 | 0.7 | 0.0 | 1 | 2 |
| SOC/14$^{B}$ | 1.6 | 0.9 | 1 | 3.5 | 3.9 | 5 | 0.6 | 0.0 | 1 | 2 |
| SOC/15$^{A}$ | 2.6 | 1.3 | 8 | 4.0 | 3.7 | 5 | 0.7 | 0.2 | 1 | 2 |
| SOC/15$^{B}$ | 1.9 | 0.9 | 1 | 4.0 | 3.3 | 4 | 1.0 | 0.0 | 2 | 2 |

A: Cont'

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| CT/2 | 1.4 | 0.9 | 2 | 2.4 | 2.1 | 3 | 0.9 | 0.0 | 1 | 1 |
| CT/3 | 0.8 | 0.4 | 1 | 1.6 | 1.6 | 1 | 1.7 | 0.0 | 1 | 1 |
| CT/4 | 0.7 | 1.2 | 1 | 1.2 | 1.1 | 1 | 1.5 | 0.0 | 1 | 1 |
| CT/5 | 1.0 | 1.0 | 1 | 1.1 | 1.0 | 1 | 0.8 | 0.0 | 1 | 1 |
| CT/6 | 0.8 | 0.9 | 0 | 0.1 | 0.3 | 0 | 0.1 | 0.0 | 1 | 1 |
| RK/1 | 0.8 | 1.5 | 1 | 0.3 | 0.4 | 0 | 2.9 | 0.0 | 1 | 1 |
| RK2 | 1.6 | 0.9 | 1 | 0.1 | 0.4 | 1 | 6.5 | 0.0 | 1 | 1 |
| RK/3 | 1.0 | 1.2 | 1 | 1.0 | 1.0 | 1 | 1.3 | 0.0 | 1 | 1 |
| FLG/1 | 3.1 | 1.1 | 6 | 6.5 | 11.9 | 2 | 0.2 | 0.2 | 1 | 1 |
| FLG/2 | 1.5 | 0.6 | 2 | 5.4 | 12.0 | 2 | 0.1 | 0.0 | 0 | 1 |
| FLG/3$^{A}$ | 36.5 | 6.4 | 563 | 9.5 | 195.0 | 7 | 2.3 | 2.0 | 1 | 1 |
| FLG/3$^{B}$ | 4.2 | 2.0 | 63 | 4.1 | 23.3 | 2 | 2.1 | 0.2 | 1 | 1 |
| FLG/4 | 0.7 | 1.0 | 2 | 3.0 | 2.1 | 1 | 1.9 | 0.0 | 1 | 1 |
| FLG/5$^{A}$ | 2.2 | 2.3 | 12 | 2.7 | 4.9 | 4 | 0.9 | 0.2 | 1 | 2 |
| FLG/5$^{B}$ | 1.2 | 1.0 | 15 | 3.6 | 8.3 | 2 | 2.5 | 0.0 | 1 | 1 |
| FLG/6$^{A}$ | 4.7 | 20.1 | 30 | 4.7 | 5.6 | 5 | 1.9 | 1.2 | 1 | 2 |
| FLG/6$^{B}$ | 1.2 | 1.5 | 2 | 2.9 | 3.9 | 3 | 1.6 | 0.0 | 1 | 1 |
| FLG/7$^{A}$ | 2.3 | 1.4 | 6 | 3.5 | 3.0 | 4 | 0.6 | 0.2 | 1 | 2 |
| FLG/7$^{B}$ | 1.2 | 1.2 | 2 | 3.5 | 2.9 | 3 | 0.7 | 0.0 | 1 | 2 |
| FLG/8 | 1.0 | 1.0 | 1 | 3.0 | 1.9 | 2 | 0.6 | 0.0 | 1 | 2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| FLG/9$^{A}$ | 5.1 | 2.0 | 8 | 5.0 | 6.9 | 10 | 0.9 | 0.6 | 1 | 2 |
| FLG/9$^{B}$ | 2.7 | 1.3 | 3 | 4.0 | 5.9 | 11 | 0.6 | 0.0 | 1 | 2 |
| FLG/10$^{A}$ | 1.8 | 1.0 | 1 | 3.5 | 5.9 | 9 | 0.5 | 0.0 | 1 | 1 |
| FLG/10$^{B}$ | 1.8 | 1.0 | 1 | 4.3 | 5.1 | 6 | 0.7 | 0.0 | 1 | 1 |
| FLG/11 | 9.9 | 3.2 | 28 | 6.0 | 9.0 | 16 | 0.8 | 1.1 | 1 | 2 |
| MAP/1$^{A}$ | 6.4 | 6.8 | 86 | 5.6 | 9.3 | 11 | 0.3 | 2.0 | 0 | 1 |

A: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| MAP/1$^{B}$ | 3.8 | 0.9 | 17 | 4.0 | 10.4 | 12 | 0.2 | 0.0 | 1 | 1 |
| MAP/2 | 18.7 | 14.8 | 81 | 10.0 | 8.7 | 6 | 1.5 | 4.0 | 1 | 2 |
| MAP/3$^{A}$ | 30.2 | 5.0 | 347 | 21.8 | 61.9 | 7 | 1.7 | 1.6 | 1 | 2 |
| MAP/3$^{B}$ | 17.3 | 3.2 | 195 | 15.9 | 31.4 | 6 | 1.7 | 1.0 | 1 | 2 |
| AWD/1 | 6.2 | 2.1 | 44 | 5.8 | 9.9 | 14 | 0.3 | 1.0 | 1 | 1 |
| AWD/2 | 2.1 | 1.1 | 6 | 5.3 | 15.3 | 5 | 0.5 | 0.0 | 1 | 1 |
| AWD/3$^{A}$ | 3.2 | 7.5 | 39 | 4.7 | 5.4 | 5 | 1.0 | 3.4 | 1 | 2 |
| AWD/3$^{B}$ | 1.3 | 1.6 | 5 | 3.8 | 2.4 | 3 | 0.8 | 0.4 | 1 | 2 |
| AWD/4$^{A}$ | 4.6 | 8.4 | 26 | 4.5 | 11.4 | 5 | 1.3 | 0.7 | 1 | 2 |
| AWD/4$^{B}$ | 1.6 | 1.7 | 3 | 3.2 | 2.6 | 2 | 1.1 | 0.0 | 1 | 2 |
| AWD/5$^{A}$ | 29.0 | 14.7 | 101 | 9.3 | 60.1 | 13 | 1.3 | 9.0 | 1 | 2 |
| AWD/5$^{B}$ | 25.6 | 11.8 | 90 | 8.5 | 14.4 | 7 | 1.7 | 4.0 | 1 | 2 |
| AWD/6$^{A}$ | 32.9 | 17.1 | 124 | 15.0 | 16.6 | 12 | 1.7 | 9.6 | 1 | 4 |
| AWD/6$^{B}$ | 5.8 | 5.2 | 19 | 4.9 | 6.4 | 3 | 1.3 | 1.8 | 2 | 3 |
| AWD/7 | 5.0 | 2.5 | 24 | 4.6 | 4.6 | 5 | 1.2 | 0.9 | 1 | 2 |
| AWD/8 | 64.4 | 24.6 | 288 | 14.1 | 49.4 | 8 | 2.3 | 11.2 | 1 | 3 |
| MWM/1 | 4.4 | 1.9 | 13 | 5.8 | 11.1 | 4 | 0.8 | 0.4 | 1 | 2 |
| MWM/2$^{A}$ | 11.5 | 17.3 | 46 | 11.2 | 10.7 | 5 | 1.1 | 1.4 | 1 | 2 |
| MWM/2$^{B}$ | 6.5 | 6.5 | 25 | 6.6 | 6.9 | 3 | 0.6 | 0.7 | 0 | 1 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/2$^{A}$ | 14.4 | 10.0 | 29 | 7.9 | 6.7 | 4 | 2.6 | 1.2 | 1 | 2 |
| MWM/3$^{A}$ | 10.0 | 10.5 | 26 | 10.9 | 3.9 | 2 | 0.7 | 1.1 | 0 | 1 |
| MWM/3$^{B}$ | 6.8 | 17.1 | 24 | 5.5 | 6.7 | 3 | 1.0 | 0.6 | 1 | 2 |
| MWM/4$^{A}$ | 21.3 | 18.0 | 233 | 8.8 | 31.4 | 8 | 1.2 | 6.8 | 0 | 1 |
| MWM/4$^{B}$ | 4.0 | 3.2 | 16 | 3.3 | 2.9 | 3 | 1.3 | 0.8 | 1 | 2 |
| MWM/5 | 31.0 | 31.9 | 140 | 24.5 | 15.7 | 6 | 1.9 | 9.6 | 1 | 3 |

A: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/6$^{A}$ | 23.4 | 79.4 | 63 | 13.2 | 10.7 | 12 | 1.6 | 8.6 | 1 | 2 |
| MWM/6$^{B}$ | 2.4 | 2.3 | 3 | 3.6 | 3.9 | 9 | 1.0 | 0.2 | 1 | 1 |
| MWM/7$^{A}$ | 4.7 | 1.7 | 8 | 2.0 | 1.4 | 1 | 0.5 | 0.4 | 0 | 1 |
| MWM/7$^{B}$ | 1.7 | 1.2 | 2 | 3.4 | 4.3 | 6 | 1.3 | 0.2 | 1 | 2 |
| MWM/8 | 3.3 | 4.0 | 7 | 4.6 | 5.3 | 4 | 0.6 | 0.2 | 1 | 1 |
| MWM/9 | 158.2 | 58.7 | 350 | 101.7 | 35.4 | 21 | 3.0 | 20.6 | 1 | 5 |
| MWM/10 | 33.3 | 11.6 | 82 | 12.7 | 8.9 | 3 | 1.4 | 2.8 | 1 | 2 |
| MWM/11 | 147.7 | 23.6 | 148 | 107.5 | 30.4 | 24 | 4.7 | 10.6 | 1 | 13 |
| MWM/12$^{A}$ | 4.2 | 2.1 | 16 | 5.5 | 5.6 | 8 | 0.8 | 0.6 | 1 | 2 |
| MWM/12$^{B}$ | 2.1 | 1.4 | 5 | 6.5 | 5.4 | 6 | 1.7 | 0.2 | 2 | 2 |
| MWM/13$^{A}$ | 4.2 | 4.1 | 6 | 5.3 | 4.4 | 6 | 1.1 | 0.2 | 1 | 2 |
| MWM/13$^{B}$ | 2.4 | 1.2 | 2 | 4.2 | 4.1 | 6 | 0.7 | 0.2 | 1 | 2 |
| MWM/14 | 23.6 | 57.6 | 92 | 19.4 | 12.0 | 6 | 1.3 | 12.0 | 1 | 4 |
| MWM/15$^{A}$ | 8.8 | 4.5 | 20 | 8.8 | 4.0 | 3 | 1.3 | 1.4 | 1 | 2 |
| MWM/15$^{B}$ | 2.3 | 1.2 | 2 | 4.2 | 3.4 | 4 | 2.2 | 0.2 | 1 | 1 |
| MWM/16$^{A}$ | 32.8 | 95.1 | 105 | 14.8 | 12.9 | 9 | 1.9 | 5.7 | 1 | 4 |
| MWM/16$^{B}$ | 17.8 | 111.3 | 68 | 8.9 | 8.6 | 12 | 1.1 | 4.8 | 1 | 2 |
| MWM/17$^{A}$ | 16.4 | 13.2 | 508 | 12.2 | 11.9 | 7 | 0.8 | 20.4 | 1 | 2 |
| MWM/17$^{B}$ | 3.4 | 1.6 | 23 | 4.6 | 6.1 | 11 | 0.8 | 1.6 | 1 | 1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/18 | 11.8 | 11.9 | 41 | 11.0 | 10.9 | 5 | 1.0 | 1.2 | 1 | 2 |

