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Volume 1

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Scope of the Journal

The Journal of International Medical Geologists- Nigeria publishes original research and review articles in the field of Medical Geology and its allied disciplines such as Environmental/Urban Geochemistry, Hydrogeochemistry, Medical Geography, Pharmacy, Agrogeology, Medical/Environmental Microbiology, Physics (Radiation/Medical Physics), and Environmental Toxicology and Management. Research articles that detail the effects of the interaction between man and the environment are welcome.

Instruction to Authors

Note to Contributors

Manuscripts of unpublished original contributions to knowledge in the broad area of Medical Geology and Environmental Geochemistry are acceptable for submission to the Journal for publication consideration. Such manuscripts must not be under simultaneous publication consideration in another Journal. The official language of the Journal is English.

Requirements

All manuscripts must be in editable MS-word format and must be line numbered. All pages must be numbered consecutively. Contributors must ensure correctness in the language of expression, including spelling, hyphenation, punctuation, notation, and structure. In addition, write-ups must be concise and lucid. Authors must acknowledge the sources of materials obtained elsewhere, and if applicable, secure the rights of reproduction. A major policy of the Journal is space optimization and easy reproduction. All tables and figures must be legible, titled and appropriately referenced. There may be need for tables and figures to be remade to suit the requirements of the Journal.

Front Cover

This should contain the title of the paper, plus the name(s) and affiliation(s) / contact(s) of the author(s). The title which must be brief and appropriate to the subject of the article, should exclude complex symbols. To facilitate the indexing, it is recommended that author's full name is given, with SURNAME being FIRST and written in BLOCK LETTERS.

Abstract

The abstract should not exceed **250 words** and must clearly outline the essential contents of the paper without citing references. It should not be mere description of intent and expectation and must be vividly informative and adequate for separate publication in abstracted outlets.

Text

The general format for the text should comprise the following: Introduction, Study area description, Methods / Techniques, Results/Discussion, Conclusions and Acknowledgements (i.e. funding, non-author contributors, etc). Headings of, and sub-heading in these major sections, should be differentiated by use of appropriate point or style (e.g. normal text for headings, *italics for sub-headings*).

The Methods/Techniques section must be explicitly stated, in a way that allows reproducibility by an independent researcher. If the methods/techniques used in the research follows one/those already published in renowned outlets, the published researcher(s) should be quoted, instead of repeating the methodology process.

There should normally be **no more than three categories of heading**; and hence, sub-headings should not exceed second level. **Headings and subheading should not be numbered**.

References

References cited in all parts of the manuscript (text, tables, illustrations) are to be listed on separate sheet following the end of the text, in alphabetical order of the first author, and sequence of year for the same author. **Titles of journals should be given in full.** To ensure the required conformity with the Journal's style in textual citations and referencing, find below example of how references should be listed:

Journal

Afolabi, O.A., Kolawole, L.L., Abimbola, A.F., Olatunji, A.S. and Ajibade, O.M. (2013). Preliminary study of geology and structural trends of Lower Proterozoic basement rocks in Ogbomoso, SW Nigeria. *Journal of Environment and Earth Science,* Vol. 3. No. 8: 82-95

Edited Publication

Laniyan, T.A., Olatunji, A.S. and Fagade, O.G. (2014). Environmental risk assessment of Cement Dust on Soils and Vegetables in an Urban City of Southwestern Nigeria. In Brebbia C.A. (Ed.) *Risk Analysis.* WIT Press Ashurst Lodge, Ashurst, Southampton. 133-139pp. ISSN1743-3517

Book

Peters, S.W. (1991). Regional Geology of Africa, Springer-Verleg, Berlin, 722p.

Unpublished work

Olatunji, A.S. (2006). Geochemical Characterisation of the Lagos lagoon sediments. *Ph.D. Thesis*, University of Ibadan, 174pp.

Tables

All tables must be referred to and numbered in the order of mention in the text. They should be adequately compact. Compactness can be achieved by utilising the appropriate data reduction or statistical techniques to generate necessary summary. The number and suitable brief heading should be indicated on top of the Tables. The appropriate notations or units of the columns and rows must be specified.

Figures

Illustrations (diagrams, plots, maps, sections, photographs, plates) must all be indicated as figures, and numbered according to the sequence of citing in the text. Each figure must be clearly labelled with the appropriate number. **Figures should be written in the text and captions, in the abbreviated form of Fig.**

Units and numerals

The metric system is mandatory, and SI units in the acceptable abbreviations, should normally be used. All numbering must be in Arabic figures.

Equations, formulae, and symbols

The Equation editor should be used for the rendering of all equations in the texts, and they must be numbered. Formulae and symbols should be written in their acceptable international standard format.

Manuscript submission and processing

Manuscripts can only be submitted by email to conference.imganigeria@gmail.com. All submitted manuscripts should be accompanied by a Cover Letter from the corresponding author, stating the contributing authors and detailing salient information about the research. Each submission would be subjected to the blind review process by selected experts in that area at the discretion of the Editorial Committee.

Proofs, Copyright, reprints, and charges

Copyright form and proof of accepted article will be dispatched to the corresponding author, for completion and correction, respectively. The completed form and corrected proof must be sent together, and promptly to the Editorial Committee.

Forward

From Editor-in-Chief

The Journal of International Medical Geologists Association- Nigeria provides an avenue to publish high quality articles in the relatively novel, but quite promising field of Medical Geology. As Medical Geology is a field at the heart of many disciplines, research from allied fields such as Chemistry, Environmental Science, Hydrology, Pharmacy, Agro-geology, Microbiology, Medical Physics, Geography, Health Sciences, amongst others are welcome for publication consideration. Novel and innovative research or review articles within the scopes highlighted below are sought:

Physico-chemical, chemical and microbiological qualities of geologic and environmental media [dust, particulate matter, soil, rocks, water, air and living organisms plants, animals and microorganisms].

Levels and Health Risk Assessment of inorganic (e.g., trace, major and rare earth elements) or organic (e.g., total petroleum hydrocarbons [TPH], polycyclic aromatic hydrocarbons [PAHs], BTEX [benzene, toluene, ethyl benzene and xylene]) substances in consumed products.

Levels of inorganic or organic parameters in human biomarkers such as urine, blood, milk, nails and hair in population exposed to geologic or environmental media.

Presentation of the abundance and spatio-temporal relationships of these parameters using Models.

I recommend the Journal of IMGA-Nigeria as a great outlet for researchers in the Natural, Health and Earth Sciences to publish their findings.

Prof. A.M. Gbadebo
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Physico-chemical and Mineralogical Assessment of Geophagy Clays from Northern Bida Basin, Nigeria and their Health Implications

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Abstract

Geophagy is the consumption of earth materials such as clays and this is commonly practiced in some communities in Nigeria, but there is potential for serious health problems accompanying the consumption which require investigations. This research is focused on assessing the geophagic clays from parts of Northern Bida Basin, Nigeria with the aim of determining their compositions and the potential human health risks that may be associated with their consumption. Thirteen clay samples were collected and analyzed for physico-chemical parameters including colour, Particle Size Distribution (PSD), pH, Electrical Conductivity (EC), Dissolved Oxygen (DO), Total Dissolved Solids (TDS), salinity and Cation Exchange Capacity (CEC). X-Ray Diffractometry (XRD) and Fourier Transform Infra-Red Spectroscopy (FTIR) were used to determine the mineralogy of the clays. The clays are texturally classified as clay, clayey-silt and silty-clay; dominantly whitish coloured with occasional red-stains which might be attractive to geophagists. Results of the physico-chemical results; pH 3.18-5.52, DO 7.46-11.10 mg/L, TDS 5.36-231 mg/L, CEC 4.71-10.27 $cmol^{(+)}/kg$, EC 10.06-460.00 µS/cm and salinity 0.10-0.30 (ppt) fall within the ranges of acceptable standard. Mineralogical analysis revealed quartz and kaolinite enrichment which suggest the ability to the clays to hold nutrients, soothe upset stomach, act as protective and detoxifying agents, treat soreness in the digestive track that may be caused by ulcers as well as prevent diarrhea. This study concluded that the colour and other physico-chemical parameters of the clays meet some tolerable standards for ingestion. However, beneficiation is recommended to improve the quality before ingestion.

Keywords: Geophagia, Total Dissolved Solids, Kaolinite, Health implications, Bida Basin.

Introduction

Clay is defined as a natural, earthy, fine-grained material, composed largely of a group of crystalline hydrous silicate minerals (Velde, 1995). Velde (1995) further submitted that clay minerals are composed mainly of silica, alumina, and water; but they may also contain appreciable quantities of iron, alkalis and alkaline earths. Abrahams (2002), Wilson (2003), Hooda et al. (2004) and Momoh et al. (2015) defined the habitual, intended consumption of earthy materials suchas clays by humans and animals as geophagia. This act has been practiced in almost all the continents in the world, including Africa, Asia, Australia, Europe, North America and South America (Ngole and Ekosse, 2012). Young (2007), Bisi-Johnson et al. (2010) and Ekosse et al. (2011) have reported the practice on the African continent in Botswana, Cameroon, Ghana, Guinea, Ivory Coast, Kenya, Malawi, Nigeria, Senegal, Sierra Leone, Tanzania, Uganda, South Africa and Swaziland. Cases of geophagic practice in Nigeria were also reported by Okunlola and Owoyemi (2011), Odewumi (2013), Lar et al. (2014), and Olatunji et al. (2014).

Researchers including Reilly and Henry (2001), Wilson (2003) and Diko and Ekosse (2014) have recently devoted more attention to the health risks associated with physico-chemical characteristics of several geophagic materials. The World Health Organization/Food and Agriculture Organization ofthe United Nations (2004), Songca et al. (2010), and Ngole-Jeme and Ekosse (2015) submitted that clays can be harmful and cause an adverse effect on human health in some cases. Reilly and Henry (2001), and Wilson (2003) stated that any ingested components of soils can be beneficial to human health by serving as active excipients in pharmaceutical preparations, in spas, and in beauty therapy medicine. According to Young et al. (2011) and Dikko (2013), beneficial

properties of clays also include nutrient supplementation, detoxification, and alleviation of gastrointestinal disorders such as diarrhea, cravings and relief from morning sickness.

In this study, clays from Enagi Formation in northern Bida Basin, Nigeria (Figure 1) were studied to assess their physico-chemical and mineralogical compositions. Within the study area, investigation from clay vendors confirmed the consumption by some pregnant women during and after delivery. Local herb sellers within the locality also confirmed the mixture of the clay with palm wine in the cure of some skin infections. Although, several studies have been carried out on clays from the northern Bida Basin especially on sedimentological, geochemical and mineralogical studies (e.g. Ojo et al., 2011; Ojo, 2012; Ojo and Akande, 2012; Adepoju, 2019; Adepoju et al., 2020; 2021), few have focused on the characterization of the clays as geophagic materials (e.g. Odewumi, 2013). There is also a dearth of data in literature on the physico-chemical and mineralogical compositions of the clay within the study area. The aim of the study therefore, is to assess the physico-chemical and mineralogical characteristics of the geophagic clays, and evaluate the potential health risk that could result from their consumption. This study will also provide baseline data for future studies.

Geological Setting

The Bida Basin is a northwest-southeast trending intra-cratonic sedimentary basin extending from Kontagora in its northern part to areas slightly beyond Lokoja in the southern part. It is delimited in the northeast and southwest by the Basement Complex. The Basin has been divided geographically into northern and southern portions. The northern Bida Basin comprises the basal Campanian Bida Formation which comprises mainly conglomerate and sandstone lithologies, in alluvial to fluvial depositional system (Ojo and Akande, 2012). It is overlain by Maastrichtian Sakpe and Enagi Formations. These older formations are succeeded by the Batati Formation, which is the youngest. Their stratigraphic equivalents in southern Bida Basin (Figure 2) are Lokoja Formation, Maastrichtian Patti Formation and the youngest Agbaja Formation (Ojo and Akande 2009).

Methods

Thirteen clay samples were collected from six locations (Share-SHA, Tshonga-TSG, Enagi-ENG, Kutigi-KUT, Manigi-MNG and Rabba-RAB) within the study area and the lithological logs representing the field occurrences were constructed (Figures 3a and b; lithologies from which samples were collected are arrowed).

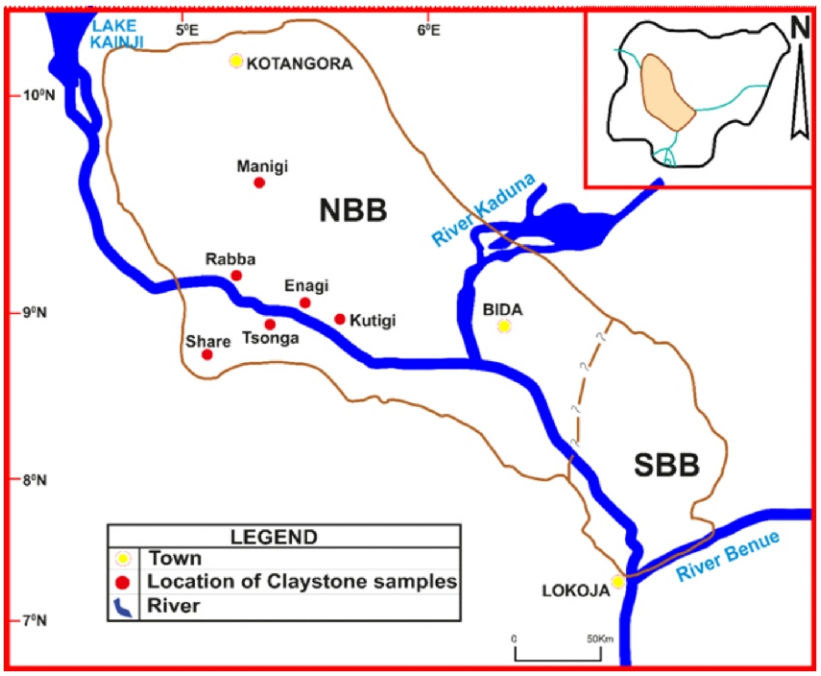


Figure 1: Sampling locations of Geophagia samples within Bida Basin [Inset: Map of Nigeria] (Modified after Adepoju et al., 2020).