B: Results of the calculated Contamination Factor for Sediments of the study area

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| ID/1 | 8.1 | 6.6 | 35 | 7.5 | 9.6 | 3 | 1.0 | 1.2 | 1 | 1 |
| ID/2 | 10.1 | 6.6 | 40 | 8.4 | 14.4 | 4 | 1.1 | 1.2 | 1 | 1 |
| ID/3 | 10.1 | 6.9 | 40 | 8.8 | 12.3 | 3 | 1.1 | 1.2 | 1 | 1 |
| ID/4 | 11.6 | 8.2 | 46 | 8.5 | 8.9 | 3 | 1.2 | 1.5 | 1 | 1 |
| ID/5 | 11.5 | 9.9 | 52 | 9.0 | 10.0 | 4 | 1.4 | 1.8 | 1 | 1 |
| ID/6 | 11.2 | 8.1 | 47 | 8.5 | 8.7 | 3 | 1.2 | 1.6 | 1 | 1 |
| ID/7 | 2.6 | 1.1 | 7 | 7.4 | 16.1 | 4 | 0.1 | 0.2 | 1 | 0 |
| ID/8 | 4.5 | 1.4 | 16 | 3.0 | 5.1 | 3 | 1.7 | 0.0 | 1 | 1 |
| ID/9 | 14.7 | 6.5 | 20 | 18.3 | 11.7 | 5 | 1.3 | 1.0 | 1 | 1 |
| ID/10 | 6.3 | 3.5 | 21 | 5.7 | 5.9 | 3 | 1.9 | 0.6 | 1 | 1 |
| NK/11 | 7.5 | 3.5 | 25 | 6.0 | 5.9 | 4 | 2.1 | 1.0 | 1 | 1 |
| NK/12 | 3.0 | 1.4 | 10 | 3.6 | 5.4 | 10 | 3.3 | 0.0 | 2 | 1 |
| NK/13 | 2.9 | 2.0 | 10 | 4.0 | 3.7 | 3 | 2.5 | 0.5 | 1 | 1 |
| NK/14 | 10.9 | 4.6 | 37 | 7.5 | 9.0 | 5 | 2.6 | 1.5 | 1 | 1 |
| NK/15 | 5.0 | 2.4 | 13 | 3.7 | 4.0 | 2 | 2.6 | 0.6 | 1 | 1 |
| NK/17 | 6.5 | 3.5 | 22 | 5.5 | 6.0 | 3 | 2.0 | 0.4 | 1 | 1 |
| NK/18 | 1.9 | 1.3 | 8 | 3.7 | 5.3 | 14 | 4.0 | 0.2 | 1 | 1 |
| NK/19 | 2.8 | 1.9 | 10 | 3.7 | 3.7 | 3 | 2.8 | 0.6 | 1 | 1 |
| NK/20 | 7.2 | 4.0 | 24 | 6.2 | 7.4 | 5 | 2.6 | 0.8 | 1 | 1 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/1 | 5.5 | 2.5 | 6 | 6.0 | 5.9 | 3 | 0.9 | 0.2 | 1 | 1 |
| RSD/2 | 17.0 | 3.6 | 13 | 5.6 | 5.3 | 4 | 1.2 | 0.8 | 1 | 1 |
| RSD/3 | 4.0 | 3.0 | 12 | 5.5 | 5.6 | 3 | 0.8 | 0.4 | 1 | 1 |
| RSD/4 | 7.2 | 3.6 | 24 | 5.6 | 6.0 | 4 | 1.5 | 0.6 | 1 | 1 |
| RSD/5 | 6.7 | 2.7 | 15 | 6.3 | 5.1 | 3 | 0.8 | 0.8 | 0 | 1 |
| RSD/6 | 7.9 | 4.1 | 21 | 6.8 | 6.4 | 4 | 1.0 | 1.0 | 1 | 1 |
| RSD/7 | 11.7 | 29.7 | 29 | 8.5 | 8.4 | 5 | 1.2 | 1.4 | 1 | 1 |
| RSD/8 | 17.2 | 18.2 | 70 | 20.7 | 15.3 | 8 | 1.3 | 3.2 | 1 | 1 |
| RSD/9 | 7.8 | 4.9 | 24 | 11.1 | 10.9 | 6 | 1.0 | 1.0 | 1 | 1 |

B: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/10 | 5.4 | 4.5 | 20 | 6.4 | 6.1 | 8 | 1.5 | 1.0 | 1 | 1 |
| RSD/12 | 16.9 | 17.6 | 31 | 7.2 | 8.7 | 4 | 1.4 | 1.2 | 1 | 1 |
| RSD/13 | 6.5 | 4.9 | 19 | 5.1 | 7.4 | 4 | 0.6 | 0.6 | 0 | 0 |
| RSD/11 | 14.7 | 8.3 | 39 | 12.2 | 8.6 | 5 | 1.9 | 2.0 | 1 | 1 |
| RSD/14 | 18.2 | 7.7 | 35 | 10.7 | 11.4 | 5 | 1.6 | 1.3 | 1 | 1 |
| RSD/15 | 8.6 | 3.9 | 26 | 5.5 | 5.3 | 4 | 1.1 | 0.6 | 1 | 1 |
| RSD/16 | 9.2 | 8.0 | 48 | 7.0 | 15.3 | 5 | 1.2 | 1.1 | 1 | 1 |
| RSD/20 | 9.8 | 6.9 | 79 | 10.5 | 10.4 | 5 | 1.5 | 1.2 | 1 | 1 |
| RSD/21 | 9.5 | 3.3 | 25 | 16.0 | 12.3 | 6 | 0.9 | 0.7 | 1 | 1 |
| RSD/22 | 31.9 | 6.9 | 49 | 41.3 | 25.0 | 17 | 2.1 | 3.2 | 0 | 2 |
| RSD/23 | 17.4 | 7.7 | 65 | 11.4 | 8.0 | 6 | 0.9 | 2.8 | 0 | 1 |
| RSD24 | 22.6 | 22.5 | 58 | 16.4 | 14.6 | 8 | 2.1 | 2.2 | 0 | 1 |

Appendix 6

A: Results of the calculated Metal Ratio for Soils of the study area

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/1 | 0.75 | 1.74 | 5.04 | 0.23 | 0.50 | 0.52 | 0.64 | 1.00 | 0.52 | 0.54 |
| RA/2 | 0.60 | 1.66 | 3.03 | 0.18 | 0.47 | 0.50 | 0.34 | 1.00 | 0.43 | 0.44 |
| RA/3 | 1.69 | 12.87 | 16.77 | 0.23 | 0.37 | 0.69 | 0.66 | 5.67 | 0.65 | 0.63 |
| RA/4 | 1.55 | 10.68 | 13.57 | 0.28 | 0.36 | 1.03 | 0.59 | 6.07 | 0.48 | 0.56 |
| RA/5$^{A}$ | 0.55 | 1.96 | 1.10 | 0.09 | 0.21 | 1.26 | 0.18 | 1.00 | 0.32 | 0.34 |
| RA/5$^{B}$ | 0.50 | 1.15 | 0.40 | 0.12 | 0.23 | 1.35 | 0.42 | 0.33 | 0.78 | 0.52 |
| RA/6 | 1.13 | 6.99 | 4.89 | 0.19 | 0.21 | 0.52 | 0.67 | 2.00 | 0.71 | 0.63 |
| RA/7 | 0.46 | 2.20 | 1.30 | 0.12 | 0.17 | 0.50 | 0.81 | 0.67 | 0.89 | 0.52 |
| RA/10 | 0.73 | 2.72 | 6.58 | 0.15 | 0.16 | 0.80 | 0.63 | 1.67 | 0.79 | 0.57 |
| RA/11$^{A}$ | 0.33 | 0.86 | 1.52 | 0.08 | 0.10 | 0.19 | 0.55 | 0.33 | 0.48 | 0.54 |
| RA/11$^{B}$ | 0.28 | 1.15 | 0.80 | 0.09 | 0.11 | 0.27 | 0.62 | 0.33 | 0.69 | 0.56 |
| RA/12 | 0.52 | 1.43 | 2.01 | 0.10 | 0.12 | 0.28 | 0.57 | 1.00 | 0.69 | 0.58 |
| RA/13$^{A}$ | 0.50 | 0.89 | 0.43 | 0.10 | 0.15 | 0.87 | 0.47 | 0.33 | 0.68 | 0.49 |
| RA/13$^{B}$ | 0.50 | 1.15 | 1.02 | 0.10 | 0.17 | 1.14 | 0.45 | 0.33 | 0.62 | 0.60 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/14 | 2.91 | 8.04 | 28.41 | 0.28 | 0.46 | 2.50 | 0.91 | 7.33 | 0.44 | 0.84 |
| RA/15$^{A}$ | 1.09 | 3.77 | 5.16 | 0.15 | 0.16 | 0.43 | 0.69 | 1.73 | 0.56 | 0.67 |
| RA/15$^{B}$ | 0.16 | 1.32 | 0.39 | 0.05 | 0.05 | 0.12 | 0.57 | 0.33 | 0.60 | 0.41 |
| RA/16$^{A}$ | 0.54 | 4.14 | 2.81 | 0.13 | 0.15 | 0.52 | 0.58 | 2.33 | 0.60 | 1.25 |
| RA/16$^{B}$ | 0.34 | 1.56 | 1.02 | 0.11 | 0.20 | 0.61 | 0.55 | 1.33 | 0.75 | 0.69 |
| RA/17 | 0.80 | 2.56 | 4.03 | 0.18 | 0.32 | 1.03 | 0.63 | 2.33 | 0.65 | 0.68 |
| RA/17$^{B}$ | 0.55 | 1.65 | 1.07 | 0.13 | 0.22 | 1.00 | 0.45 | 1.00 | 0.68 | 0.47 |
| RA/18 | 1.71 | 7.91 | 13.99 | 0.27 | 0.26 | 0.72 | 0.51 | 3.13 | 0.28 | 0.48 |
| RA/19 | 0.22 | 0.63 | 0.17 | 0.01 | 0.02 | 0.01 | 0.05 | 0.33 | 0.32 | 0.24 |

A: Cont'

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RA/20$^{A}$ | 0.47 | 2.85 | 3.18 | 0.14 | 0.18 | 0.61 | 0.4 | 1.33 | 0.72 | 0.78 |
| RA/20$^{B}$ | 0.17 | 1.04 | 0.26 | 0.11 | 0.10 | 0.29 | 0.33 | 0.33 | 0.93 | 0.71 |
| RA/21 | 0.74 | 6.50 | 3.13 | 0.13 | 0.22 | 0.50 | 0.33 | 1.67 | 0.64 | 0.47 |
| SOC/1$^{A}$ | 0.27 | 0.60 | 0.69 | 0.13 | 1.01 | 0.84 | 0.05 | 0.33 | 0.25 | 0.24 |
| SOC/1$^{B}$ | 0.18 | 0.50 | 0.41 | 0.13 | 0.31 | 0.14 | 0 | 0.00 | 0.25 | 0.26 |
| SOC/2$^{A}$ | 0.70 | 8.15 | 4.50 | 0.11 | 0.14 | 0.56 | 0.27 | 1.67 | 0.38 | 0.43 |
| SOC/2$^{B}$ | 0.04 | 0.32 | 0.12 | 0.02 | 0.03 | 0.12 | 0 | 0.00 | 0.12 | 0.15 |
| SOC/3 | 0.30 | 1.26 | 0.52 | 0.10 | 0.22 | 0.92 | 0.31 | 0.00 | 0.70 | 0.47 |
| SOC/4 | 0.37 | 1.60 | 1.37 | 0.10 | 0.12 | 0.48 | 0.71 | 0.67 | 0.78 | 0.45 |
| SOC/5 | 0.70 | 8.30 | 5.01 | 0.27 | 0.24 | 0.88 | 0.67 | 2.00 | 0.63 | 0.51 |
| SOC/6 | 0.95 | 12.66 | 4.39 | 0.21 | 0.19 | 0.40 | 1.28 | 1.33 | 0.75 | 0.76 |
| SOC/7$^{A}$ | 0.75 | 4.97 | 4.29 | 0.16 | 0.20 | 0.65 | 0.7 | 3.00 | 0.58 | 0.66 |
| SOC/7$^{B}$ | 0.40 | 2.16 | 1.41 | 0.11 | 0.13 | 0.62 | 0.59 | 1.00 | 0.69 | 0.59 |
| SOC/8$^{A}$ | 0.64 | 2.26 | 4.03 | 0.13 | 0.10 | 0.39 | 0.3 | 2.00 | 0.32 | 0.44 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| SOC/8$^{B}$ | 0.36 | 1.79 | 1.23 | 0.09 | 0.10 | 0.30 | 0.79 | 0.67 | 0.80 | 0.56 |
| SOC/9 | 0.29 | 1.59 | 2.18 | 0.10 | 0.10 | 0.40 | 0.47 | 0.33 | 0.64 | 0.50 |
| SOC/10$^{A}$ | 0.26 | 1.68 | 0.84 | 0.07 | 0.10 | 0.35 | 0.33 | 0.00 | 0.41 | 0.37 |
| SOC/10$^{B}$ | 0.31 | 0.93 | 0.26 | 0.08 | 0.11 | 0.46 | 0.46 | 0.00 | 0.58 | 0.44 |
| SOC/11 | 0.63 | 3.02 | 0.69 | 0.09 | 0.07 | 0.18 | 0.39 | 0.33 | 0.76 | 0.45 |
| SOC/12$^{A}$ | 2.46 | 10.35 | 5.03 | 0.13 | 0.19 | 0.45 | 1.1 | 1.27 | 0.57 | 0.70 |
| SOC/12$^{B}$ | 0.24 | 0.79 | 0.44 | 0.06 | 0.09 | 0.35 | 1.32 | 0.00 | 0.75 | 0.41 |
| SOC/13 | 0.70 | 3.45 | 4.59 | 0.11 | 0.09 | 0.30 | 0.23 | 0.00 | 0.36 | 0.51 |
| SOC/14$^{A}$ | 0.36 | 0.95 | 0.43 | 0.12 | 0.20 | 0.83 | 0.28 | 0.00 | 0.76 | 0.78 |
| SOC/14$^{B}$ | 0.23 | 0.83 | 0.21 | 0.10 | 0.14 | 0.46 | 0.27 | 0.00 | 0.85 | 0.57 |

A: Cont'

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| SOC/15$^{A}$ | 0.37 | 1.21 | 1.39 | 0.11 | 0.13 | 0.46 | 0.3 | 0.27 | 0.81 | 0.72 |
| SOC/15$^{B}$ | 0.27 | 0.85 | 0.20 | 0.11 | 0.12 | 0.36 | 0.4 | 0.00 | 0.94 | 0.60 |
| CT/2 | 0.20 | 0.79 | 0.39 | 0.07 | 0.08 | 0.28 | 0.38 | 0.00 | 0.73 | 0.44 |
| CT/3 | 0.11 | 0.36 | 0.11 | 0.05 | 0.06 | 0.12 | 0.69 | 0.00 | 0.62 | 0.27 |
| CT/4 | 0.11 | 1.11 | 0.10 | 0.03 | 0.04 | 0.08 | 0.62 | 0.00 | 0.64 | 0.35 |
| CT/5 | 0.14 | 0.93 | 0.17 | 0.03 | 0.04 | 0.12 | 0.35 | 0.00 | 0.64 | 0.33 |
| CT/6 | 0.11 | 0.81 | 0.03 | 0.00 | 0.01 | 0.01 | 0.05 | 0.00 | 0.42 | 0.24 |
| RK/1 | 0.11 | 1.40 | 0.24 | 0.01 | 0.02 | 0.04 | 1.2 | 0.00 | 0.34 | 0.45 |
| RK2 | 0.23 | 0.79 | 0.19 | 0.00 | 0.02 | 0.05 | 2.73 | 0.00 | 0.62 | 0.28 |
| RK/3 | 0.14 | 1.10 | 0.09 | 0.03 | 0.04 | 0.07 | 0.56 | 0.00 | 0.53 | 0.29 |
| FLG/1 | 0.44 | 0.97 | 1.07 | 0.18 | 0.42 | 0.23 | 0.08 | 0.30 | 0.42 | 0.35 |
| FLG/2 | 0.21 | 0.55 | 0.41 | 0.15 | 0.42 | 0.18 | 0.04 | 0.00 | 0.29 | 0.28 |
| FLG/3$^{A}$ | 5.19 | 5.79 | 93.28 | 0.26 | 6.83 | 0.68 | 0.98 | 3.33 | 0.55 | 0.47 |
| FLG/3$^{B}$ | 0.60 | 1.82 | 10.38 | 0.11 | 0.82 | 0.19 | 0.88 | 0.33 | 0.70 | 0.39 |
| FLG/4 | 0.11 | 0.92 | 0.30 | 0.08 | 0.08 | 0.13 | 0.8 | 0.00 | 0.69 | 0.38 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| FLG/5$^{A}$ | 0.31 | 2.05 | 1.93 | 0.08 | 0.17 | 0.37 | 0.39 | 0.33 | 0.49 | 0.64 |
| FLG/5$^{B}$ | 0.17 | 0.92 | 2.46 | 0.10 | 0.29 | 0.15 | 1.03 | 0.00 | 0.82 | 0.42 |
| FLG/6$^{A}$ | 0.67 | 18.31 | 5.01 | 0.13 | 0.20 | 0.46 | 0.8 | 2.00 | 0.67 | 0.56 |
| FLG/6$^{B}$ | 0.17 | 1.41 | 0.39 | 0.08 | 0.14 | 0.30 | 0.65 | 0.00 | 0.82 | 0.47 |
| FLG/7$^{A}$ | 0.32 | 1.27 | 1.00 | 0.10 | 0.11 | 0.42 | 0.24 | 0.33 | 0.65 | 0.53 |
| FLG/7$^{B}$ | 0.17 | 1.11 | 0.41 | 0.10 | 0.10 | 0.32 | 0.28 | 0.00 | 0.88 | 0.58 |
| FLG/8 | 0.14 | 0.92 | 0.23 | 0.08 | 0.07 | 0.16 | 0.26 | 0.00 | 0.80 | 0.59 |
| FLG/9$^{A}$ | 0.72 | 1.80 | 1.31 | 0.14 | 0.24 | 0.92 | 0.36 | 1.00 | 0.67 | 0.59 |
| FLG/9$^{B}$ | 0.39 | 1.23 | 0.56 | 0.11 | 0.21 | 1.03 | 0.25 | 0.00 | 0.66 | 0.53 |
| FLG/10$^{A}$ | 0.26 | 0.92 | 0.19 | 0.10 | 0.21 | 0.82 | 0.22 | 0.00 | 0.58 | 0.37 |