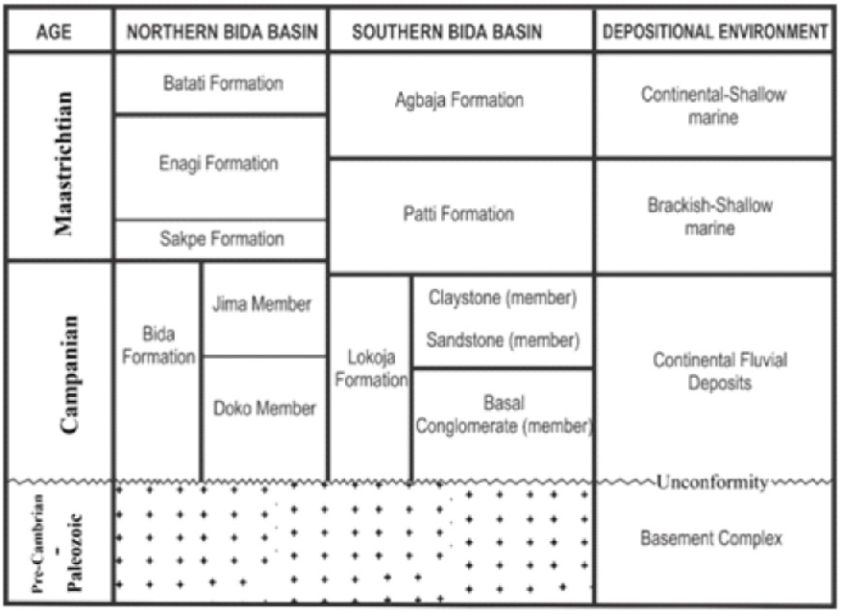


Figure 2: Generalized stratigraphic sequence of the Bida Basin (Adapted from Akande et al., 2005).

The samples were air-dried according to the methods of Tan (1996) and Van Reeuwijk (2002). Particle Size Distribution analysis was conducted after Brown et al.(2016) at GeoTechnics Laboratory, Lagos using sieves of 200 µm and 50 µm. Calculations were made to estimate the gravel, sand and fine contents and their weight percentages plotted in a ternary diagram to determine the texture of the samples. Prior to analysis, a dispersant (sodium hexametaphosphate in deionised water) was added to the samples while organic matter was oxidized using hydrogen peroxide.

The clay samples were also analyzed for physico-chemical characteristics including Colour, Potential of Hydrogen (pH), Cation Exchange Capacity (CEC), Electrical Conductivity (EC), Dissolved Oxygen (DO), Total Dissolved Solids (TDS) and salinity at the Chemistry Department, Landmark University, Omu-Aran, Kwara State. The pH of the clay samples was determined using a 1:2.5 clayey soil-water suspension ratio according to the methods of Van Reevwijk (2002), while the EC of the samples were measured on the saturated paste extract of each sample as described in the United States Soil Survey Laboratory Manual (1996). Determination of CEC was done using the Ammonium Acetate (NH_4OAc) method in accordance with procedures in Brown et al. (2016). 1g of soil was leached with a 1M ammonium acetate solution of pH 7. The NH_4OAc-washed soil was transferred to 50 ml plastic bottles and shaken with a reciprocating shaker for 15minutes. The exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) in the NH_4OAc extract were determined by ionchromatography and the values for CEC were expressed as the sum of the exchangeable base cations.

The mineralogical composition of the clays was determined at the University of Pretoria, South Africa. Prior to analysis, about 100 g of each dried clay samples were gently crushed and sieved, while Moore and Reynolds (1989) method was adopted for the separation of the clay fraction extraction. The samples were later analyzed using a ANalytical X'Pert Pro powder diffractometer in èè configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Ká radiation (ë=1.789Å). The phases were identified using X'Pert High score plus software. Percentage mineralogical composition was also estimated based on the relative peak intensities of the respective minerals in the XRD charts. Infra-red spectra were recorded in diffuse reflectance mode using a Bruker Fourier Transform Interferometer IFS 55 at the Chemistry Department, Kwara State University, Malete, Kwara State.

Results and Discussion

Colour

Colour and texture of the clay, according to Brime (1985), are the physical properties that help in

describing specific characteristics that usually appeals togeophagists. Young et al. (2008) and Reilly and Henry (2001) opined that it is a wide spread belief amongst geophagists that yellowish and reddish clays are likely to contain iron, and could be a source of iron supplement in humans. However, Ngole et al. (2010) submitted that the reddish tint is not necessarily an indicator of the quantities or availability of iron. In this study, colour descriptions were based on the degree of lightness. Out of the 13geophagicsamples studied,3 are whitish, 8 aredirty-white, 1 is brownish and 1 is grey (Figure 4; Table 1). Therefore, on account of colour, as suggested by Young et al. (2008) and Reilly and Henry (2001), several geophagic individuals would prefer consuming the studied clays based on their colour. The colour of the studied clay compared well with other geophagic clays from Nigeria, Cameroon, Swaziland and South Africa (Table 5).

Particle Size Distribution and Textural classification

PSD result of the clay samples revealed textural classification, viz: clay: KUT-1K, KUT-1L, KUT-1Q, MNG-1C and SHA-1J; silty-clay: ENG-1K, SHA-1I-1, SHA-1I-2 and TSG-1K; and clayey-silt: KUT-1M, RAB-1A, TSG-1I and TSG-1J (Table 1; Figures 5a and 5b).

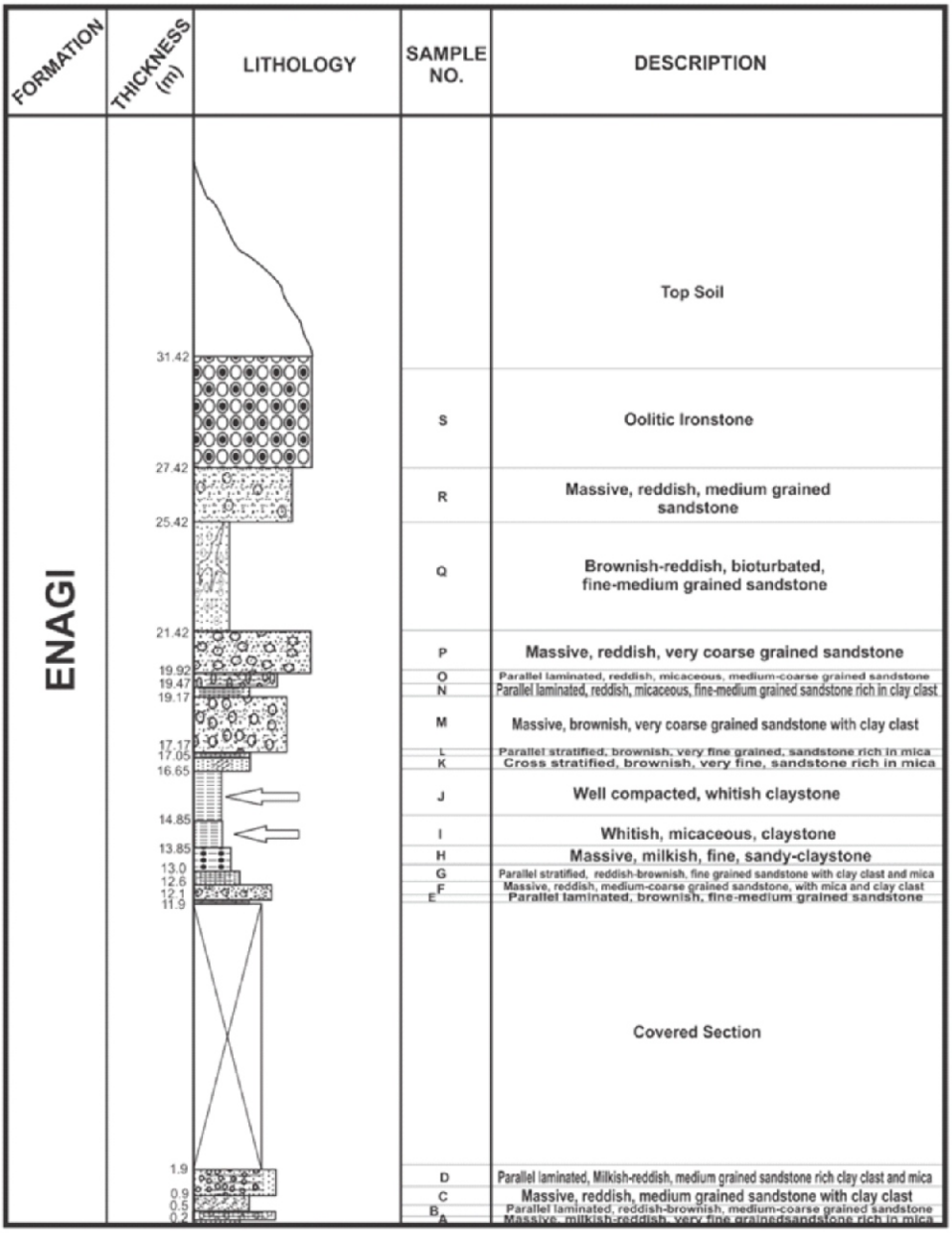


Figure 3a: Lithological section of Enagi Formation exposed at Share (SHA); Longitude: 004°58'26.9"E; Latitude: 08°49'30.3"N.

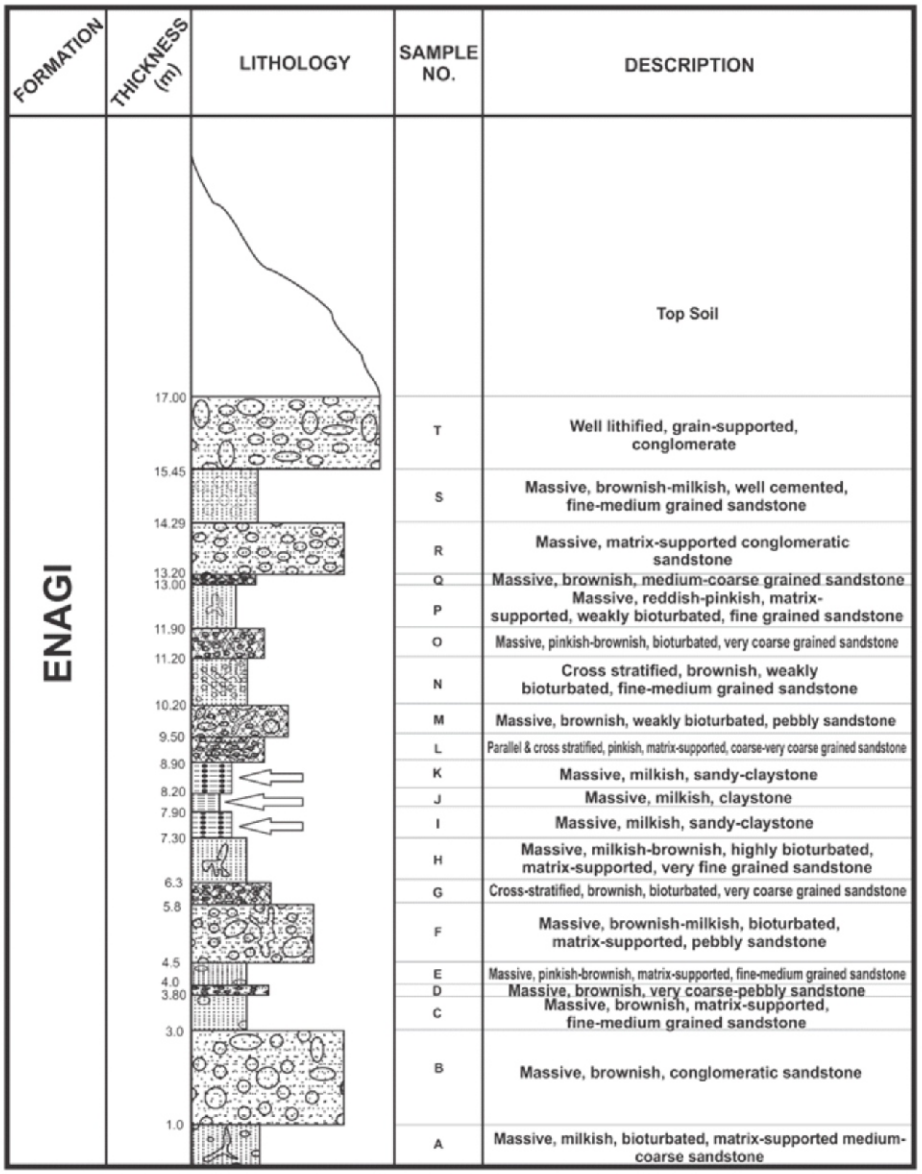


Figure 3b: Lithological section of Enagi Formation exposed at Tshonga (TSG); Longitude: 005°08'50.1"E; Latitude: 09°01'27.4"N.



Figure 4: (a) Exposed clay mine with the samples collected (red circle) at the Agbonna Ridge, Share; (b) Grey samples broken down and ready for collection at Tshonga; (c) Exposed clay section at Kutigi and (d) Clay at the exposed part of the section at Manigi.

It is noted that the results of the particle size distribution in this study is compared well with Meka'a geophagic clay from West Cameroon (Ninla et al., 2018) and geophagic clayey soils from South Africa and Swaziland (Ngole et al., 2010); affirming its geophagic characteristic.

Table 1: Particle Size Distribution and sample classification with their respective colours

Sample No	Sand (%)	Silt (%)	Clay (%)	Textural Classification	Colour
ENG-1K	0	34	66	Silty Clay	Dirty White
KUT-1K	1	16	83	Clay	Dirty White
KUT-1L	0	9	91	Clay	Dirty White
KUT-1M	2	65	33	Clayey Silt	Whitish
KUT-1Q	0	9	91	Clay	Whitish
MNG-1C	0	7	93	Clay	Dirty White
RAB-1A	4	63	33	Clayey Silt	Brownish
SHA-11-1	0	22	78	Silty Clay	Dirty White
SHA-1I-2	0	26	74	Silty Clay	Dirty White
SHA-1J	0	0	100	Clay	Whitish
TSG-1I	0	67	33	Clayey Silt	Grey
TSG-1J	1	56	43	Clayey Silt	Dirty White
TSG-1K	0	20	80	Silty Clay	Dirty White

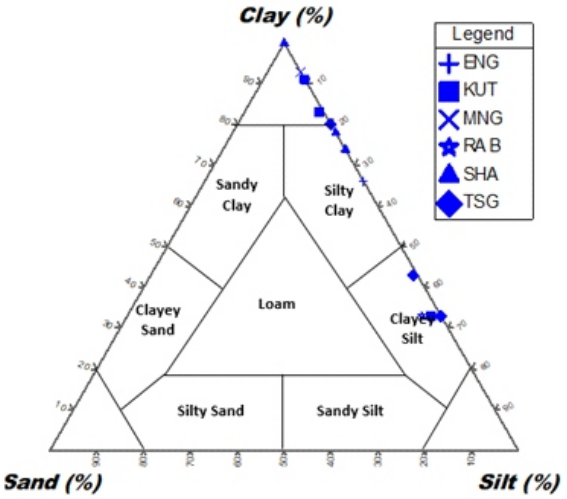


Figure5a:Particle size distributionofthe studiedgeophagic claysamples showing Sand-Silt-Clay ratios (After Shepard, 1954).