A: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| FLG/10$^{B}$ | 0.26 | 0.88 | 0.19 | 0.12 | 0.18 | 0.53 | 0.3 | 0.00 | 0.66 | 0.38 |
| FLG/11 | 1.41 | 2.87 | 4.60 | 0.17 | 0.32 | 1.55 | 0.32 | 1.77 | 0.65 | 0.54 |
| MAP/1$^{A}$ | 0.91 | 6.23 | 14.16 | 0.16 | 0.33 | 1.01 | 0.14 | 3.37 | 0.24 | 0.37 |
| MAP/1$^{B}$ | 0.55 | 0.82 | 2.77 | 0.11 | 0.37 | 1.11 | 0.08 | 0.00 | 0.46 | 0.37 |
| MAP/2 | 2.65 | 13.51 | 13.49 | 0.28 | 0.31 | 0.62 | 0.64 | 6.67 | 0.37 | 0.51 |
| MAP/3$^{A}$ | 4.29 | 4.51 | 57.43 | 0.60 | 2.17 | 0.70 | 0.72 | 2.70 | 0.40 | 0.57 |
| MAP/3$^{B}$ | 2.46 | 2.90 | 32.21 | 0.44 | 1.10 | 0.55 | 0.7 | 1.67 | 0.63 | 0.75 |
| AWD/1 | 0.89 | 1.92 | 7.28 | 0.16 | 0.35 | 1.33 | 0.11 | 1.67 | 0.47 | 0.39 |
| AWD/2 | 0.30 | 1.02 | 0.93 | 0.15 | 0.54 | 0.51 | 0.21 | 0.00 | 0.55 | 0.40 |
| AWD/3$^{A}$ | 0.46 | 6.79 | 6.49 | 0.13 | 0.19 | 0.49 | 0.41 | 5.67 | 0.70 | 0.78 |
| AWD/3$^{B}$ | 0.18 | 1.44 | 0.89 | 0.10 | 0.09 | 0.32 | 0.32 | 0.67 | 0.92 | 0.68 |
| AWD/4$^{A}$ | 0.66 | 7.65 | 4.32 | 0.12 | 0.40 | 0.48 | 0.55 | 1.10 | 0.70 | 0.74 |
| AWD/4$^{B}$ | 0.22 | 1.56 | 0.58 | 0.09 | 0.09 | 0.21 | 0.45 | 0.00 | 0.80 | 0.61 |
| AWD/5$^{A}$ | 4.12 | 13.38 | 16.73 | 0.26 | 2.11 | 1.26 | 0.56 | 15.00 | 0.46 | 0.75 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| AWD/5$^{B}$ | 3.64 | 10.77 | 14.86 | 0.23 | 0.51 | 0.72 | 0.72 | 6.67 | 0.71 | 0.78 |
| AWD/6$^{A}$ | 4.67 | 15.60 | 20.61 | 0.41 | 0.58 | 1.15 | 0.72 | 16.00 | 0.73 | 1.18 |
| AWD/6$^{B}$ | 0.82 | 4.72 | 3.13 | 0.13 | 0.23 | 0.27 | 0.56 | 3.00 | 0.95 | 0.83 |
| AWD/7 | 0.71 | 2.24 | 3.92 | 0.13 | 0.16 | 0.50 | 0.5 | 1.50 | 0.72 | 0.51 |
| AWD/8 | 9.14 | 22.42 | 47.76 | 0.39 | 1.73 | 0.74 | 0.96 | 18.67 | 0.63 | 0.85 |
| MWM/1 | 0.62 | 1.75 | 2.19 | 0.16 | 0.39 | 0.40 | 0.33 | 0.67 | 0.53 | 0.58 |
| MWM/2$^{A}$ | 1.63 | 15.73 | 7.63 | 0.31 | 0.38 | 0.49 | 0.44 | 2.33 | 0.38 | 0.59 |
| MWM/2$^{B}$ | 0.93 | 5.95 | 4.07 | 0.18 | 0.24 | 0.27 | 0.26 | 1.23 | 0.22 | 0.35 |
| MWM/2$^{A}$ | 2.04 | 9.14 | 4.81 | 0.22 | 0.24 | 0.34 | 1.08 | 2.00 | 0.66 | 0.67 |
| MWM/3$^{A}$ | 1.41 | 9.60 | 4.24 | 0.30 | 0.14 | 0.24 | 0.29 | 1.83 | 0.18 | 0.43 |
| MWM/3$^{B}$ | 0.97 | 15.53 | 3.97 | 0.15 | 0.24 | 0.25 | 0.41 | 1.00 | 0.47 | 0.59 |

A: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/4$^{A}$ | 3.03 | 16.35 | 38.64 | 0.24 | 1.10 | 0.72 | 0.5 | 11.30 | 0.26 | 0.48 |
| MWM/4$^{B}$ | 0.57 | 2.93 | 2.59 | 0.09 | 0.10 | 0.27 | 0.53 | 1.33 | 0.42 | 0.52 |
| MWM/5 | 4.40 | 29.03 | 23.10 | 0.68 | 0.55 | 0.61 | 0.78 | 16.00 | 0.34 | 0.96 |
| MWM/6$^{A}$ | 3.32 | 72.22 | 10.43 | 0.36 | 0.38 | 1.17 | 0.68 | 14.33 | 0.39 | 0.69 |
| MWM/6$^{B}$ | 0.35 | 2.06 | 0.56 | 0.10 | 0.14 | 0.90 | 0.42 | 0.33 | 0.63 | 0.43 |
| MWM/7$^{A}$ | 0.67 | 1.55 | 1.34 | 0.06 | 0.05 | 0.14 | 0.2 | 0.67 | 0.22 | 0.29 |
| MWM/7$^{B}$ | 0.24 | 1.14 | 0.27 | 0.09 | 0.15 | 0.60 | 0.53 | 0.33 | 0.91 | 0.55 |
| MWM/8 | 0.47 | 3.63 | 1.23 | 0.13 | 0.19 | 0.37 | 0.27 | 0.33 | 0.84 | 0.49 |
| MWM/9 | 22.46 | 53.38 | 57.98 | 2.80 | 1.24 | 2.00 | 1.25 | 34.33 | 0.45 | 1.57 |
| MWM/10 | 4.73 | 10.58 | 13.64 | 0.35 | 0.31 | 0.33 | 0.59 | 4.67 | 0.53 | 0.70 |
| MWM/11 | 20.98 | 21.47 | 24.53 | 2.96 | 1.07 | 2.26 | 1.98 | 17.67 | 0.39 | 4.43 |
| MWM/12$^{A}$ | 0.59 | 1.90 | 2.63 | 0.15 | 0.20 | 0.72 | 0.35 | 1.00 | 0.72 | 0.70 |
| MWM/12$^{B}$ | 0.29 | 1.24 | 0.86 | 0.18 | 0.19 | 0.57 | 0.72 | 0.33 | 0.93 | 0.78 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| MWM/13$^A$ | 0.59 | 3.69 | 1.02 | 0.15 | 0.16 | 0.54 | 0.46 | 0.33 | 0.82 | 0.60 |
| MWM/13$^B$ | 0.34 | 1.12 | 0.31 | 0.12 | 0.15 | 0.60 | 0.31 | 0.33 | 0.78 | 0.54 |
| MWM/14 | 3.36 | 52.40 | 15.25 | 0.53 | 0.42 | 0.57 | 0.55 | 20.00 | 0.38 | 1.21 |
| MWM/15$^A$ | 1.25 | 4.10 | 3.33 | 0.24 | 0.14 | 0.26 | 0.54 | 2.33 | 0.32 | 0.58 |
| MWM/15$^B$ | 0.33 | 1.12 | 0.37 | 0.12 | 0.12 | 0.41 | 0.93 | 0.33 | 0.71 | 0.47 |
| MWM/16$^A$ | 4.65 | 86.53 | 17.45 | 0.41 | 0.45 | 0.89 | 0.8 | 9.57 | 0.53 | 1.18 |
| MWM/16$^B$ | 2.53 | 101.32 | 11.31 | 0.24 | 0.30 | 1.17 | 0.45 | 8.00 | 0.62 | 0.67 |
| MWM/17$^A$ | 2.33 | 11.99 | 84.09 | 0.34 | 0.42 | 0.68 | 0.32 | 33.97 | 0.45 | 0.67 |
| MWM/17$^B$ | 0.49 | 1.43 | 3.84 | 0.13 | 0.22 | 1.06 | 0.34 | 2.67 | 0.62 | 0.45 |
| MWM/18 | 1.67 | 10.86 | 6.80 | 0.30 | 0.38 | 0.47 | 0.42 | 2.00 | 0.42 | 0.54 |

B: Results of the calculated Metal Ratio for Sediments of the study area

| S/N | Cu | Pb | Zn | Ni | Co | Mn | Cd | V | Cr | As |
|---|---|---|---|---|---|---|---|---|---|---|
| ID/1 | 1.15 | 5.98 | 5.76 | 0.21 | 0.34 | 0.41 | 2.00 | 0.59 | 0.51 | 0.41 |
| ID/2 | 1.44 | 6.00 | 6.66 | 0.23 | 0.51 | 0.46 | 2.00 | 0.64 | 0.54 | 0.46 |
| ID/3 | 1.43 | 6.32 | 6.63 | 0.24 | 0.43 | 0.45 | 2.03 | 0.55 | 0.54 | 0.45 |
| ID/4 | 1.65 | 7.50 | 7.63 | 0.23 | 0.31 | 0.50 | 2.53 | 0.63 | 0.61 | 0.5 |
| ID/5 | 1.64 | 9.02 | 8.62 | 0.25 | 0.35 | 0.57 | 3.00 | 0.68 | 0.60 | 0.57 |
| ID/6 | 1.59 | 7.39 | 7.70 | 0.23 | 0.31 | 0.50 | 2.67 | 0.71 | 0.60 | 0.5 |
| ID/7 | 0.37 | 0.99 | 1.12 | 0.20 | 0.57 | 0.06 | 0.33 | 0.39 | 0.33 | 0.06 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| ID/8 | 0.64 | 1.26 | 2.66 | 0.08 | 0.18 | 0.73 | 0.00 | 0.90 | 0.58 | 0.73 |
| ID/9 | 2.09 | 5.87 | 3.26 | 0.50 | 0.41 | 0.55 | 1.67 | 0.53 | 0.57 | 0.55 |
| ID/10 | 0.89 | 3.17 | 3.54 | 0.16 | 0.21 | 0.79 | 1.00 | 0.88 | 0.59 | 0.79 |
| NK/11 | 1.06 | 3.22 | 4.20 | 0.16 | 0.21 | 0.87 | 1.67 | 0.88 | 0.58 | 0.87 |
| NK/12 | 0.43 | 1.29 | 1.71 | 0.10 | 0.19 | 1.36 | 0.00 | 0.93 | 0.51 | 1.36 |
| NK/13 | 0.42 | 1.82 | 1.62 | 0.11 | 0.13 | 1.05 | 0.77 | 0.80 | 0.49 | 1.05 |
| NK/14 | 1.55 | 4.19 | 6.18 | 0.21 | 0.32 | 1.09 | 2.50 | 0.72 | 0.58 | 1.09 |
| NK/15 | 0.71 | 2.20 | 2.18 | 0.10 | 0.14 | 1.07 | 1.00 | 0.84 | 0.48 | 1.07 |