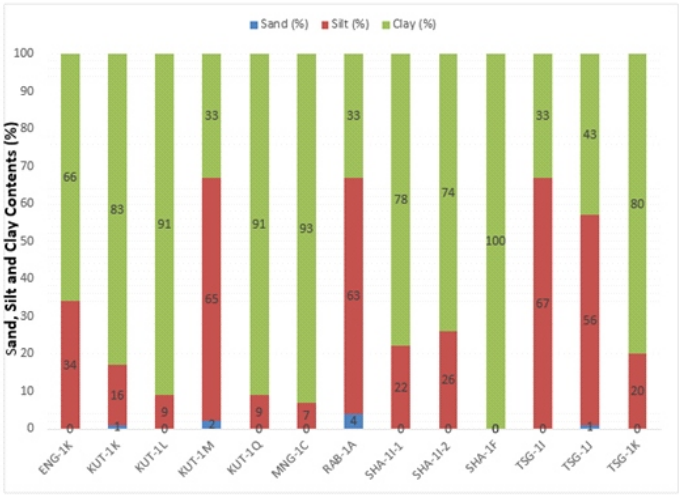


Figure5b: Particle size distribution of the studied geophagic claysamples.

Physico-chemical characteristics of the geophagic clays

The physico-chemical parameters of eight of the samples were determined, the results are presented in Tables 2 and 3.

Cation exchange capacity (CEC)

CEC is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil (Addis and Abebaw, 2014). TheCECof the investigated clay varied from1.68to5.77 **cmol$^{(+)}$/kg** (Table 3; Figure 6) which according to Brady and Weil (2008), falls within the standard values (2-5 **cmol$^{(+)}$/kg**) suggested for soil composed of kaolinite mineral.

PotentialofHydrogen(pH)

The investigated clay samples by its pH values are acidic to moderately acidic (3.18-5.52; Table 3; Figure 7). According to Abrahams and Parsons (1997), acidic clays have potential to impart a sour taste when consumed. Also, Ngole et al. (2010) and Ibeanu et al. (1997) concluded that acidic nature of the consumed samples may generate an astringent effect in the mouth, therefore having an ability to overcome nausea and control excessive salivation in pregnant women.

According to Olatunji et al. (2014), the acidic nature of the clays would neutralize the alkalinity of saliva, thereby leading to a tasteless feeling for individual

geophagists. The pH values of the clay (less than 7) also indicate a stream draining clay type which according to Keller and Matlack (1990), are usually composed essentially of kaolinite. The pH values of the samples in this study also compare well with pH values of other geophagic clays consumed in other parts of Africa (Table 6).

Electrical Conductivity (EC) and Salinity

The quantity of dissolved salts in soils in addition to pH, determines the electrical conductivity (Young et al., 2008). Generally, the higher the dissolved material in a soil sample, the higher the EC. According to Ngoleet al. (2006), geophagic samples thatexhibit very low EC may indicate presence of low amount of dissolved salts. The investigated clay samples have variable electrical conductivity values; 6 samples have values ranging from 10.06 to 27.4 µS/cm which indicate low dissolved salt contents, while the remaining 2 samples with relatively higher values of 132.0 and 460.0 µS/cm Is likely due to the presence of relatively higher dissolved salt contents in the clays (Table 3; Figure 8).

Table 2: Cation Exchange Capacity of the analyzed clays

Sample Code	Na^+	K^+	Mg^{2+}	Ca^{2+}	CEC ($cmol^{(+)}/kg$)
ENG-1K	0.28	0.18	1.00	0.75	2.21
KUT-1K	0.27	0.16	0.60	0.65	1.68
KUT-1L	0.28	0.19	0.50	0.75	1.72
KUT-1M	0.28	0.17	0.65	0.85	1.95
KUT-1Q	0.64	1.91	0.95	1.20	4.70
MNG-1C	1.92	2.25	1.10	0.50	5.77
RBA-1A	1.28	2.05	1.05	0.40	4.78
SHA-1I-1	0.28	0.16	1.15	0.40	1.99
SHA-1I-2	0.58	0.21	0.25	1.00	2.04
SHA-1J	0.64	1.38	0.80	0.50	3.32
TSG-1I	0.26	0.17	0.65	0.90	1.98
TSG-1J	0.28	0.16	1.15	0.45	2.04
TSG-1K	0.64	1.36	0.55	0.45	3.00
Minimum	0.26	0.16	0.25	0.40	1.68
Maximum	1.92	2.25	1.15	1.20	5.77

Table 3: Physico-chemical parameters of the analyzed geophagic clays

Sample Code	PH	Electrical Conductivity (S/cm)	Dissolved Oxygen (mg/L)	TDS (mg/L)	Salinity (ppt)
ENG-1K	4.69	21.90	7.55	11.50	0.10
KUT-1K	3.92	19.64	8.63	10.80	0.10
KUT-1L	4.43	27.40	11.10	14.50	0.10
KUT-1M	5.52	24.60	7.46	12.70	0.10
KUT-1N	4.51	132.00	10.81	69.20	0.30
SHA-1I-1	3.18	460.00	9.65	231.00	0.10
SHA-1J	3.47	21.60	10.50	11.70	0.10
TSG-1J	3.36	10.06	9.38	5.36	0.10
Minimum	3.18	10.06	7.46	5.36	0.10
Maximum	5.52	460.00	11.10	231.00	0.30

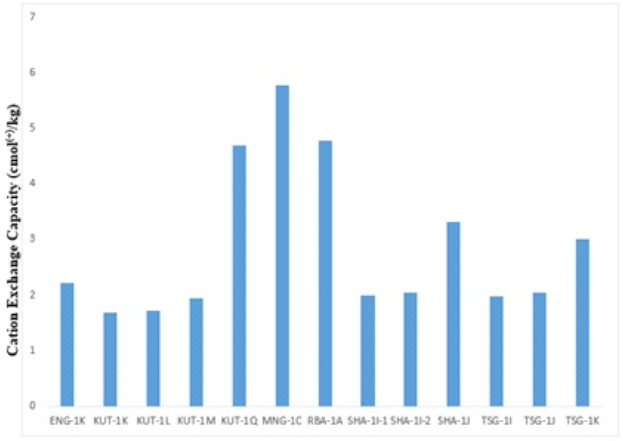


Figure 6: Cation Exchange Capacity (cmol$^{(+)}$/kg) of the studied geophagic clay samples.

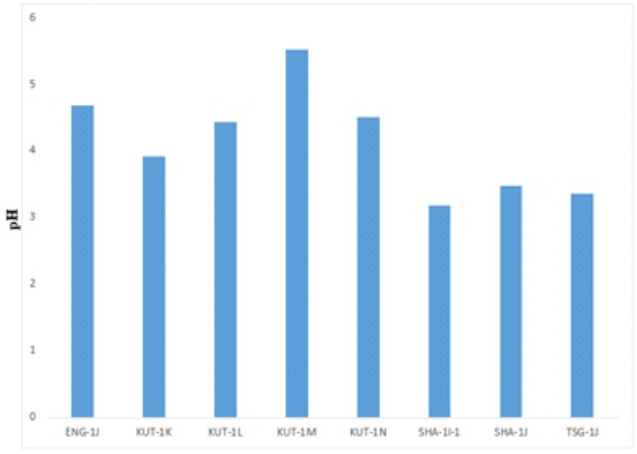


Figure 7: pH of studied geophagic claysamples.

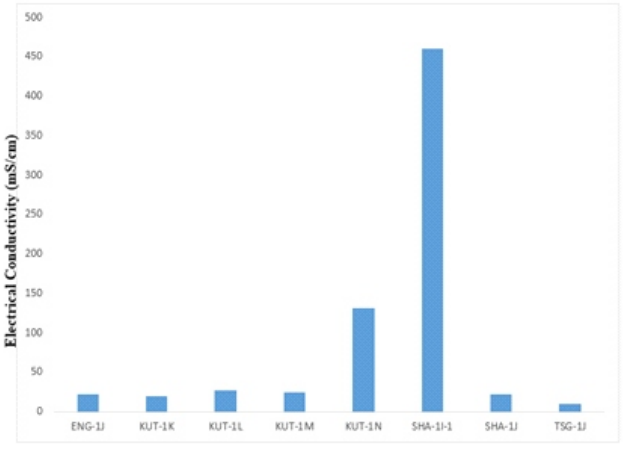


Figure 8: Electrical conductivity of studied geophagic clay samples.

Total Dissolved Salts (TDS) and Dissolved Oxygen (DO)

The TDS of the claystone samples ranges from **5.36 to 231.00mg/L.** World Health Organization and International Programme on Chemical Safety (ý1996) described the following TDS classes **for** palatability:excellent (< 300 mg/L), good (300 - 600 mg/L); fair (600 - 900 mg/L), poor (900 -1200 mg/L) and unacceptable (>1200 mg/L). The TDS values for the studied clay **classifies as excellent and therefore are a**cceptable for consumption.

The DO values in the studied clays range from **7.46 to 11.10 mg/L and the results** falls stradles the range of standard values of non-contaminated soil (0.5 - 8.0 **mg/L**) presribed by British Geological Survey and Department of Public Health Engineering (2001).

Mineralogical Characteristics by X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR) Spectroscopy

Thequalitative and quantitative mineralogical composition and functional group evaluation of four clay sampleswere done using XRD and FTIR analyses, respectively. Qualitative XRD result revealed quartz as the dominant mineral, kaolinite as the only clay mineral, with other non-clay minerals such as mica and anatase (Figure 9). The FTIR results presented in Figure 10 are based on the functional groups with spectrum of bands Si-O stretching, C-H stretching and Al-OH bending vibration. According to Madejovà (2006), FTIR spectrum of 4000400 cm^{-1} permits detailed examination of the OH stretching region, while the region below 1200 cm^{-1} (fingerprint region) characterizes SiO transmission and OH bending bands.

The results obtained from the FTIR spectrums revealed presence of quartz and kaolinite, corroborating the XRD results. The compositions of the minerals present in the investigated geophagic clay are: quartz (40-79 %), kaolinite (12 to 37 %), mica (9-10 %) and anatase (0-13 %) (Table 4; Figure 9). According to Osredkar (2011), higher quartz content in the clays and the presence of kaolinite could have resulted from the alteration of feldspathic sandstones.

Table 4: XRD result showing the percentage mineralogical composition for the geophagic clay samples (%)

Sample Code	Quartz	Kaolinite	Mica	Anatase
MNG -1C	40	37	10	13
SHG -1I-1	79	12	9	0
SHR -1I-2	73	13	9	5
SHR -1J	58	23	10	9

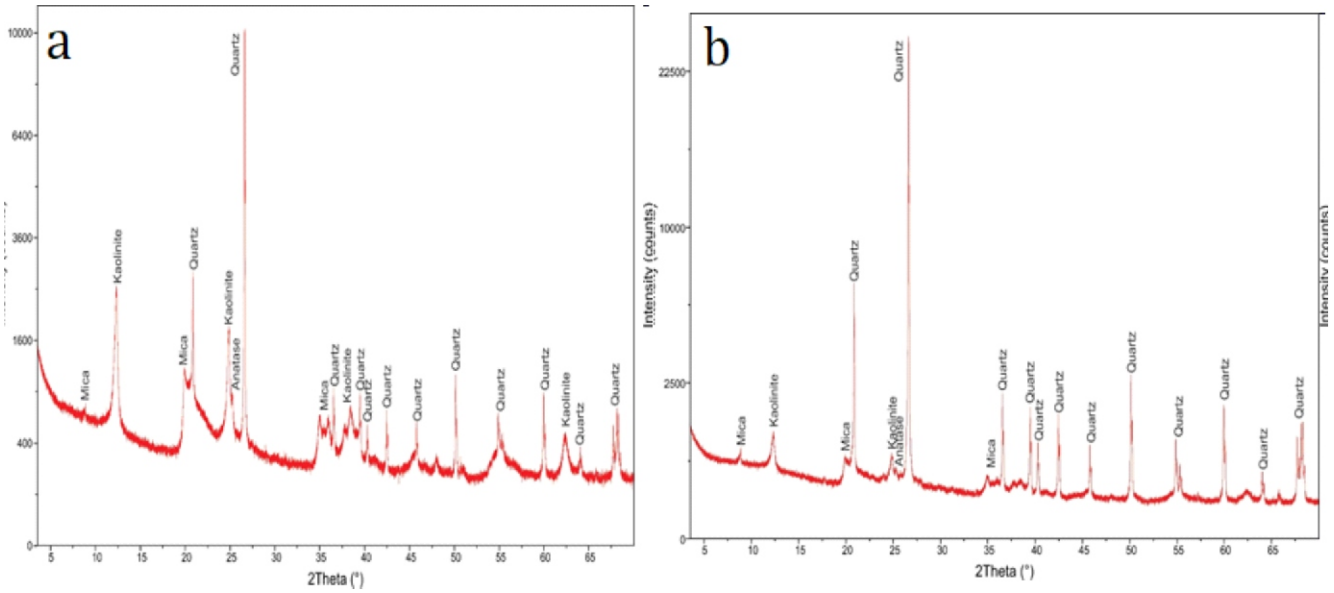


Figure 9: XRD diffractogram showing the mineralogical compositions for samples (a) MNG-1C and (b) SHA-1J.

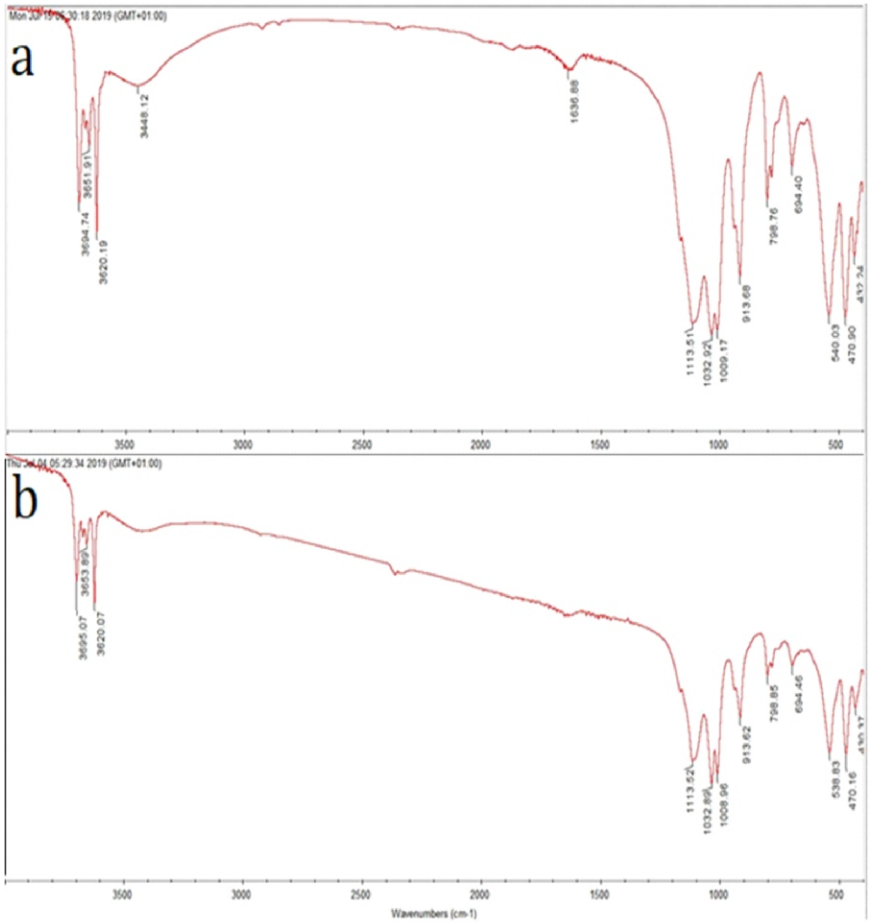


Figure 10: FTIR chart showing functional group present in samples (a) SHG-1I-2 and (b) SHR-1J.

Table 5: Comparison of the studied clays with others from some selected locations

Features		Locations					
		Northern Bida Basin, Nigeria (Present Study)	Geophagic Clays in Southern Nigeria (Olatunji et al., 2014)	Meka'a Clay, West Cameroon (Ninla et al., 2018)	Geophagic clayey soils from South Africa and Swaziland (Ngole et al., 2010)	Clay Soil from South Africa (Okereafor et al, 2016)	Geophagic Clay from Limpopo, South Africa (Mashao, 2018)
Particle Size Distribution (%)		Sand (0 4.0) Silt (0 67.0) Clay (33.0 100.0)	Not Reported	Sand (1.30 17.3) Silt (2.20 28.1) Clay (59.7 70.5)	Sand (0 55.0) Silt (18.0 58.0) Clay (25.0 70.0)	Not Reported	Sandy; Sandy loam; Clay; Sandy Clay; Silty loam.
Physico-Chemical Characteristics	pH	3.18 5.52	3.9 6.9	4.68 6.44	5.5 7.3	4.47 6.36	5.4 7.6
	EC (S/cm)	10.06 - 460.00	0.3 377.7	Not Determined	15.0 200.0	121.5 1028.5	112.0 245.0
Color		Dirty White; Whitish; Brownish; Grey.	Not Reported	Pink; White; Pale red; Pale yellow; Yellow	Brown; Light grey; Red; Yellowish brown Reddish brown; Dark red	Yellowish orange; Yellowish brown; Brownish grey	Reddish; Reddish yellow; Reddish brown; Brown; Brownish yellow; Red; Dark brown.
Mineralogy (%)	Kaolinite	12.0 37.0	23.6 60.0	64.71 85.37	Not Reported	39.24 96.96	4.0 90.0
	Quartz	40.0 79.0	14.4 75.7	Not Reported		8.30 57.0	4.0 45.0
	Anatase	0 13.0	Not Reported	2.25 8.82		Not Reported	Not Reported
	Geothite/Hematite	Not Determined	Not Reported	6.38 14.71		0.7 5.50	Not Reported
	Others	Minor	Minor	Minor		Minor	Minor

Health Implications

The textural analyses of the studied geophagic clays revealed that few samples (KUT-1K, KUT-1L, KUT-1Q, MNG-1C and SHA-1J) were dominantly clay (fine), while others (ENG-1K, SHA-1I-1, SHA-1I-2 and TSG-1K) and (KUT-1M, RAB-1A, TSG-1I and TSG-1J) are silty-clay and clayey-silt, respectively which indicate relatively higher gritty contents. According to Ngole and Ekosse (2012), geophagists always prefer soft, silky or powdery clays over gritty ones. Meanwhile, Lohn et al. (2000), Woywodt and Kiss (2002), Ngole-Jeme and Ekosse (2015) concluded

that problems linked with abdominal complications, such as intestinal perforations and rupturing, indigestible intestinal contents, intestinal obstruction and constipation with ulcer may be experienced when ingested coarse particles passes through and gets deposited in the colon. Therefore, consumption of samples with dominant fine contents may pose no threat to an individual's dental enamel and colon; whereas continual ingestion of samples with higher gritty contents (silty-clay and clayey-silt) would be unsuitable as they pose threats to the health of an individual especially during mastication and ingestion.

The acidic nature of the clays and their moderate electrical conductivity values suggests ability to relieve nausea andvomiting that are usually experienced by pregnant women. Okereafor et al. (2016) reported that moderate to high EC values in geophagic clays makes them suitable for absorbing diarrhea-causing enterotoxins and protect the gastrointestinal epithelium. Therefore, the moderate EC values in some of the studied clays make them suitable as protection for the gastrointestinal epithelium of the geophagists against diarrhea-causing enterotoxins.

The presence of appreciable amount of kaolinite in the geophagic clays suggests its useful in pharmaceutical formulations due to its ability to coat and adhere to the gastric and intestinal mucus membrane tocurb gastrointestinal ailments. According to Levison et al. (1982) and Carretero (2002), clays enriched with kaolinite are widely used as anti-diarrheals, because it has a high specific surface area and sorption capacity, and act by reducing the quantity of liquid that arrives in the colon from the bowel. Based on the presence of kaolinite in the studied clay, it can also be used traditionally for curbing gastritis, colitis and other gastrointestinal ailments. The clay might also be more preferable by dermatologists in the production of creams, powders and ointments especially after processing to remove the impurities present.

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Conclusion

This study assessed the physico-chemical characteristics and mineralogical composition of the geophagic clays from different locations within northern Bida Basin, and evaluated the possible health implications of their consumptions.

The clays areprimarily whitish, dirty-whitish,brownish and greyish in colour and are textually classified as clay, silty-clay and clayey-silt. Samples KUT-1K, KUT-1L, KUT-1Q, MNG-1C and SHA-1J with little or no gritty contents are safe for consumption while the other samples with more gritty contents are unsuitable for consumptions. However, such samples could be used as raw materials by the dermatologists especially after processing to remove the impurities.

Physico-chemical parameters of the clay samples indicate acidic to moderate nature which have tendency to impact a sour taste that will serve as a remedy for nausea and curb salivation associated with pregnancy. The kaolinite content in the clays make them usable in pharmaceutical formulations and as local antacids if properly beneficiated.

However, further geochemical studies to assess bioavailability of essential elements in the geophagic clays as well as the microbial constituents are recommended for more understanding on health implications. This will also help an individual geophagist identify suitable strategies to make the ingested clays safer since the age-long practices cannot be eradicated.

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Heavy Metal contamination and accumulation in Soils and Plants around a Granite Quarry Site in Ibadan, Southwestern Nigeria

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Abstract

This study investigated heavy metal contents in soils and plants around a granite quarrysite and assessed their contamination risk. Soil and plant samples collected at 0m, 25m, 50m, 100m, 200m and 400m from the quarry site, as well as those from acontrol location were analysed for heavy metals (Fe, Mn, Pb, Zn, Cu, Cr, Co, Ni and Cd) using Atomic Absorption Spectrophotometer (AAS). Heavy metal concentrations were assessed for pollution using Enrichment Factor (EF), ContaminationFactor (CF), Degree of Contamination (CD)and Pollution Load Index (PLI). Accumulation Factor (AF) and Translocation Factor (TF) were used to assess the potential of the plant samples for heavy metal accumulation. Heavy metals concentration (mg/kg) in soils from the downslope side of the quarry site were Fe: 61.98- 112.09;Mn: 70.29-120.22;Zn: 22.23-50.45;Cu: 16.11-45.09;Pb: 22.34-52.89; Co: 2.01-11.09; Cr: 4.89-12.11;Ni: 0.31-3.70 and Cd: 0.19-0.47. These values were higher than those obtained from control soil samples. The negative correlation coefficient (-0.80 to -0.14) indicated reduction in the values of these heavy metals in soil with distances from the quarry site. Heavy metals concentrations in the soil also showed deficiency to moderate enrichment, low to moderate contamination, and background levels of pollution for calculated PLI.The values of AF (0.51- 0.97)and TF (0.15- 1.25) for the plant samplesindicated their potentials for heavy metals accumulation.This study has shown the influence of the quarry on the soil and plant samples and their contamination risk on the study area.

Keywords: Quarry, Heavy metals, Contamination, Accumulation Factor.

Introduction

Soil plays a significant role in biogeochemical cycling and acts as a sink to different contaminants in the environment (Sheng et al., 2012; Tripathee et al., 2018). These contaminants present in the soil could be transferred to various environmental media such as plants, aquatic life and water resources, affecting theecosystem and human health (Xie et al. 2014;Akintola, 2019;Akintola et al., 2019a). Heavy metals, product of biological and geochemical processes, are naturally present in agricultural soils at low concentrations but can increase to high levels through anthropogenic activities such as industrial processes, mining, agriculture, waste disposal, and transportation (Uwah et al., 2011; Chen et al. 2012; Gao et al., 2012; Ogunkunle and Fatoba 2013). They are persistent and can bioaccumulate in plants and percolate into groundwater resources; impacting the environment and public health (Chen et al. 2012; Akintola, 2014). Previous studies have shown thatheavy metalsare major contaminants in food and agricultural products (Akintola, 2014).Observing these contaminants in the human food chain and devising ways to reduce their concentration levels in source emissions is anultimate concern for health policymakers (Gao et al., 2015; Karbasdehi et al., 2016). Generally, their metabolic roles in the human body are classified into two major groups: essential and non-essential (Esmaeilzadeh et al., 2019). The essential metals such as iron (Fe), copper (Cu), zinc (Zn), selenium (Se), manganese (Mn), nickel (Ni), cobalt (Co) and chromium (Cr) play an important role in metabolic activities. Non-essential metals such as arsenic (As), lead (Pb), cadmium (Cd) and mercury (Hg) can bioaccumulatein the tissues of microorganisms and the human body;becoming hazardous even at low concentrations (Akintola, 2014; Safari et al., 2018, Quadeer et al., 2020). Exposure to heavy metals hasresulted in various health problems such as Itai-Itai disease, cancers, gastrointestinal colitis, and brain function disorders(Yang et al., 2007;

Nogawa et al., 2017). Apart from these, it has been proven that heavy metals are also common causes of non-communicable diseases such as diabetes, cardiovascular disease, and high blood pressure (Agarwal et al., 2011; Lee et al., 2013). Soils and plants can be contaminated with heavy metals through various ways such as leaching, cultivation, irrigation, infiltration, use of pesticides, organic and chemical fertilizers, and proximity to industries (Gola et al., 2016; Akintola et al, 2019a; Habibollahi et al., 2019; Sharafi et al., 2019).Mining and mineral exploration have led to environmental degradation such as air pollution, destruction of natural flora, ecological disturbance, land degradation, water and soil pollution, among others (Bada et al.,2013). A quarry is an open-pit mine from which rocks or rock minerals are extracted through processes such as removal of topsoil, drilling, blasting with explosives, and using machinery to crush and grade rock materials. The aforementioned processes release particulate matter and dust containing metallic constituents into the environment (Bada and Fagbayibgo, 2009; Ayodele et al., 2014). This study investigated the heavy metal concentrations in soils and plants around a granite quarry site and assessed the contamination risk posed by the metals.

Study Area description

RatconQuarry site is located within OluyoleArea, south of Ibadan in Southwestern Nigeria (Figure1).Ithas a humid and tropical climate with a mean annual rainfall of approximately 1270mm and a mean maximum temperature of 32ºC. The area is well drained by rivers and streams which have adendritic pattern, andfalls within the Basement Complex terrain consisting of crystalline igneous and metamorphic rocks. It is characterized by banded gneiss with few occurrences of granite and quartzite (Akintola and Bodede, 2019).

Methods

Sample collection and analyses

Soil and plant samples were collected at 0m, 25m, 50m, 100m, 200m and 400m away from the downslope side of the quarry site. The control samples (soil and plant) were also collected at 500m upslope side of the quarry. Based on the availability of the plants in the area, *Chromolaenaodorata* (Siam weeds) and *Talinumtriangulare* (Water leaf) were selected for this study. Two (2) soil and plant samples were collected at each of the sampling points. A total of fourteen (14) soil samples and twenty-eight (28) plant samples (14 samples each for *Chromolaenaodorata and Talinumtriangulare*) were collected for further investigation. Soil samples were air-dried, disaggregated, and sieved through 1 mm mesh to remove debris and roots before analysis. Plant samples (shoots and roots) were also air-dried and ground prior to heavy metal analysis. Soil and plant (shoots: stem and leaves; and roots) samples were analysed for Fe, Mn, Pb, Zn, Cu, Cr, Co, Ni and Cd at Forestry Research Institute of Nigeria, Ibadan using Atomic Absorption Spectrophotometer (AAS). 2g of soil samples were digested with 10ml of 0.30 HCl and 3.50ml of 0.65 HNO_3 at 150°C for 90 minutes before heating at 230°C for another 30 minutes. The digestion tubes were removed and allowed to cool before washing the contents into 50ml volumetric flasks. The digestion of 0.5g plant samples was also done with 5ml of the acid mixture using the same procedure. The analyses were done in triplicate, and the appropriate quality procedures and precautions were taken in order to obtain reliable results.