B: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| NK/17 | 0.92 | 3.23 | 3.61 | 0.15 | 0.21 | 0.84 | 0.67 | 0.90 | 0.61 | 0.84 |
| NK/18 | 0.27 | 1.21 | 1.29 | 0.10 | 0.19 | 1.69 | 0.33 | 0.90 | 0.46 | 1.69 |
| NK/19 | 0.40 | 1.75 | 1.60 | 0.10 | 0.13 | 1.17 | 1.00 | 0.88 | 0.49 | 1.17 |
| NK/20 | 1.02 | 3.62 | 3.97 | 0.17 | 0.26 | 1.10 | 1.33 | 0.89 | 0.62 | 1.1 |
| RSD/1 | 0.78 | 2.29 | 1.06 | 0.16 | 0.21 | 0.38 | 0.33 | 0.43 | 0.68 | 0.38 |
| RSD/2 | 2.41 | 3.31 | 2.08 | 0.15 | 0.19 | 0.50 | 1.33 | 0.78 | 0.55 | 0.5 |

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/3 | 0.56 | 2.72 | 2.00 | 0.15 | 0.20 | 0.33 | 0.67 | 0.48 | 0.50 | 0.33 |
| RSD/4 | 1.02 | 3.25 | 4.06 | 0.15 | 0.21 | 0.63 | 1.00 | 0.54 | 0.79 | 0.63 |
| RSD/5 | 0.95 | 2.49 | 2.47 | 0.17 | 0.18 | 0.35 | 1.33 | 0.29 | 0.56 | 0.35 |
| RSD/6 | 1.12 | 3.74 | 3.40 | 0.19 | 0.23 | 0.41 | 1.67 | 0.36 | 0.60 | 0.41 |
| RSD/7 | 1.66 | 27.01 | 4.88 | 0.23 | 0.30 | 0.52 | 2.33 | 0.47 | 0.57 | 0.52 |
| RSD/8 | 2.44 | 16.57 | 11.61 | 0.57 | 0.54 | 0.55 | 5.33 | 0.43 | 0.82 | 0.55 |
| RSD/9 | 1.10 | 4.50 | 3.93 | 0.31 | 0.38 | 0.41 | 1.67 | 0.52 | 0.58 | 0.41 |
| RSD/10 | 0.76 | 4.06 | 3.26 | 0.18 | 0.22 | 0.64 | 1.67 | 0.68 | 0.51 | 0.64 |
| RSD/12 | 2.41 | 16.03 | 5.21 | 0.20 | 0.31 | 0.59 | 2.00 | 0.37 | 0.42 | 0.59 |

B: Cont’

| S/N | Cu | Pb | Zn | Ni | Co | Mn | As | Cd | V | Cr |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/13 | 0.93 | 4.50 | 3.08 | 0.14 | 0.26 | 0.26 | 1.00 | 0.27 | 0.33 | 0.26 |
| RSD/11 | 2.09 | 7.56 | 6.47 | 0.34 | 0.30 | 0.79 | 3.37 | 0.67 | 0.64 | 0.79 |
| RSD/14 | 2.59 | 7.04 | 5.77 | 0.29 | 0.40 | 0.68 | 2.17 | 0.52 | 0.56 | 0.68 |
| RSD/15 | 1.23 | 3.53 | 4.33 | 0.15 | 0.19 | 0.45 | 1.00 | 0.43 | 0.49 | 0.45 |
| RSD/16 | 1.31 | 7.30 | 7.95 | 0.19 | 0.54 | 0.52 | 1.80 | 0.50 | 0.57 | 0.52 |
| RSD/20 | 1.39 | 6.25 | 13.03 | 0.29 | 0.37 | 0.64 | 2.00 | 0.35 | 0.63 | 0.64 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| RSD/21 | 1.35 | 3.01 | 4.14 | 0.44 | 0.43 | 0.36 | 1.17 | 0.52 | 0.64 | 0.36 |
| RSD/22 | 4.53 | 6.27 | 8.19 | 1.14 | 0.88 | 0.86 | 5.33 | 0.27 | 1.23 | 0.86 |
| RSD/23 | 2.46 | 7.04 | 10.72 | 0.31 | 0.28 | 0.38 | 4.67 | 0.23 | 0.46 | 0.38 |
| RSD24 | 3.21 | 20.51 | 9.62 | 0.45 | 0.51 | 0.86 | 3.67 | 0.30 | 0.77 | 0.86 |

Appendix 7: A: Lead Isotope compositions of soils, sediments, coal, vehicle exhaust and Ore-galena in the study area.

| S/N | $^{207}$Pb/$^{204}$Pb | $^{208}$Pb/$^{204}$Pb | $^{206}$Pb/$^{204}$Pb | $^{207}$Pb/$^{206}$Pb | $^{208}$Pb/$^{206}$Pb | $^{208}$Pb/$^{207}$Pb | $^{206}$Pb/$^{207}$Pb |
|---|---|---|---|---|---|---|---|
| RA/04 | 15.11 | 34.23 | 17.44 | 0.87 | 1.96 | 2.27 | 1.15 |
| RA/14 | 15.19 | 35.48 | 17.65 | 0.86 | 2.01 | 2.34 | 1.16 |
| RA/15A | 15.34 | 37.13 | 17.72 | 0.87 | 2.1 | 2.42 | 1.15 |
| RA/18 | 15.36 | 35.96 | 17.69 | 0.87 | 2.03 | 2.34 | 1.15 |
| SOC/12A | 14.85 | 34.35 | 17 | 0.87 | 2.02 | 2.31 | 1.14 |
| SOC/15A | 15.52 | 38.45 | 18.12 | 0.86 | 2.12 | 2.48 | 1.17 |
| MAP/1A | 15.37 | 36.04 | 17.62 | 0.87 | 2.04 | 2.35 | 1.15 |
| MAP/3A | 15.27 | 36.15 | 17.5 | 0.87 | 2.07 | 2.37 | 1.15 |
| MWM/2A | 15.4 | 36.06 | 17.95 | 0.86 | 2.01 | 2.34 | 1.17 |
| MWM/3A | 15.07 | 33.16 | 17.21 | 0.88 | 1.93 | 2.2 | 1.14 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| MWM4A | 14.82 | 33.54 | 16.84 | 0.88 | 1.99 | 2.26 | 1.14 |
| MWM/5 | 13.97 | 33.81 | 16.09 | 0.87 | 2.1 | 2.42 | 1.15 |
| MWM/11 | 14.21 | 33.72 | 16.34 | 0.87 | 2.06 | 2.37 | 1.15 |
| MWM/14 | 14.06 | 33.99 | 16.09 | 0.87 | 2.11 | 2.42 | 1.14 |
| MWM/16A | 14.11 | 33.82 | 16.22 | 0.87 | 2.09 | 2.4 | 1.15 |
| MWM/17A | 15 | 33.35 | 17.1 | 0.88 | 1.95 | 2.22 | 1.14 |
| FLG/01 | 15.92 | 39.27 | 18.62 | 0.86 | 2.11 | 2.47 | 1.17 |
| AWD/4A | 14.91 | 34.5 | 17.28 | 0.86 | 2 | 2.31 | 1.16 |
| AWD/7 | 15.28 | 36.09 | 17.52 | 0.87 | 2.06 | 2.36 | 1.15 |
| FLG/11 | 15.78 | 36.79 | 18.3 | 0.86 | 2.01 | 2.33 | 1.16 |
| ID/3 | 15.34 | 35.59 | 17.53 | 0.87 | 2.03 | 2.32 | 1.14 |
| 1D/4 | 14.96 | 34.9 | 17.31 | 0.86 | 2.02 | 2.33 | 1.16 |
| NK/13 | 15.69 | 36.55 | 18.08 | 0.87 | 2.02 | 2.33 | 1.15 |
| NK/14 | 15.55 | 36.34 | 18.06 | 0.86 | 2.01 | 2.34 | 1.16 |
| RSD/11 | 15.21 | 35.66 | 17.46 | 0.87 | 2.04 | 2.34 | 1.15 |
| RSD/14 | 15.3 | 35.16 | 17.58 | 0.87 | 2 | 2.3 | 1.15 |

A: Cont’

| S/N | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{206}Pb$ | $^{208}Pb/^{206}Pb$ | $^{208}Pb/^{207}Pb$ | $^{206}Pb/^{207}Pb$ |
|---|---|---|---|---|---|---|---|
| RSD/16 | 15.47 | 35.8 | 17.54 | 0.88 | 2.04 | 2.31 | 1.13 |
| RSD/21 | 15.52 | 36.66 | 17.75 | 0.87 | 2.06 | 2.36 | 1.14 |
| RK/1 | 15.54 | 37.59 | 17.82 | 0.87 | 2.11 | 2.42 | 1.15 |
| CT/2 | 16.05 | 39 | 18.76 | 0.86 | 2.08 | 2.43 | 1.17 |
| Coal | 14.41 | 34.83 | 17.64 | 0.82 | 1.97 | 2.42 | 1.22 |
| Galena | 16.32 | 39.22 | 20.3 | 0.8 | 1.93 | 2.4 | 1.24 |
| Vehicle exhust | 15.21 | 36.3 | 18.9 | 0.81 | 1.92 | 2.39 | 1.15 |
| Battery cell | 14.43 | 34.15 | 17.23 | 0.84 | 1.98 | 2.37 | 1.19 |

Appendix 8

A : Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Ni | Ni | Ni | Ni | Ni |
| PPB | PPB | PPB | PPB | PPB |
| 5 | 50 | 50 | 50 | 50 |
| 165 | 1224 | 4181 | 4450 | 7613 |
| 51 | 844 | 1623 | 3638 | 1449 |
| 466 | 740 | 1144 | 9190 | 8962 |

|  |  |  |  |  |
|---|---|---|---|---|
| 1932 | 9501 | 3173 | 42637 | 51865 |
| 99 | 879 | 635 | 2460 | 2811 |
| 4875 | 3480 | 5999 | 11637 | 6804 |
| 134 | 1831 | 3376 | 4861 | 2708 |
| 124 | 10229 | 6043 | 42060 | 65927 |
| 493 | 284 | 1023 | 1398 | 1158 |
| 1863 | 843 | 2435 | 4972 | 3419 |

B : Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Cd | Cd | Cd | Cd | Cd |
| PPB | PPB | PPB | PPB | PPB |
| 0.5 | 20 | 20 | 20 | 20 |
| 0.9 | 1193 | 472 | 1383 | 837 |
| 0.5 | 251 | 26 | 155 | 44 |
| 1.5 | 390 | 172 | 554 | 227 |

|  |  |  |  |  |
|---|---|---|---|---|
| 5.8 | 1511 | 253 | 1496 | 1155 |
| 5.9 | 1499 | 227 | 1059 | 467 |
| 1.1 | 197 | 56 | 357 | 122 |
| 2.5 | 470 | 163 | 215 | 65 |
| 0.7 | 2483 | 534 | 2500 | 1835 |
| 3.8 | 399 | 129 | 235 | 36 |
| 1.5 | 496 | 225 | 591 | 162 |

C: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Pb | Pb | Pb | Pb | Pb |
| PPB | PPB | PPB | PPB | PPB |
| 3 | 20 | 20 | 20 | 20 |
| 67 | 7289 | 19802 | 912 | 55696 |

| | | | | |
|---|---|---|---|---|
| 25 | 35842 | 16113 | 46321 | 55191 |
| 57 | 21119 | 37004 | 22991 | 141844 |
| 76 | 17474 | 7537 | 3385 | 135692 |
| 13 | 21795 | 12897 | 24816 | 88445 |
| 40 | 1367 | 3766 | 2403 | 29679 |
| 114 | 4735 | 10005 | 12355 | 38478 |
| 43 | 35182 | 20711 | 6134 | 388629 |
| 122 | 9351 | 10867 | 25513 | 32926 |
| 108 | 4223 | 14206 | 16891 | 76221 |

D: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Zn | Zn | Zn | Zn | Zn |
| PPB | PPB | PPB | PPB | PPB |

| | | | | |
|---|---|---|---|---|
| 100 | 100 | 100 | 100 | 100 |
| 1192 | 362314 | 286517 | 531058 | 327422 |
| 157 | 145731 | 64184 | 190814 | 48743 |
| 2592 | 189741 | 148967 | 331210 | 176246 |
| 3502 | 504530 | 92592 | 417348 | 405089 |
| 6707 | 1111990 | 218032 | 345119 | 154408 |
| 19914 | 1298953 | 606482 | 1242079 | 493837 |
| 39817 | 2645735 | 1083503 | 1068344 | 551845 |
| 419 | 636731 | 258725 | 831510 | 967747 |
| 9170 | 441101 | 194721 | 223601 | 89945 |
| 5029 | 289902 | 237633 | 402772 | 159129 |

E: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|

| Mn | Mn | Mn | Mn | Mn |
|---|---|---|---|---|
| PPB | PPB | PPB | PPB | PPB |
| 50 | 50 | 50 | 50 | 50 |
| 177 | 42401 | 53106 | 552175 | 104552 |
| 91 | 26997 | 25553 | 204463 | 35323 |
| 388 | 46312 | 79921 | 265831 | 48516 |
| 9300 | 219810 | 46546 | 526791 | 225468 |
| 2030 | 52040 | 20835 | 126214 | 64449 |
| 3941 | 87201 | 58048 | 143668 | 52161 |
| 1721 | 49249 | 49414 | 280874 | 41783 |
| 195 | 115401 | 105749 | 533818 | 224038 |
| 862 | 95434 | 124980 | 359768 | 27074 |
| 610 | 42071 | 81362 | 696597 | 80217 |

F: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Ba | Ba | Ba | Ba | Ba |
| PPB | PPB | PPB | PPB | PPB |
| 10 | 50 | 50 | 50 | 50 |
| 164 | 33719 | 8105 | 51023 | 114024 |
| 260 | 33217 | 3895 | 78748 | 9439 |
| 469 | 37655 | 5199 | 66338 | 30423 |
| 3293 | 73596 | 2944 | 169186 | 113346 |
| 1263 | 46251 | 2705 | 81438 | 21816 |
| 201 | 14750 | 3940 | 72175 | 46337 |
| 473 | 50559 | 19859 | 139530 | 76361 |
| 660 | 65752 | 2369 | 132350 | 123095 |
| 350 | 44464 | 6754 | 71849 | 8517 |
| 199 | 21435 | 7240 | 76169 | 25258 |

G: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Cu | Cu | Cu | Cu | Cu |
| PPB | PPB | PPB | PPB | PPB |
| 5 | 20 | 20 | 20 | 20 |
| 1247 | 2590 | 46990 | 571 | 15100 |
| 1091 | 7612 | 31279 | 10249 | 22699 |
| 3231 | 1693 | 25561 | 657 | 8761 |
| 22306 | 94284 | 146410 | 38899 | 213002 |
| 4722 | 11656 | 35065 | 3006 | 27169 |
| 7648 | 4974 | 29190 | 2680 | 13382 |
| 723 | 7249 | 76457 | 9279 | 28967 |
| 2951 | 102881 | 179121 | 21415 | 158755 |
| 2360 | 915 | 7829 | 820 | 2530 |
| 8284 | 2305 | 20818 | 1698 | 7739 |

H : Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| Co | Co | Co | Co | Co |
| PPB | PPB | PPB | PPB | PPB |
| 1 | 20 | 20 | 20 | 20 |
| 25 | 332 | 917 | 4485 | 2124 |
| 22 | 242 | 292 | 1363 | 543 |
| 59 | 156 | 547 | 2959 | 2464 |
| 109 | 1609 | 345 | 3318 | 2922 |
| 356 | 4748 | 761 | 9189 | 4317 |
| 2342 | 3658 | 4121 | 14925 | 5110 |
| 576 | 18159 | 11972 | 76289 | 15362 |
| 14 | 652 | 664 | 8510 | 3782 |
| 231 | 80 | 552 | 2419 | 466 |
| 181 | 57 | 483 | 3665 | 746 |

I: Sequence Extraction Fraction of soils and sediments in the study area

| LH1 | LH2 | LH3 | LH4 | LH5 |
|---|---|---|---|---|
| As | As | As | As | As |
| PPB | PPB | PPB | PPB | PPB |
| 5 | 100 | 100 | 100 | 100 |
| LH1 | LH2 | LH3 | LH4 | LH5 |
| 47 | 184 | 1186 | 337 | 286 |
| 35 | 491 | 2331 | 100 | 121 |
| 33 | 192 | 348 | 100 | 100 |
| 24 | 100 | 452 | 100 | 100 |
| 19 | 202 | 528 | 100 | 100 |
| 53 | 222 | 950 | 158 | 161 |
| 27 | 100 | 1209 | 157 | 231 |
| 7 | 169 | 657 | 100 | 100 |
| 50 | 170 | 366 | 100 | 100 |
| 43 | 267 | 691 | 283 | 198 |

Appendix 9: A : Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments in the study area.

| S/N | Fluorene µg/kg | Anthracene µg/kg | Phenanthrene µg/kg | Fluoranthene µg/kg | Pyrene µg/kg | Benzo[a]anthracene µg/kg | Chrysene µg/kg |
|---|---|---|---|---|---|---|---|
| RA/3 | 0,0 | 1.0 | 19.8 | 18.0 | 19.7 | 8.4 | 14.8 |
| RA/4 | 4.3 | 8.2 | 90.7 | 134.4 | 150.0 | 101.1 | 151.2 |
| RA/6 | 5.6 | 9.8 | 105.3 | 70.9 | 76.8 | 23.0 | 58.7 |
| RA14 | 0.0 | 1.0 | 39.5 | 81.1 | 79.4 | 46.6 | 80.1 |
| RA/18 | 7.0 | 14.9 | 138.7 | 217.4 | 208.9 | 115.4 | 187.8 |
| RA/20 | 0.0 | 1.0 | 4.2 | 71.5 | 62.3 | 30.5 | 47.3 |
| RA/21 | 0.0 | 0.0 | 8.2 | 11.5 | 11.7 | 2.7 | 8.1 |
| SOC/2A | 0.0 | 0.0 | 1.3 | 9.2 | 7.1 | 2.4 | 7.8 |
| SOC/5 | 0.0 | 1.0 | 8.1 | 12.9 | 14.9 | 5.0 | 14.2 |
| SOC/6 | 0.0 | 1.0 | 68.1 | 41.9 | 35.1 | 15.1 | 30.0 |
| SOC/7A | 0.0 | 1.0 | 13.0 | 37.2 | 33.8 | 12.7 | 22.5 |
| SOC/12A | 0.0 | 1.2 | 21.1 | 51.1 | 40.4 | 12.1 | 29.3 |
| CT/4 | 0.0 | n.d. | 1.0 | 1.0 | n.d. | n.d. | 1.0 |
| FLG/3A | 0.0 | 1.0 | 4.7 | 4.1 | 3.7.0 | 1.0 | 1.3 |
| RK/2 | 0.0 | 0.0 | 5.9 | 8.5 | 9.4 | 1.0 | 3.9 |
| FLG/5A | 0.0 | 1.9 | 32 | 30.6 | 37.0 | 8.7 | 19.3 |
| FLG/6A | 0.0 | 1.0 | 7.1 | 60.2 | 57.7 | 30.2 | 49.7 |
| MAP/1A | 0.0 | 1.0 | 15.0 | 11.3 | 13.1 | 3.4 | 9.9 |
| MAP/2 | 15.3 | 23.4 | 229.9 | 239.7 | 229.0 | 119.4 | 204.1 |
| MAP/3A | 1.0 | 13.0 | 186.6 | 281.7 | 259.8 | 110.8 | 159.1 |
| AWD/3A | 36.7 | 22.0 | 188.3 | 65.3 | 72.5 | 28.4 | 70.6 |
| AWD/4A | 0.0 | <1.0 | 5.0 | 30.9 | 35.0 | 23.4 | 46.6 |
| AWD/5A | 1.0 | 13.4 | 245.3 | 483.7 | 298.0 | 68.1 | 108.0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AWD/5B | 2.6 | 10.5 | 190.9 | 317.1 | 195.5 | 59.2 | 88.2 |
| AWD/6A | 4.7 | 8.7 | 124.5 | 83.7 | 85.4 | 39.3 | 97.1 |
| AWD/8 | 0.0 | 2.5 | 39.3 | 58.4 | 63.4 | 51.2 | 86.3 |

B : Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments in the study area, (μg/kg)

| S/N | Benzo[k]fluoranthene | Benzo[a]pyrene | Benzo[b]fluoranthene | Benzo[ghi]perylene | Indeno(1,2,3-cd)pyrene | Dibenz[ah]anthracene |
|---|---|---|---|---|---|---|
| RA/3 | 8.7 | 20.0 | 27.8 | 25.2 | 23.2 | 1.9 |
| RA/4 | 87.9 | 248.7 | 247.2 | 190.6 | 185.8 | 22.8 |
| RA/6 | 16.7 | 38.9 | 64.2 | 77.3 | 51.5 | 4.2 |
| RA14 | 43.0 | 103.8 | 128.6 | 107.2 | 100.4 | 6.5 |
| RA/18 | 95.5 | 253.9 | 290.1 | 273.0 | 243.0 | 20.0 |
| RA/20 | 23.1 | 48.2 | 70.5 | 48.4 | 50.9 | 4.5 |
| RA/21 | 3.6 | 4.3 | 14.6 | 9.8 | 10.5 | 1.0 |
| SOC/2A | 2.4 | 2.8 | 8.7 | 5.6 | 5.2 | 1.0 |
| SOC/5 | 4.7 | 11.3 | 19.7 | 16.5 | 15.0 | 1.0 |
| SOC/6 | 11.3 | 27.2 | 38.5 | 29.4 | 26.0 | 2.1 |
| SOC/7A | 10.4 | 23.8 | 30.9 | 22.5 | 20.2 | 1.4 |
| SOC/12A | 8.2 | 9.3 | 27.1 | 18.4 | 15.0 | 1.4 |
| CT/4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| FLG/3A | 1.0 | 1.0 | 1.1 | 1.0 | 1.0 | n.d. |
| RK/2 | 1.0 | 1.0 | 2.8 | 1.3 | 1.1 | n.d. |
| FLG/5A | 7.4 | 11.9 | 26.4 | 19.7 | 18.9 | 1.0 |
| FLG/6A | 19.6 | 49.7 | 60.0 | 41.6 | 40.1 | 3.8 |
| MAP/1A | 2.1 | 3.8 | 9.2 | 8.5 | 6.2 | 1.0 |
| MAP/2 | 84.9 | 259.7 | 286.9 | 231.4 | 203.6 | 15.8 |
| MAP/3A | 56.7 | 124.4 | 163.6 | 90.9 | 98.7 | 10.5 |
| AWD/3A | 18.7 | 56.3 | 72.9 | 182.3 | 63.0 | 4.0 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| AWD/4A | 28.3 | 76.5 | 101.5 | 103.8 | 98.2 | 6.1 |
| AWD/5A | 23.4 | 53.5 | 78.7 | 53.0 | 47.5 | 4.4 |
| AWD/5B | 39.5 | 109.8 | 117.8 | 91.8 | 87.0 | 8.0 |
| AWD/6A | 26.6 | 77.8 | 96.4 | 82.4 | 67.1 | 6.5 |
| AWD/8 | 55.3 | 145.5 | 175.8 | 165 | 164.2 | 12.9 |

C: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments in the study area, (µg/kg).

| S/N | Fluorene | Anthracene | Phenanthrene | Fluoranthene | Pyrene | Benzo[a]anthracene | Chrysene |
|---|---|---|---|---|---|---|---|
| MWM/2A | 16.9 | 19 | 147.6 | 115.8 | 191.3 | 53.1 | 103.4 |
| MWM/2B | 1.8 | 3.4 | 29.6 | 11.6 | 18.0 | 6.0 | 10.4 |
| MWM/3A | 4.4 | 16.6 | 140.8 | 130.6 | 431.5 | 50.0 | 146.8 |
| MWM/3B | 1.7 | 2.0 | 24.8 | 25.0 | 40.5 | 11.4 | 18.9 |
| MWM/4A | 0.0 | 1.0 | 25.7 | 59.0 | 48.3 | 27.1 | 63.3 |
| MWM/5 | 17.3 | 18.8 | 162.4 | 79.8 | 282.3 | 46.2 | 95.5 |
| MWM/6A | 1.8 | 3.7 | 33.4 | 32.3 | 50.5 | 12.4 | 23 |
| MWM/9 | 33.7 | 41.8 | 414.0 | 387.5 | 404.2 | 222.0 | 306.5 |
| MWM/10 | 6.9 | 26.4 | 343.0 | 154.9 | 267.3 | 27.5 | 426.4 |
| MWM/11 | 122.2 | 55.3 | 2045.8 | 463.5 | 533.4 | 127.8 | 348.5 |
| MWM/14 | 5.1 | 13.1 | 77.7 | 57.9 | 89.2 | 32.9 | 44.7 |
| MWM/16A | 15.3 | 17.6 | 151.0 | 114.8 | 310.9 | 67.1 | 162.9 |
| MWM/16B | 2.1 | 5.0 | 49.9 | 62.1 | 62.2 | 37.2 | 51.5 |
| MWM/17A | 3.0 | 2.7 | 49.4 | 41.4 | 50.2 | 23.0 | 55.0 |
| MWM/18 | 4.9 | 21.7 | 91.4 | 110.3 | 379.5 | 57.0 | 117.5 |
| SSD/7 | 2.1 | 4.4 | 55.2 | 58.9 | 58.0 | 14.3 | 29.7 |
| SSD/8 | <1.0 | n.d. | 47.9 | 72.5 | 73.6 | 40.8 | 83 |
| SSD/11 | 6.5 | 12.7 | 75.3 | 91.7 | 116.4 | 47.7 | 105.9 |
| SSD/12 | 4.4 | 12.3 | 89.9 | 204.3 | 198 | 86.1 | 172.2 |
| SSD/14 | 9.8 | 27.7 | 155 | 149.3 | 183.9 | 86.4 | 155.4 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| SSD/16 | <1 | 1.7 | 22.2 | 13.4 | 14.1 | 5.6 | 10 |
| SSD/20 | 4.2 | 33.6 | 227.9 | 602.9 | 474.9 | 298.3 | 336.8 |
| SSD/22 | 3.7 | 11.9 | 74.9 | 129.4 | 117.5 | 69.8 | 92.6 |
| SSD/23 | 1.7 | 5.7 | 57.6 | 100.4 | 95.2 | 58.9 | 88.7 |
| SSD/24 | 3.3 | 11.9 | 103.1 | 209.5 | 170.4 | 112.9 | 166.3 |
| ID/3 | 20.1 | 27.9 | 208.6 | 188.3 | 182 | 86.4 | 147 |
| ID/4 | 31.1 | 37.1 | 266.2 | 245.7 | 244.5 | 119.6 | 196.6 |

C: Cont’

| S/N | Fluorene µg/kg | Anthracene µg/kg | Phenanthrene µg/kg | Fluoranthene µg/kg | Pyrene µg/kg | Benzo[a]anthracene µg/kg | Chrysene µg/kg |
|---|---|---|---|---|---|---|---|
| ID/6 | 20.2 | 30.0 | 213.7 | 211.0 | 208.5 | 99.5 | 168.0 |
| ID/9 | 12.9 | 46.0 | 236.5 | 494.6 | 531.8 | 226.6 | 385.6 |
| NK/14 | 8.6 | 14.3 | 111.8 | 180.1 | 185.6 | 83.1 | 150.4 |
| NK/20 | 10.5 | 16.2 | 103.0 | 115.1 | 139.6 | 59.5 | 101.9 |
| ∑ PAHs | 453.0 | 669.6 | 7455.6 | 7038.3 | 7936.4 | 3029.0 | 5650.6 |

D: Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in soils and sediments in the study area.

| S/N | Benzo[k]fluorante µg/kg | Benzo[a]pyre µg/kg | Benzo[b]fluoranthee µg/kg | Benzo[ghi]perylee µg/kg | Indeno(1,2,3-cd)pyrene µg/kg | Dibenz[ah]anthracee µg/kg |
|---|---|---|---|---|---|---|
| MWM/2A | 32.1 | 96.4 | 120.9 | 197.6 | 108.1 | 8.4 |
| MWM/2B | 4.5 | 15.9 | 14.8 | 50.1 | 24.3 | 1.0 |
| MWM/3A | 50.0 | 130.4 | 221.7 | 406.8 | 186.2 | 3.4 |
| MWM/3B | 7.4 | 17.6 | 26.9 | 29.3 | 16.3 | 1.0 |
| MWM/4A | 31.9 | 24.2 | 118.4 | 108.2 | 107.4 | 9.1 |
| MWM/5 | 29.8 | 139.8 | 134.8 | 426.5 | 143.4 | 6.7 |
| MWM/6A | 6.3 | 27.5 | 25.5 | 205.4 | 39.3 | 1.3 |
| MWM/9 | 166.5 | 525.9 | 502.6 | 500.9 | 412.2 | 33.4 |
| MWM/10 | 22.3 | 35.3 | 122.8 | 101.0 | 55.3 | 3.2 |
| MWM/11 | 39.2 | 94.8 | 164.6 | 184.5 | 97.6 | 4.2 |
| MWM/14 | 17.1 | 67.0 | 64.5 | 359.7 | 85.4 | 4.0 |
| MWM/16A | 62.2 | 240.1 | 235.2 | 557.8 | 305.2 | 14.8 |
| MWM/16B | 33.4 | 102.6 | 100.2 | 105.1 | 91.7 | 8.3 |
| MWM/17A | 20.0 | 50.5 | 67.8 | 57.1 | 48.1 | 5.4 |
| MWM/18 | 39.1 | 160.0 | 176.7 | 415.9 | 194.1 | 11.5 |
| RSD/7 | 9.5 | 24.6 | 32.1 | 38.2 | 27.1 | 2.3 |
| RSD/8 | 43.1 | 99.7 | 143.2 | 126.4 | 119.1 | 8.9 |
| RSD/11 | 38.9 | 121.9 | 130.5 | 237.0 | 151.3 | 9.3 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| RSD/12 | 48.6 | 110.5 | 181.6 | 167.5 | 121.0 | 11.1 |
| RSD/14 | 57.3 | 216.9 | 199.4 | 449.8 | 326.0 | 18.1 |
| RSD/16 | 4.0 | 12.9 | 14.1 | 25.5 | 14.9 | 1.0 |
| RSD/20 | 163.5 | 514.9 | 452.9 | 329.3 | 300.2 | 37.0 |
| RSD/22 | 47.1 | 143.1 | 138.9 | 144.8 | 124.2 | 9.3 |
| RSD/23 | 47.1 | 134.3 | 146.6 | 149.3 | 136.6 | 9.8 |
| RSD/24 | 83.7 | 223.9 | 263.5 | 203.9 | 192.6 | 17.8 |
| ID/3 | 61.4 | 181.8 | 210.3 | 204.2 | 174.6 | 12.3 |
| ID/4 | 82.2 | 253.0 | 280.2 | 273.4 | 234.4 | 16.0 |
| ID/5 | 72.0 | 225.1 | 249.1 | 264.3 | 227.0 | 15.2 |