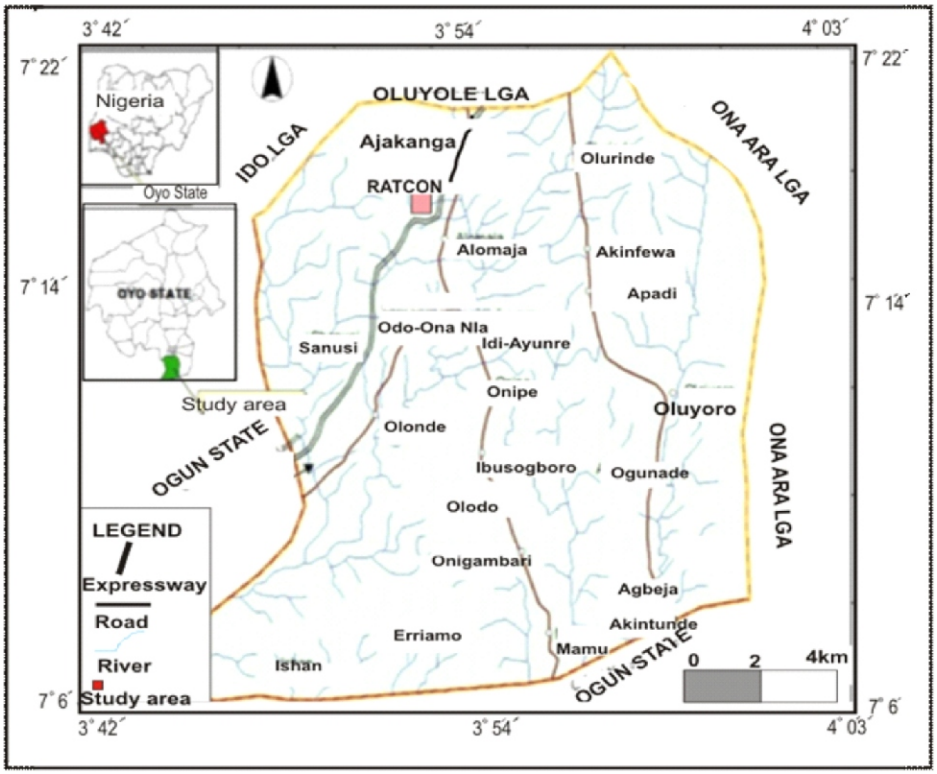


Figure 1: Location map of the study area

Descriptive statistics and correlation coefficients (r) were done using the Statistical Package for the Social Sciences (SPSS) software 20.0. The pollution status of the soils was determined using enrichment factor (EF), contamination factor (CF),contamination degree (CD) and pollution load index (PLI) as expressed in Equations 1-4.

Contamination factor (CF) and contamination degree(CD) as proposed by Hakanson (1980) are used to assess soil contamination through comparison of the concentrations in the surface layer to background values. It is expressed in equation 1 and 2:

$$CF = \frac{Cn}{Cb} \qquad Equation\ 1$$

CF is the Contamination factor (CF), *Cn is* the mean of the concentrations of individual heavy metals from at least five sampling locations, *Cb is* the baseline or background concentration of the individual heavy metal. The world average elemental concentrations in mg/kg for Fe (47,200), Cu (45), Zn (95), Pb(20), Mn(850), Ni(68), Cd(0.30), Cr(90) and Co (19) given by Barbalace (1995) were used as background values.

$$Cd = \sum Cf \qquad Equation\ 2$$

Contamination factor (C*F*) is classified into: CF<1- Low contamination; 1<CF<3- Moderate contamination; 3<CF<6- Considerable contamination and 6<CF- Very high contamination while CD is classified as CD<6- Low degree of contamination; 6<CD<12- Moderate degree of contamination; 12<CD<24- Considerable degree of contamination and CD≥24- Very high degree of contamination.

Enrichment Factor (EF): is an index used in evaluating the degree of metal enrichment of an area (Hakanson, 1980).It is calculated as:

$$EF = \frac{Cns/Cis}{\left(\frac{Cnb}{Cib}\right)} \qquad Equation\ 3$$

Cns is the concentration of heavy metals in the samples; Cis is the concentration of immobile elements in the samples, while *Cnb*is the concentration of heavy metals in the background environment, and*Cib* is the concentration of immobile elements in the background environment. The immobile element is often taken to be Al, Li, Sc, Zr, Ti, Fe, Mn (Hakanson, 1980; Blaser et *al.,* 2000; Sutherland, 2000; Chatterjee et al., 2007). The immobile element that was used in this study is Fe(also one of the immobile and abundant elements in plants). The classification of enrichment factor according to Sutherland (2000) is given as EF<2-

Depletion to minimal; 2<EF<5- Moderate; 5<EF<20- Significant; 20<EF<40- Very high and EF>40- Extremely high.

Pollution Load Index (PLI): is used to assess the total degree of contamination in soil: proving the deterioration of the soil conditions based on the accumulation of heavy metals (Varol, 2011). Itis expressed using the relation:

$$PLI = \sqrt[n]{CF_1 \ X \ Cf_2 \ X \ Cf_3 \ X - - - - - CFn} \quad Equation\ 4$$

where n - the number of analysed heavy metals and CF - calculated values for the Contamination Factor. PLI classes are given as PLI< 1- denotes no pollution, PLI=1- baseline levels of pollution and PLI>1 deterioration of soil quality.

AccumulationFactor (AF) and Translocation Factor (TF) were used to assess the ability of the plants to uptake the available heavy metals in the soil and the potential of the plants to transfer them into their different parts.

The Accumulation Factor (AF), according to Baker (1981), is calculated using the relation in Equation 5. AF with values greater than 1 are classified as accumulators while plants with AF values less than 1 are excluders.

$$AF = \frac{\text{heavy metal concentration in studied plants (mg/kg)}}{\text{heavy metal concentration in soil (mg/kg)}} \quad Equation\ 5$$

Translocation Factor (TF) is calculated using the formula:

$$TF = \frac{\text{heavy metal concentration in shoot of the studied plants (mg/kg)}}{\text{heavy metal concentration in root of the studied plants (mg/kg)}} \quad Equation\ 6$$

The values of TF greater than one are classified as high potential for plants in transferring heavy metals from roots to their shoots (Malik et al. 2010).

Results and Discussion

Heavy metals concentrations in soils

Heavy metals concentration (mg/kg) in soils from sampling points at the downslope side of the quarry site were Fe: 61.98- 112.09, Mn: 70.29-120.22, Zn: 22.23-50.45, Cu: 16.11-45.09, Pb: 22.34-52.89, Co: 2.01-11.09, Cr: 4.89-12.11, Ni: 0.31-3.70 and Cd: 0.19-0.47(Table 1). These values were higher than those obtained from control soil samples: Fe: 67.22, Mn: 41.10, Zn: 15.10, Cu: 13.01, Pb: 18.22, Co: 3.06, Cr: 4.10, Ni: 1.20 and Cd: 0.13. This indicated the influence of the quarry site on the soils within the vicinity studied. The concentrations of the heavy metals in the studied soils were lower than the recommended values given by Food and Agriculture Organisation (FAO)/World Health Organisation (WHO) (2011) and Veceraet al. (1999) as shown in Table 1.Heavy metals concentration in soils were in the order: Fe> Mn> Zn> Cu> Pb> Cr> Co> Ni> Cd. Regression equation and correlation coefficient (r) values of heavy metals concentrations in soil samples with distances from the quarry siteis presented in Table 2.The regression equation and the negative correlation coefficient (-0.80 to-0.14) indicated reductions in the heavy metals concentration in the soils with distances away from the quarry site, and also the contamination effect of the quarry site on the soils sampled.

Table 1: Mean values of heavy metals in soils from the sampling points

Heavy metals in mg/kg	Distances from downslope side of the quarry site (n=2)						Mean	Upslope control	Recommended Levels (FAO/WHO, 2011*; Vecera et al.,1999)
	0m	25m	50m	100m	200m	400m			
Fe	112.09	99.61	87.09	76.38	69.11	61.98	84.37	67.22	100-700*
Zn	50.45	37.25	31.01	28.22	27.11	22.23	32.71	15.10	300
Cu	45.09	32.09	27.21	23.93	18.89	16.11	27.22	13.01	100
Pb	52.89	40.11	34.26	28.99	26.81	22.34	34.23	18.22	100
Mn	120.22	84.68	78.76	74.11	73.87	70.29	83.65	41.10	500
Co	11.09	6.11	3.21	2.11	1.41	2.09	3.34	3.06	50
Ni	3.70	2.58	1.51	0.84	0.52	0.31	1.57	1.20	50
Cr	12.11	5.09	1.59	2.01	1.87	4.69	4.56	4.10	100
Cd	0.47	0.20	0.32	0.19	0.21	0.41	0.3	0.13	3

Table 2. Regression equation and Correlation coefficient (r) values of heavy metals concentrations in soil samples and distances from the quarry site

Heavy metals	Regression Equation y= heavy metal concentrations and x= distances from the quarry site	Correlation Coefficient (r)
Fe	y = -0.103x + 95.6	-0.79
Zn	y = -0.050x + 39.26	-0.76
Cu	y = -0.055x + 34.44	-0.80
Pb	y = -0.059x + 42.05	-0.81
Mn	y = -0.082x + 95.94	-0.67
Co	y = -0.010x + 4.643	-0.42
Ni	y = -0.004x + 1.548	-0.39
Cr	y = -0.007x + 5.561	-0.30
Cd	y = 0.000x + 0.284	-0.14

Contamination assessment of the heavy metals in soils

Contamination factor and degree, enrichment factor and pollution load index were used to assess the contamination status of the heavy metals in soils from the studied area. The mean CF descended in the order: Zn>Cu>Mn>Pb>Fe>Cr>Co>Ni>Cd (Table 3). Based on the classification of contamination level given by Hakanson (1980),the CFs of Cr, Co, Ni and Cd indicate low contamination while those of Zn, Cu, Mn, Pb and Fe show moderate contamination. The CD alsoshows moderate degree of contamination in soils of the study area. EF values of heavy metals in soils show depletion to minimal enrichmentof Zn, Cu, Mn, Cr, Co, Ni and Cd while the soil samplesare moderately enriched with Pb. The PLI value for all the studied heavy metals in the soil is 0.92 (Table 3). Thisindicates background levels of pollution (Varol, 2011).

Heavy metals in plants

The mean total values of heavy metal concentrations in *Talinumtriangulare* (water leaf) and *Chromolaenaodorata (siam weeds) shoot and root* samples are presented in Tables 4a and 4b. It was observed that Fe has the highest concentration in both plant samples. Also, higher concentrations of the studied heavy metals were recorded in *Talinumtriangulare compared to Chromolaenaodorata. This result agreed with the findings of Akintola (2014) and* Moreno-Garido*et al. (2005), that Talinumtriangulare has more potential to accumulate heavy metals than Chromolaenaodorata.*

Heavy metal concentrations in the plant samples from the downslope side mostly decreased with distances from the quarry site (Table 4a and 4b). Also, their values were higher than those from the control sampling points except at 200m and 400m. The recorded values of heavy metals in the studied plants were lower than the recommended standard values for plants given by FAO/WHO (2011). Generally, heavy metal concentrations in the studied plants showed the order of Fe>Zn>Cu>Pb>Ni>Cd. Higher concentration levels of Fe, Zn Cu, Pb and Ni in plants could be attributed to the importance of these metals in the proper functioning of the biological system and plant growth(Harrison and Chirgawi, 1989; Akintola, 2014). Low concentration levels of Cd could be attributed to the metal being non-essential for plant growth and metabolism (Shuaibu and Ayodele, 2002).

The AF and TF values for *Chromolaenaodorata* and *Talinumtriangulare* ranged from 0.11-0.98 and 0.16-1.25, respectively (Table 5). The AF of metals in the plant signifies the amount of heavy metal in the soil that ended up in plants. *Talinumtriangulare* showed higher accumulation factors of the heavy metals than *Chromolaenaodorata* except Cd. One of the vital indices used in assessing the potential of plants for phytoremediation is the translocation factor(TF); which is the ratio of concentrations of metals in shoots to metal concentrations in roots (Mohammed et al, 2014; Liu et al., 2015; Akintola et al, 2019b). High values of AF and TF of Fe in *Chromolaenaodorata* and *Talinumtriangulare* showed their potential for Fe accumulation.

Table 3: Mean values of CF, EF,CD and PLI

Heavy metals	CF	EF	CD	PLI
Fe	1.22	-	11.36	0.92
Zn	2.10	1.72		
Cu	2.08	1.73		
Pb	1.88	2.05		
Mn	1.98	1.63		
Co	0.61	0.67		
Ni	0.45	0.13		
Cr	0.82	0.85		
Cd	0.22	0.16		

Table 4a:Mean totalvalues of heavy metals in *Talinumtriangulare* (shoot and root) from the sampling points

Heavy metals	Distances from downslope side of the quarry site						Upslope control	Recommended Levels (FAO/WHO, 2011; **Vecera et al.,1999)
	0m	25m	50m	100m	200m	400m		
Fe	70.22	52.91	48.06	38.78	36.01	30.22	35.22	425
Zn	21.71	19.01	17.09	16.66	12.08	10.22	11.79	99.40
Cu	11.63	10.66	7.03	6.21	4.98	4.11	5.03	73.30
Pb	6.60	4.49	3.84	3.29	3.08	2.78	3.11	18**
Ni	1.48	1.03	0.89	0.85	0.82	0.81	0.99	10
Cd	0.10	0.08	0.06	0.04	0.04	0.04	0.09	0.2

Table 4b: Mean total values of heavy metals in Chromolaeea*odorata (shoot and root)* from the sampling points

Heavy metals in mg/kg	Distances from downslope side of the quarry site						Upslope control	Recommended Levels (FAO/WHO, 2011; **Vecera et al.,1999)
	0m	25m	50m	100m	200m	400m		
Fe	65.78	45.98	43.63	34.31	31.57	26.01	30.98	425
Zn	15.30	13.42	12.29	11.87	9.98	9.68	10.01	99.40
Cu	9.99	7.81	7.09	6.62	5.89	5.85	6.06	73.30
Pb	4.87	4.24	3.89	3.73	3.41	3.08	3.51	18**
Ni	1.01	0.87	0.86	0.85	0.82	0.81	0.84	10
Cd	0.04	0.03	0.02	0.01	0.01	0.01	0.02	0.2

Table 5: Accumulation and Translocation Factors (AF and TF)

Heavy metals	*Talinumtriangulare (water leaf)*		*Chromolaneaodorata* (Siam weeds)	
	AF	**TF**	**AF**	**TF**
Fe	0.55	1.25	0.51	1.20
Zn	0.55	0.88	0.39	0.91
Cu	0.31	0.61	0.27	0.52
Pb	0.19	0.31	0.11	0.28
Cd	0.33	0.21	0.67	0.18
Ni	0.97	0.16	0.88	0.15

Conclusion

This study examined the concentrations and contamination of heavy metals in soils and plants around a quarry site. Heavy metals concentration in soils showed the order of Fe>Mn>Zn>Cu>Pb>Cr>Co>Ni>Cd and these were higher when compared with those from the control samples. A reduction in the heavy metal concentrations from both soil and plant samples with distances at the downslope side of the quarry site indicated negative influence of the quarry on the study area. Heavy metals showed deficiency to moderate enrichment, low to moderate contamination and background levels for calculated PLI. High values of accumulation and translocation factors of Fein *Chromolaenaodorata* and *Talinumtriangulare* showed their potential for Fe accumulation. This study has shown that quarrying activity causes increase in the concentration and contamination of heavy metals in soils and plants. Thus, cleaning up technologies for reducing harmful effects of heavy metals in contaminated sites such as excavation, stabilization of metals in the soil and the use of tree plantings to reduce the spread of the heavy metals in the environment should be adopted.

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Geochemistry and Risk Assessment of Stream Sediments from Active and Abandoned Quarry sites in Oban Massif and Calabar Flank, Southeastern Nigeria

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Abstract

This study examined the impact of quarrying activities on the quality of sediments around active and abandoned sites in Oban massif and Calabar flank, Nigeria.Twelve representative composite samples were collected from the streams of AyipOjong-Ita, Etap-Ayip, Ikpaya, Iwiri and Monayip-Netim which flow through the selected quarry sites. Three samples used as control were collected from a nearby reserve forest (National Park) about 5km away from the quarries.Physical parameters of the sediments were analysed and their elemental composition was determined by Inductively Coupled Plasma Mass Spectrophotometry. Results for the physical properties showed that the sediments were generally sandy (≥80%), slightly acidic (pH 5.7-6.4),with low organic matter (<16%).Trace element concentrations(mg/kg)were: Oban massif active site; Cu (19.2±7.81), Pb (35.7±11.90), Zn (91.5±30.90), As (0.51±0.35), Cd (0.16±0.10), Cr (26.7±8.17), Mn (261±71.60), and Fe (0.12±.46). Oban massif abandoned sites;Cu (18.1±7.56), Pb (32.9±12.40), Zn (86.2±32.30), As (0.44±0.31), Cd (0.15±0.09), Cr (33.7±33.90), Mn (290±134.00) and Fe (2.21±.0.83). Calabar flankquarry had Cu (10.5±5.18), Pb (26.1±2.50), Zn (43.0±15.30), As (3.67±2.00), Cd (0.10±0.05), Cr (30.7±17.90), Mn (509±101.10) and Fe (2.18±.1.04).Cd and Sr recorded the highest Enrichment Factor (EF) (1.17- 9.13 and1.96-5.31) inactive and abandoned sites of Oban massif;and 2.44-3.92 in Calabar flank.Results for Geo-accumulation index showed that the sediments are polluted by As(Igeo 8.56-17.3)and Sr (Igeo 1.22-3.60) in the Calabar flank. Long term contamination of sediments may pose hazard to fish, crops and ultimately, human health.

Keywords: Quarry, Sediment quality, Enrichment Factor, Geo-accumulation index, Oban Massif, Calabar Flank

Introduction

The contamination of the environmentas a result of quarrying activities has recently become an issue of concern due to the potential environmental/health implications associated with it. In the study area, over thirty quarry operators are involved in extensive quarrying of rock types such as granite, schists, gneiss, granodiorite, limestone, and shale. These rocks are quarried with neither pre-development planning against environmental pollution nor proper management of the pits/waste materials. The waste materials in the area are left to litter the environment in piles/heaps and during rains, these materials are washed into the drainage system. The result of this, is a possible increase in the heavy metal content in stream sediments around the area. Abua and Eyo (2013) stated that quarrying impacts negatively on agriculture because of the complex catena of interactions that occur as waste become part of the ecosystem into which it is deposited. Oxidation of metal sulphides from quarry waste induces soil acidification; impeding natural growth of vegetation and causing soil erosion. When the contaminated soil finds its way into the aquatic environment, degradation occurs (Li, Wai, Coles, Ramsey and Thornton, 2000).

Stream sediments survey was used in the past to prospect for ore bodies that could be of economic value but more recently, the primary interest has shifted to assessing whether heavy metals have concentrated to dangerous levels. They are very germane in environmental studies as they are products of weathered rocks and soil materials upstream from sampling points (Olubunmi *and* Olorunsola, 2010). According to Siegel (2002), they are used as important tool to assess the health status of aquatic ecosystem and are to a large extent, major component for the

functioning of ecological integrity. Heavy metal content of sediment therefore reflects more or less that of the host rocks and soil in the catchment area (Idris, 2008; Mohiuddin, Zakir, Otomo, Sharimin and Shikazono,2010). The general representative nature of sediments makes them useful sampling medium for the detection of trace element anomalies related to mineralization and for environmental studies related to pollution (Chakrapani, 2002).

The intensity of quarrying activities in the study area yields high volume of quarry waste, which are most likely leached into nearby streams. The quarry waste is rich in heavy metals; which are contaminants that persistent in the environment for a very long time (Vincent, Joseph and Raphael, 2012). Heavy metals in the quarry waste will also most likely be found in agricultural soils and food crops.The streams in the area are the cheapest source of drinking water to the local population and some quarry staff. Therefore, heavy metals contamination in the streams poses significant potential health risks to humans and animals in the vicinity of the quarries.

Studies by Lim, Lee, Chon and Sager (2008) reported carcinogenic risk of cancer due to As exposure from intake of soil, plant and water from the abandoned Songcheon Au-Ag mine in Korea. Risk assessment studies by the World Health Organization (WHO) in communities of Mitrovica exposed to Pb from mining indicated Pb level in children's blood to be dangerously high with soil contamination as source of exposure (Prathumratana, Kim and Kim, 2008). Due to the toxic effect of heavy metals associated with quarrying activities on the environment, there is a need to do a novel assessment of the level of metal contamination in sediments of the study area and also quantify the extent of pollution using sediment quality indices. Few previous studies conducted on quarrying activities in the area were limited to the environmental impact of aggregate mining on soil and the assessment of soils around the quarry terrain (Ukpong, 2012; Abua and Eyo, 2013).

Study Area description

The study area lies between latitudes 05° 06' - 05° 23' and longitudes 08° 15' - 08° 30'. It covers parts of the Basement Complex (the Oban Massif) and sedimentary terrains (Calabar Flank) in southeastern Nigeria (**Figure 1**). It is situated within the subequatorial climatic region of Nigeria with total annual rainfall varying between 180 and 200cm, with annual temperature in the range of 25°C and 30°C (Iloeje, 2001). The topography of the area is generally rugged and undulating, with alternating plains and hills. The area is drained mainly by the Cross River, its tributaries (Ayipojong-Ita and Etap-Ayip) as well as some perennial streams (Ikpaya, Iwiri and Monayip-Netim). The dendritic and linear drainage patterns are suggestiveof structural control (Abua and Eyo, 2013).

The Oban Massif forms part of the giant spurs of the western elongation of the Cameroon Mountain into the Cross-River plains of Southern Nigeria (Ekwueme, 2003). It is bordered to the south by the Cretaceous sedimentary fill known as the Calabar Flank, and to the north by the theMamfe Embayment. To the southeast, it is flanked by the Cameroon Volcanic Line and on the northwest by the Benue Trough**.** Rocks of the Oban Massif are mainly phyllites, schists, gneisses and amphibolites. These rocks are intruded by pegmatites, granites, granodiorites, tonalites and charnockites which occur as enclaves in gneisses (Rahman, Ukpong and Azumutullah 1981; Ekwueme, 1993; Adamu,Nganje and Edet, 2014). The Calabar Flank, which is a part of the Benue Trough, consists of the Albian to lower Cenomanian Asu River Group made up of continental arkosic sandstones of the Awi Formation and Mamfe Formation (Reyment, 1965; Adeleye and Fayose 1978). According to Petters and Ekweozor (1982), the Awi Formation is overlain by shallow marine Mfamosing limestone formation. This is overlain by the Middle Cenomanian to Early Santonian Odukpani, EzeAku and Awgu Shale Formations, linking regressive sandstones such as the Amaseri, Agbani, Agala and Makurdi Formations (Offodile, 1976). Petters and Ekweozor (1982) grouped the sediments of this age into the Cross-River Group and designated the Odukpani, Eze-Aku and Awgu Shale Formations as Nkalagu Formation.

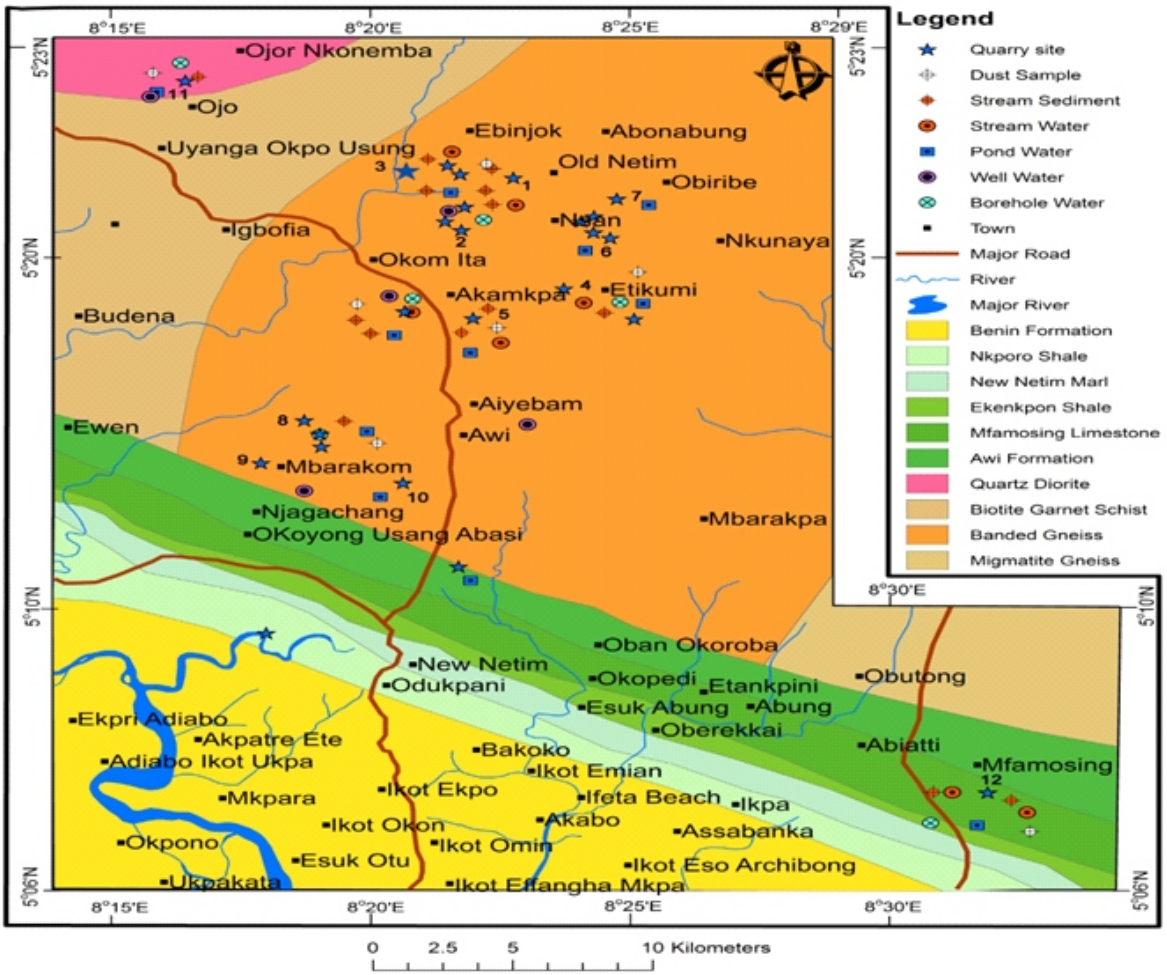


Figure 1: Geological map of the study area showing sampling locations (Modified from Nigeria Geological Survey Agency; NGSA, 2004)

Methods

Sampling collection and analyses

Twelve (12) quarry sites were considered for this study based on the underlying geology and mining status (active and abandoned). Eleven of the quarries were underlain by the Basement Complex while one was underlain by the Calabar Flank. The quarries were further divided into active and abandoned (Figure 2, Table 1).A total of fifteen composite sediment samples were obtained in all (Active quarry = 9, abandoned quarry = 3, Control sites = 3). Out of these, seven samples were collected from the active quarry sites in Oban Massif, three samples from abandoned quarry sites in Oban Massif and two samples were collected from the active quarry site in Calabar Flank. Another set of three samples (one sample from each of the sites) were taken from streams about 5km away from the quarry sites (reserved area) which were used as control samples.