D: Cont’

| S/N | Benzo[k]fluorante | Benzo[a]pyre | Benzo[b]fluoranthee | Benzo[ghi]perylee | Indeno(1,2,3-cd)pyrene | Dibenz[ah]anthracee |
|---|---|---|---|---|---|---|
|  | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg |
| ID/9 | 106.6 | 256.0 | 373.0 | 326.6 | 213.9 | 21.7 |
| NK/14 | 62.4 | 171.7 | 218.5 | 208.1 | 177 | 11.3 |
| NK/20 | 43.5 | 140.2 | 136.6 | 185.1 | 134.8 | 8.7 |
| SHALE | 14.8 | 104.4 | 19.8 | 4.7 | 1.0 | 2.3 |
| ∑ PAHs | 2046.0 | 5970.7 | 6930.5 | 8502.6 | 5828.2 | 428.2 |

E: Selected Polycyclic Aromatic Hydrocarbons (PAHs) ratios and TOC values in soils and sediments in the study area.

| S/N | Phe/Ant | Flu/Pyr | BaA/(BaA+Chr) | IcdP/(IcdP + BiP) | TOC | Flu/(Flu+Pry) | Ant/(Ant+Pyr) |
|---|---|---|---|---|---|---|---|
| RA/3 | 19.8 | 0.9 | 2.76 | 0.48 | 1.05 | 0.48 | 0.05 |
| RA/4 | 11.1 | 0.9 | 2.50 | 0.49 | 2.87 | 0.47 | 0.05 |
| RA/6 | 10.7 | 0.9 | 3.55 | 0.40 | 2.31 | 0.48 | 0.11 |
| RA14 | 39.5 | 1.0 | 2.72 | 0.48 | 1.13 | 0.51 | 0.01 |
| RA/18 | 9.3 | 1.0 | 2.63 | 0.47 | 2.07 | 0.51 | 0.07 |
| RA/20 | 4.2 | 1.1 | 2.55 | 0.51 | 1.98 | 0.53 | 0.02 |
| RA/21 | 0.0 | 1.0 | 4.00 | 0.52 | 1.3 | 0.50 | 0.00 |
| SOC/2A | 0.0 | 1.3 | 4.25 | 0.48 | 0.38 | 0.56 | 0.00 |
| SOC/5 | 8.1 | 0.9 | 3.84 | 0.48 | 1.69 | 0.46 | 0.06 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| SOC/6 | 68.1 | 1.2 | 2.99 | 0.47 | 1.2 | 0.54 | 0.03 |
| SOC/7A | 13.0 | 1.1 | 2.77 | 0.47 | 0.67 | 0.52 | 0.03 |
| SOC/12A | 17.6 | 1.3 | 3.42 | 0.45 | 0.81 | 0.56 | 0.03 |
| CT/4 | 0.0 | 0.0 | 0.00 | 0.00 | 0.12 | 0.00 | 0.00 |
| FLG/3A | 4.7 | 1.1 | 2.30 | 0.50 | 0.16 | 0.53 | 0.21 |
| RK/2 | 0.0 | 0.9 | 4.90 | 0.46 | 2.03 | 0.47 | 0.00 |

E: Cont’

| S/N | Phe/Ant | Flu/Pyr | BaA/(BaA+Chr) | IcdP/(IcdP + BiP) | TOC | Flu/(Flu+Pry) | Ant/(Ant+Pyr) |
|---|---|---|---|---|---|---|---|
| FLG/5A | 16.8 | 0.8 | 3.22 | 0.49 | 3.22 | 0.45 | 0.05 |
| FLG/6A | 7.1 | 1.0 | 2.65 | 0.49 | 1.94 | 0.51 | 0.02 |
| MAP/1A | 15.0 | 0.9 | 3.91 | 0.42 | 1.45 | 0.46 | 0.07 |
| MAP/2 | 9.8 | 1.0 | 2.71 | 0.47 | 5.12 | 0.51 | 0.09 |
| MAP/3A | 14.4 | 1.1 | 2.44 | 0.52 | 3.41 | 0.52 | 0.05 |
| AWD/3A | 8.6 | 0.9 | 3.49 | 0.26 | 10.5 | 0.47 | 0.23 |
| AWD/4A | 0.0 | 0.9 | 2.99 | 0.49 | 4.74 | 0.47 | 0.0 |
| AWD/5A | 18.3 | 1.6 | 2.59 | 0.47 | 1.86 | 0.62 | 0.04 |
| AWD/5B | 18.2 | 1.6 | 2.49 | 0.49 | 1.96 | 0.62 | 0.05 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AWD/6A | 14.3 | 1.0 | 3.47 | 0.45 | 3.49 | 0.49 | 0.09 |
| AWD/8 | 15.7 | 0.9 | 2.69 | 0.50 | 3.98 | 0.48 | 0.04 |
| MWM/2A | 7.8 | 0.6 | 2.95 | 0.35 | 2.02 | 0.38 | 0.09 |
| MWM/2B | 8.7 | 0.6 | 2.73 | 0.33 | 2.37 | 0.39 | 0.16 |
| MWM/3A | 8.5 | 0.3 | 3.94 | 0.31 | 4.87 | 0.23 | 0.04 |
| MWM/3B | 12.4 | 0.6 | 2.66 | 0.36 | 0.6 | 0.38 | 0.05 |

E: Cont'

| S/N | Phe/Ant | Flu/Pyr | BaA/(BaA+Chr) | IcdP/(IcdP + BiP) | TOC | Flu/(Flu+Pry) | Ant/(Ant+Pyr) |
|---|---|---|---|---|---|---|---|
| MWM/4A | 25.7 | 1.2 | 3.34 | 0.50 | 2.57 | 0.55 | 0.02 |
| MWM/5 | 8.6 | 0.3 | 3.07 | 0.25 | 4.19 | 0.22 | 0.06 |
| MWM/6A | 9.0 | 0.6 | 2.85 | 0.16 | 2.29 | 0.39 | 0.07 |
| MWM/9 | 9.9 | 1.0 | 2.38 | 0.45 | 2.76 | 0.49 | 0.09 |
| MWM/10 | 13.0 | 0.6 | 16.51 | 0.35 | 5.94 | 0.37 | 0.09 |
| MWM/11 | 37.0 | 0.9 | 3.73 | 0.35 | 4.02 | 0.46 | 0.09 |
| MWM/14 | 5.9 | 0.6 | 2.36 | 0.19 | 5.08 | 0.39 | 0.13 |
| MWM/16A | 8.6 | 0.4 | 3.43 | 0.35 | 6.06 | 0.27 | 0.05 |
| MWM/16B | 10.0 | 1.0 | 2.38 | 0.47 | 3.07 | 0.50 | 0.07 |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| MWM/17A | 18.3 | 0.8 | 3.39 | 0.46 | 1.68 | 0.45 | 0.05 |
| MWM/18 | 4.2 | 0.3 | 3.06 | 0.32 | 3.31 | 0.23 | 0.05 |
| SSD/7 | 12.5 | 1.0 | 3.08 | 0.42 | 0.76 | 0.50 | 0.07 |
| SSD/8 | 0.0 | 1.0 | 3.03 | 0.49 | 3 | 0.50 | 0.0 |
| SSD/11 | 5.9 | 0.8 | 3.22 | 0.39 | 2.56 | 0.44 | 0.10 |
| SSD/12 | 7.3 | 1.0 | 3.00 | 0.42 | 1.86 | 0.51 | 0.06 |

E: Cont'

| S/N | Phe/Ant | Flu/Pyr | BaA/(BaA+Chr) | IcdP/(IcdP + BiP) | TOC | Flu/(Flu+Pry) | Ant/(Ant+Pyr) |
|---|---|---|---|---|---|---|---|
| SSD/14 | 5.6 | 0.8 | 2.80 | 0.42 | 2.79 | 0.45 | 0.13 |
| SSD/16 | 13.1 | 1.0 | 2.79 | 0.37 | 0.54 | 0.49 | 0.11 |
| SSD/20 | 6.8 | 1.3 | 2.13 | 0.48 | 2.29 | 0.56 | 0.07 |
| SSD/22 | 6.3 | 1.1 | 2.33 | 0.46 | 0.99 | 0.52 | 0.09 |
| SSD/23 | 10.1 | 1.1 | 2.51 | 0.48 | 1.03 | 0.51 | 0.06 |
| SSD/24 | 8.7 | 1.2 | 2.47 | 0.49 | 1.22 | 0.55 | 0.07 |
| ID/3 | 7.5 | 1.0 | 2.70 | 0.46 | 3.03 | 0.51 | 0.13 |
| ID/4 | 7.2 | 1.0 | 2.64 | 0.46 | 3.29 | 0.50 | 0.13 |
| ID/5 | 7.8 | 1.0 | 2.67 | 0.46 | 3.35 | 0.50 | 0.11 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ID/6 | 7.1 | 1.0 | 2.69 | 0.46 | 3.13 | 0.50 | 0.13 |
| ID/9 | 5.1 | 0.9 | 2.70 | 0.40 | 3.25 | 0.48 | 0.08 |
| NK/14 | 7.8 | 1.0 | 2.81 | 0.46 | 4.18 | 0.49 | 0.07 |
| NK/20 | 6.4 | 0.8 | 2.71 | 0.42 | 2.8 | 0.45 | 0.10 |
| Total PAHs | 657.1 | 53.3 | 182.85 | 24.42 | 152.34 | 27.92 | 4.03 |