The samples were dried, disaggregated using an agate mortar and sieved using a 63µm sieve. The pH of the samples was measured from a slurry formed by mixing 0.5g of sample with 10ml distilled water. After mixing for 5 seconds, the slurry was left to stand for 5 minutes before the pH was measured using a Calomel Glass Electrode pH meter. The pH in each case was taken to 0.01 units after the reading was stabilized for 10 minutes (Bates, 1954). Organic Matter content (OM) for the sediments was estimated from Loss-On-Ignition (LOI). Empty porcelain crucibles were heated at 550°C for about 30 minutes and then cooled in desiccators at ambient temperature for 2 hours and later weighed. 5mg of sediment sample was put into a crucible and ignited in a muffler furnace at 550°C for 4 hours. The samples were then removed into desiccators

and allowed to cool down for 2 hours at ambient temperature. The difference in mass or loss-on-ignition, which is an estimation of organic matter content, was then expressed as percentage of dry sediment weight as shown in the expression below (European Union Standard, 2003):

$$LOI = \text{OM}\ (\%) = \frac{\textit{Oven dried sediment} - \text{ignited sediment}}{\text{Mass of sediment sample used}} \quad 1$$

Particle Size Analysis of sediments was carried out using Bouycous (hydrometer) method (Abua and Eyo, 2013). About 50g of sediment was placed in a baffled cup. Half of the cup was filled with distilled water and 50ml of sodium hexametaphosphate reagent, and was allowed to stand overnight. The cup was placed on a stirrer until all the sediment aggregates were broken down. The suspension was then transferred to a 100ml cylinder filled with distilled water to the lower mark while the Bouycous hydrometer was in suspension. The percentage of sand was determined by removing the hydrometer and the cylinder. The content was thoroughly mixed by inverting the cylinder several times and then set down on a desk. The hydrometer was inserted and read at the end of 40 seconds which represented the time sand settled to the bottom of the cylinder and also gave the amount of silt and clay in suspension. The following equations were used to calculate weight of sand, percentage sand, percentage clay and percentage silt (European Union Standard, 2003):

Weight of sand = Total weight of sample Corrected hydrometer reading 2

$$\%\ Sand = \frac{\textit{Weight of Sand } x\ 100}{\text{Weight of sample}} \quad 3$$

% Clay = Re-shaking suspension and taking reading after 2hours 4

$$\%\ \text{Silt} = 100\ (\%\ \text{sand} + \%\ \text{Clay}). \quad 5$$

For elemental content, 0.5g of the sample was digested using 2ml HNO_3, 1ml $HClO_4$ and 5ml HF according to Li *et al*., 2000. The samples were heated on an electrothermal plate at a temperature of 90^0C - 190^0C for 16 hours. After cooling, the residues were then filtered into polythene volumetric tubes and diluted to 25ml with deionized water for further detection of metals. The samples were analysed using Inductively Coupled Plasma Mass Spectroscopyusing an ICP198MS model Perkin Elmer Elan 6000/9000 in Acme Laboratories Limited, Vancouver, Canada. The accuracy of the analytical procedures was checked with CRM30 (Sediment reference material) and replicate analysis of the CRM 320 showed good accuracy with recovery rates for metals between 96% and 105%. The precision of the analytical processes was determined by analysing three samples in duplicates. A batch of samples included one procedural blank, two sample duplicates, and one in-house reference material (CRM 320); verified against stand reference materials (SRMS) such as SLRS-4 (National Research Council. Ottawa, Canada).

The results of the analysis were subjected to Pearson's Correlation in order to evaluate the elemental relationship and estimate the degree of interrelationship (Davis, 1986).



Figure 2: (a) Active and (b) Abandoned quarry sites in the study area

Table 1: Location and physical setting of the quarry sites

S/N	Quarry	Lithology	Lat.	Long.	Elev. (m)	Estab.	Formation	Lithology	Age	Status
1	Crushed rock	OM[1]	05^0 21.83	08 21.62	126	1976	Basement	Gneiss, Pegmatite Schist	Precambrian	Act.[2]
2	Gitto	OM	05^0 22.30	08^0 21.94	118	2005	Basement	Gneiss, Schist, Granodiorite	Precambrian	Act.
3	Cewopi	OM	05^0 23.06	08^0 21.04	101	2014	Basement	Gneiss, Schist, pegmatite	Precambrian	Act.
4	Crush pave	OM	05^0 18.28	08^0 20.80	101	2009	Basement	Schist, Gneiss, Granite	Precambrian	Act.
5	RCC	OM	05^0 18.33	08^0 20.48	117	2007	Basement	Schist, Gneiss, Granite,	Precambrian	Act.
6	Expanded	OM	05^0 18.23	08^0 22.03	97	2009	Basement	Schist, Granite, Quartzite	Precambrian	Act.
7	S and V	OM	05^0 18.75	08^0 24.98	115	2008	Basement	Schist, Granodiorite, Gneiss	Precambrian	Act.
8	Japaul	OM	05^0 14.84	08^0 19.52	114	2011	Basement	Granite, Gneiss, Pegmatite	Precambrian	Act.
9	Encrco	OM	05^0 15.35	08^0 18.81	115	2008	Basement	Gneiss, Schist, pegmatite	Precambrian	Abd.[3]
10	Cottab	OM	05^0 15.16	08^0 20.41	130	2012	Basement	Granodiorite, pegmatite	Precambrian	Abd.
11	Sermatech	OM	05^0 21.15	08^0 16.53	111	2012	Basement	Granodiorite Metadolerite,	Precambrian	Abd.
12	Unicem	CF[4]	05^0 94.64	08^0 31.95	35	2002	Sedimentary (Mfamosing Limestone)	Marl, Limestone, Shale	Albian	Act.

[1]OM = Oban Massif; [2] Act. = Active; [3]Abd. = Abandoned; [4]CF = Calabar flank

Enrichment factor (EF) was used in evaluating the contamination in the sediments by comparing the concentration of specific elements in the crust or background values (Adamu,*Nganje and Edet,* 2015). Enrichment factor takes into consideration geological variation of elemental abundances of rock types and mineralization, and practices of human induced changes. It is usually calculated with respect to Al, Fe, Ti, or Zr because these elements are relatively immobile and natural sources vastly dominate their inputs (Kabata-Pendias *and Mukherjee*, 2007). The enrichment factor for this study was normalized with Fe. In this study, background values from the control area were used for the computation of enrichment values using the formula;

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Where EF = Enrichment factor and C*x* = Concentration of element *x*.

According to Birch and Olmos (2008), five main classes of enrichment exist as follows: EF < 1 = No enrichment, EF < 3 = Minor enrichment, EF 3 - 5 = Moderate enrichment, EF 5 - 10 = Moderate to severe enrichment, EF 10 - 25 = Severe enrichment and EF 25 - 50 = Extremely severe enrichment.

The geo-accumulation index (Igeo) has been used successfully in the quantification of metal accumulation which compares the present status with the pre-civilized background values (Muller, 1979). It is calculated using the expression:

7

Where Cn is the concentration of metal in sediment samples, Bn is the metal concentration in the background sample and 1.5 is a normalization factor for possible variations in the sediments. In the present study area, metal levels from the control site with similar lithology were used as background values for the computation. Interpretation of sediments quality was based on Muller's (1979) classification as follows: < 0 (unpolluted); 0- 1(unpolluted to moderately polluted); 1-2 (moderately polluted); 2-3 (moderately to highly polluted); 3-4 (highly polluted); 4-5 (very highly polluted) and >5 (extremely polluted).

Results and Discussion

Physical characteristics

Results of the physical parameters of the sediments (texture, pH, LOI) with descriptive statistics is as

shown in Table 2.The results of Particle Size Distribution (PSD) show the sandy nature of the stream sediments in all sites. The clay and silt fractions were generally low. The silt and clay fractions from the active quarry site in Calabar Flank were observed to be higher than those from the active and abandoned quarry sites in Oban Massif area (Table 2). The minor variations in PSD of samples from the quarry sites including samples from the control areas are indications of the different sources of the sediments (Adamu *et al.,* 2015). The result of LOI is highest in sediments from the active quarry site in Calabar Flank area and lowest in sediments from the active quarry sites in Oban Massif, while pH is highest in stream sediments from the active quarry sites in Oban Massif and lowest in sediments from the abandoned quarry sites area. These differences may be attributed to the different levels in the decomposition of plant parts in the sediments and the oxidation of quarry waste materials. Jung (2001) reported that dissolved carbon dioxide from the decay of organic matter and respiration of organisms in the stream sediments is another possible source of acidity of sediments.

Table 2: Summary of physical parameters in sediments of the study area

	Sample Id.	%Sand	%Silt	%Clay	%LOI	pH
Active sites OM	S_1	38.6	46.0	15.4	10.0	6.40
	S_3	90.6	8.00	1.40	5.00	6.20
	S_5	84.6	10.0	5.40	5.50	6.30
	S_7	82.6	12.0	5.40	6.00	6.40
	S_8	86.6	12.0	1.40	6.00	6.40
	S_9	58.6	34.0	7.40	10.0	6.00
	S_{10}	50.6	38.0	11.4	7.00	6.10
	Mean ±SD*	70.3 ±19.1	22.7 ±14.7	6.83 ±4.75	7.07 ±1.94	6.26 ±0.15
	Range	38.6-90.6	8.0-46.0	1.40-15.4	6.0-10.0	6.0-6.40
	Control	82.5	15.1	2.40	12.2	6.50
Abandoned Sites OM	S_2	84.6	14.0	1.40	5.00	6.30
	S_4	74.6	22.0	3.40	6.00	6.20
	S_6	86.6	12.0	1.40	12.5	6.20
	Mean ±SD	68.9 ±21.7	20.5 ±11.9	5.46 ±4.19	6.83 ±2.64	5.74 ±1.69
	Range	74.6-86.6	12.0-22.0	1.40-3.40	5.0-12.5	6.20-6.30
	Control	85.0	15.0	3.50	12.2	6.50
Active Site CF	S11	42.6	40.0	17.4	10.00	5.90
	S12	86.6	12.0	1.40	5.50	5.90
	Mean ±SD	64.6 ±20.2	26.0 ±12.4	9.4 ±5.10	7.8 ±2.10	5.90 ±0.06
	Range	42.6-86.6	12.0-40.0	1.40-17.4	5.50-10.0	5.90-5.90
	Control	76.0	12.8	3.50	14.6	6.00

*SD = Standard Deviation

Heavy Metal Concentration

The results of heavy metals (Mn, Sr, Zn, Cr, Pb, Cu, Ni, Co, As, Mo, Se, Cd, Sb, Ag) with their descriptive statistics is as presented in Table 3. The data are compared with those from the control sites and other standards (Turekian and Wedephol, 1961; MacDonald, Ingersoll and Berger, 2000) for quality assessment. The active quarry sites recorded higher concentrations of the metals compared to the abandoned sites and the control areas. The reduced anthropogenic activities around the abandoned and control sites translates to reduced amounts of metals in the streams at those areas. Sometimes however, the variations in metal concentrations may be influenced by changes in lithological inputs, hydrological effects and type of

vegetation cover (Jain et al., 2007). In the active quarry sites in the Oban Massive area, the abundance of heavy metals was in the order: Mn > Sr > Zn > Cr > Pb > Cu > Ni > Co > As = Mo > Se > Cd > Sb > Ag.In the abandoned quarry sites in the Oban Massif area, it was in the order: Mn > Sr > Zn > Cr > Pb > Cu > Ni > Co > Mo > As > Se > Cd > Sb > Ag. The metal abundance in the active quarry site in the Calabar flank area is in the order of Mn > Sr > Zn > Cr > Pb > Ni > Cu > Co > As > Mo > Se > Sb > Cd > Ag.Sr, Mn, Zn, Pb and Cu had the highest concentration in all the sites, and the sediments in the study area are contaminated by them.

The observed elevated levels of metal composition in stream sediments from the different quarry sites compared to the levels of these metals in the control sites is a clear indication of anthropogenic contributions from activities at the quarry sites. It is most likely that the weathering/leaching of quarry waste materials is the significant source of metal concentration to the stream sediments. The metals released from the quarry waste materials are better retained in sediments with higher LOI and clay contents: often known as absorb and retain more metals due to their large surface area ratio (Azmat, Muhammad, Riffat and Zulkifi, 2014).

Enrichment Factor (EF)

The calculated EF were normalised with Fe. The values; computed to assess the level of metal enrichmentinthe sediments, are presented in Table 4. The trend of metal enrichment among the quarry groups is in the order:OM active quarries - Cd > Sr > Ag > Cu > As > Se > Mn > Zn > Mo > Sb > Co > Pb > Ni > Cr; OM abandoned quarries - Cd > Ag > Sr > Mn > Co > Mo > Cu > Ni > Zn > Cr > Se > Pb > Sb > As; CF active quarry: As > Cd > Sr > Mn > Mo > Se > Sb > Co > Ag > Cu=Ni > Cr > Zn > Pb.

Mean EF values in the OM active quarry indicated no enrichment of Ni and Cr; minor enrichment of Mo, Cu, Pb, Zn, Ag, Co, As, Sb, Mn and Se; and moderate enrichment of Sr and Cd. In the OM abandoned quarries however, mean EF values revealed no Pb, As, Sb and Se enrichment, minor enrichment of Mo, Cu, Zn, Ag, Ni, Co, Sr, Cr and Mn; and Moderate enrichment of Cd.In the CF active quarry, there was no enrichment of Pb, Zn and Cr; minor enrichment of Mo, Cu, Ag, Ni, Co, Sb, Mn and Se; moderate enrichment of Sr and Cd; and severe enrichment of As (Table 4). The enrichment of the metals is mainly from the leaching of quarry waste materials, and the elevated levels can be toxic to human and aquatic lives.

Table 3: Heavy metal concentration (mg/kg) of stream sediments in the study area

	ID	Mo	Cu	Pb	Zn	Ag	Ni	Co	As	Sr	Cd	Sb	Cr	Mn	Se	%Fe
	S_1	0.29	12.9	33.2	150	0.16	12.0	9.00	0.70	371	0.32	0.06	32.0	357	0.20	2.71
	S_3	1.18	21.8	35.7	67.4	0.08	8.50	4.00	1.20	133	0.10	0.05	27.0	206	0.40	2.55
Active	S_5	0.50	21.5	63.5	120	0.06	13.2	7.10	0.40	207	0.21	0.03	28.0	273	0.50	1.99
Site O.M.	S_7	0.37	9.60	34.8	51.7	0.07	10.0	4.60	0.30	85.0	0.03	0.07	31.0	172	0.20	1.90
	S_8	0.16	11.1	24.1	75.7	0.09	5.80	5.00	0.10	405	0.04	0.03	11.0	208	0.20	1.59
	S_9	0.23	24.4	28.6	90.8	0.02	8.30	9.40	0.70	364	0.14	0.05	20.0	372	0.20	2.89
	S_{10}	0.83	33.0	30.3	84.7	0.04	11.4	4.40	0.20	179	0.27	0.35	38.0	239	0.20	1.87
	Mean SD	0.51 0.3	19.2 7.8	35.7 11.9	91.5 31	0.07 0.04	9.89 2.4	6.21 2.1	0.51 0.4	249 119	0.16 0.1	0.09 0.1	26. 8.2	261 71.6	0.27 2.2	0.12 0.46
	Range	0.23-1.2	9.6-33.0	24.1-63.5	51.7-150	0.02-0.16	5.8-12.0	4.0-9.40	0.1-1.20	85-405	0.03-0.3	0.03-0.4	11.0-38	172-372	0.20-0.5	1.59-2.71
	Control	0.10	5.60	15.4	35.8	0.01	3.60	1.60	0.02	68.1	0.01	0.01	6.20	86.2	0.12	1.02
Aband.	S_2	1.53	18.2	43.8	125	0.13	9.60	7.00	0.10	264	0.23	0.05	18.0	468	0.20	2.70
Sites O.M	S_4	0.19	10.6	35.1	54.9	0.11	7.70	5.80	0.10	198	0.05	0.03	21.0	259	0.20	1.63
	S_6	0.29	27.4	17.8	91.9	0.03	4.70	15.9	0.60	215	0.14	0.17	143	597	0.21	4.01
	Mean SD	0.54 0.4	18.1 7.6	32.9 12.4	86.2 32	0.08 0.04	12.1 8.9	6.71 3.4	0.44 0.3	232 99	0.15 0.1	0.09 0.1	33.7 341	290 134	0.24 0.1	2.21 0.80
	Range	0.2-1.53	10.6-27	`7.8-43.8	54.9-125	0.03-0.13	47.-5.65	5.8-15.9	0.10-0.6	198-264	0.05-0.2	0.03-0.2	18.0-143	259-597	0.2-0.21	1.63-4.01
	Control	0.14	8.90	15.2	35.4	0.02	5.65	3.88	0.05	105	0.02	0.01	15.4	162	0.10	1.22
Active	S_{11}	0.41	6.10	22.9	35.7	0.03	8.80	5.30	1.30	701	0.03	0.07	20.0	369	0.20	1.63
Site C.F.	S_{12}	1.15	17.8	26.4	64.3	0.04	22.80	10.9	6.20	362	0.14	0.20	56.0	608	0.20	3.64
	Mean SD	0.73 0.3	10.5 5.2	26.1 2.50	43.0 15	0.03 0.01	12.9 7.1	6.63 3.1	3.67 2.0	467 165	0.10 0.1	0.12 0.1	30.7 18	509 101	.27 0.1	2.18 1.04
	Range	0.41-1.2	6.1-17.8	22.9-26.4	35.7-64	0.03-0.04	8.8-22.8	5.3-10.9	1.30-6.2	362-701	0.03-0.1	0.07-0.2	20-56.0	369-608	0.2-0,20	1.63-3.64
	Control	0.25	2.20	3.22	12.4	0.01	2.68	1.02	0.05	104	0.01	0.02	2.89	87.5	0.05	1.05
	ASV[1]	-	45.0	0.30	85.0	-	68.0	19.0	13.0	-	0.30	-	90.0	900	-	4.70
	TEC[2]	-	31.6	35.8	121	-	22.7	10.0	9.79	-	0.99	-	43.4	-	-	3.50
	PEC[3]	-	14.9	12.8	149	-	48.6	0.02	3.3	-	4.98	-	111	-	-	4.80

ASV[1] = Average Shale Values (Turekian and Wedephol, 1961); TEC[2] = Threshold Effect Concentration and PEC[3] = Probable Effect Concentration (MacDonald et al., 2000)

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Table 4: Enrichment Factor (EF) values of metals in sediment from the study area

		Mo	Cu	Pb	Zn	Ag	Ni	Co	As	Sr	Cd	Sb	Cr	Mn	Se
Active Quarries	S_1	0.55	0.94	2.44	2.04	3.63	0.83	1.37	0.11	3.06	7.38	0.59	0.72	1.46	0.70
OM	S_3	2.38	1.69	0.76	0.97	1.99	0.63	0.65	2.96	1.16	2.48	0.53	0.65	0.89	1.49
	S_5	1.29	2.14	1.74	2.23	3.87	1.25	1.47	1.27	2.33	6.68	0.41	0.86	1.52	2.38
	S_7	0.52	1.38	0.83	1.75	2.71	0.69	1.30	0.39	5.69	1.59	0.51	0.42	1.45	1.19
	S_8	0.50	1.67	0.54	1.15	1.92	0.54	1.34	1.53	2.82	3.06	0.47	0.42	1.42	0.66
	S_9	2.28	3.49	0.89	1.66	0.78	1.15	0.94	0.68	2.14	9.13	5.09	1.25	1.41	1.02
	S_{10}	1.29	0.74	0.77	0.80	1.70	1.02	1.34	5.05	9.61	1.17	1.16	0.75	2.50	3.50
	Mean	1.26	1.73	1.14	1.51	2.37	0.87	1.20	1.71	3.83	4.50	1.25	0.72	1.52	1.56
	Control	0.52	0.67	0.53	0.72	0.86	0.48	0.75	0.09	1.08	1.55	0.42	0.58	0.65	0.55
Abandoned Quarries OM	S_2	3.01	1.33	0.88	1.70	3.07	0.74	1.07	0.23	2.19	5.31	0.50	0.49	1.91	0.70
	S_4	0.60	1.29	1.18	1.24	2.80	0.89	1.47	0.38	2.72	1.96	0.50	0.79	1.76	1.16
	S_6	0.37	1.35	0.24	0.84	0.93	2.20	1.64	1.42	1.20	2.21	1.15	2.91	1.64	0.47
	Mean	1.33	1.32	0.77	1.25	2.28	1.26	1.39	**0.68**	2.04	3.16	0.72	1.16	1.77	0.78
	Control	0.35	1.22	0.15	0.48	0.61	0.50	1.01	0.11	0.98	1.02	0.26	0.23	0.86	0.24
Active Quarry CF	S_{11}	1.62	0.97	0.40	0.65	0.65	1.18	1.24	10.8	2.22	2.44	1.49	0.94	1.85	0.52
	S_{12}	2.49	1.15	0.40	0.83	1.83	1.03	1.19	17.3	3.42	3.92	1.70	0.78	4.05	2.97
	Mean	2.06	1.06	0.40	0.74	0.84	1.11	1.22	12.2	4.07	4.38	1.48	0.79	2.97	1.52
	Control	0.88	0.67	0.28	0.54	0.25	0.87	0.85	4.55	1.82	1.52	0.98	0.45	0.88	0.25

Geo-accumulation index (Igeo) of sediments

The mean geo-accumulation index (Igeo) values of the following metals Mo, Sr, Cu, Pb. Zn, Ag, Ni, Co, As, Sb, Cr, Mn, Se and Fe from the quarry sites in Oban Massif indicated no pollution status to moderate pollution of sediment samples. In the abandoned quarry sites in Oban Massif;the sediments were unpolluted with Mo, Cu, Pb, Zn, Ag, Ni, As, Cd, Sb, Cr, Se and Fe,and moderately polluted with Co, Sr and Mn.In the active quarry sites of Calabar Flank however, the sediments are moderately polluted with Ni, As, Cr, Mn and Sr. In all the quarry sites, the accumulation of the metals was influenced by both natural processes (geogenic) and anthropogenic(quarrying) activities.

Table 5: Geo-accumulation index values of sediment samples in the study area

		Mo	Cu	Pb	Zn	Ag	Ni	Co	As	Sr	Cd	Sb	Cr	Mn	Se	Fe
Act.	S_2	0.36	0.61	0.43	1.52	0.59	1.18	1.02	1.18	1.91	0.22	1.71	0.46	0.98	0.23	0.58
OM	S_3	1.44	1.03	0.46	0.68	0.30	0.83	0.45	0.14	0.68	0.26	0.26	0.39	0.56	0.45	0.55
	S_5	0.61	1.01	0.83	1.22	0.40	1.30	0.80	0.90	1.06	0.74	0.35	0.40	0.75	0.56	0.43
	S_7	0.45	0.38	0.42	0.52	0.11	0.98	0.52	0.68	0.44	0.68	0.16	0.44	0.47	0.23	0.41
	S_8	0.20	0.52	0.31	0.76	0.26	0.57	0.56	0.23	2.08	0.90	1.35	0.16	0.57	0.23	0.34
	S_9	0.29	1.15	0.37	0.92	0.33	0.81	1.06	1.58	1.87	0.16	0.26	0.29	1.02	0.23	0.62
	S_{10}	1.01	1.55	0.39	0.86	0.09	1.12	0.50	0.45	0.92	0.10	1.58	0.54	0.65	0.23	0.40
Mean		0.62	0.89	0.46	0.92	0.30	0.97	0.70	0.74	1.28	0.44	0.81	0.38	0.71	0.31	0.48
Control		0.19	0.42	0.25	0.48	0.12	0.36	0.40	0.22	0.32	0.12	0.21	0.12	0.26	0.11	0.25
Abd.	S_2	1.87	0.86	0.57	1.27	0.47	0.94	0.79	0.01	1.36	0.19	0.26	0.26	1.28	0.23	0.58
OM	S_4	0.23	0.50	0.46	0.56	0.27	0.76	0.65	0.23	1.02	0.13	1.35	0.30	0.71	0.23	0.36
	S_6	0.35	1.29	0.23	0.93	0.22	0.61	1.79	1.35	1.11	0.16	0.68	2.05	1.63	0.23	0.86
Mean		0.35	0.89	0.42	0.92	0.32	0.77	1.08	0.53	1.16	0.16	0.76	0.87	1.21	0.23	0.60
Control		0.12	0.46	0.22	0.44	0.14	0.45	0.52	0.12	0.89	0.66	0.18	0.22	0.65	0.12	0.32
Active	S_{11}	0.30	0.36	0.72	0.56	0.66	0.57	0.52	1.96	3.60	0.23	0.45	0.56	0.97	1.35	0.39
C. F.	S_{12}	0.84	1.04	0.83	0.65	0.56	1.47	1.07	0.30	1.86	1.05	1.29	1.58	1.60	0.45	0.86
Mean		0.57	0.70	0.78	0.61	0.37	1.22	0.81	1.13	2.73	0.64	0.87	1.06	1.29	0.90	0.63
Control		0.23	0.22	0.42	0.35	0.28	0.41	0.34	0.28	1.35	0.16	0.11	0.25	0.52	0.22	0.38

Since there are no known sediment quality criteria in Nigeria for the solid mineral/mining sector (Adamu *et al.*, 2015), the obtained result was compared with average shale values (Turekian and Wedephol, 1961) and Consensus-Based Sediment Quality Guidelines (MacDonald *et al.*, 2000) (Table 3). A comparison of the metal concentrations compared with TEC and PEC values revealed that although the levels of Cu in both the active and abandoned quarry sites are lower than TEC values, its average level in the active and abandoned quarry sites in Oban Massif area are higher than the PEC level. The mean level of Pb is higher than TEC value in the active quarry sites of Oban Massif area and higher than PEC value in all the quarry sites. Similarly, the mean level of Co is observed to be higher than PEC value in all the quarry sites while As is higher than PEC value only in the active quarry site of Calabar Flank. This may indicate that the sediments are of poor quality with regards to these metals and reflects possible contamination of aquatic life in the area. The levels of the other metals are all within the ASV, TEC and PEC ranges and do not pose any serious environmental threat. In quarry sites, dust laden metals spread on every surface in the area due to blasting and crushing of the rocks with concentration on soil, water and plants depending on distance from the quarry sites and the form in which it is transported (Jung, 2001). The metals released from these waste materials are retained more in surface sediments in streams, as they have higher LOI and clay content (Hwang, Green and Yadav, 2009).

Conclusion

High mean levels of metal concentrations were recorded in sediments from the active site. The comparatively lower concentration of metals from the abandoned sites may be linked to the reduced level of anthropogenic activities due to the present status of the quarries. The comparatively higher levels of metal concentrations in the active quarry sites may also be due to th number of quarry sites in the area and longer periods of quarrying activities. This increases the level of leaching from the piled quarry waste materials into

stream channels. Moderate pollution ofCo, Sr, Mn, Ni, As, and Cr were detected in the sediments.

As the studied areas are mostly agrarian, most of the local population depend on streams flowing from these quarry sites for irrigation, drinking and other domestic uses. The long-term metal exposures by regularly consuming crops grown within these sites and drinking water from these sites poses potential health problems on both animals and humans within the area.

Recommendations

It is important to identify possible sources, degree of contamination and the adopt appropriate remedial measures in the study area. Proper feasibility studiesfor proposed quarry sites should always be carried out by quarry operators prior to commencement of mining. Occupational and environmental health impact assessment prior to the design of the quarry and the installation of equipment and mining should be conducted. Provisions should also be made for incorporation of appropriate control technology safe handling and disposal of the resulting effluents and waste.

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The Distribution of selected Potentially Toxic Elements and their Ecological Risk Assessment in parts of Mainland Lagos, Southwestern Nigeria

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Abstract

The distribution of selected Potentially Toxic Elements (PTEs) in urban soils, road dusts and drainage sediments in Lagos Mainland were investigated to evaluate the impacts of urbanization on their quality, and consequent ecological risks. Fifty (50) samples comprising 26 top-soil, 20 road dust, and 4 drainage sediments were collected, air-dried, disaggregated, and sieved. Portions of the samples were soaked in deionized water for 48 hours prior to determination of Electrical Conductivity (EC), pH, and Total Dissolved Solids (TDS) of the soil-water mixture using digital probes. Elemental constituents of 0.5g leached with aqua regia were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The grain-size analysis revealed that the samples were predominantly silty in nature. The pH and EC ranged from 6.5-6.9 and 114-4961µS/cm respectively, while TDS ranged from 73-3168mg/l. Elemental analysis revealed the following ranges (mg/kg) for the soils, road dusts and drainage sediments respectively: Cu (29-543, 47-222 and 34-109); Pb (23-1891, 62-687 and 83-236); Zn (100-2201, 245-1256 and 291-677); Ni (9-65, 12-45 and 14-24); Co (3-18, 3-9, and 5-11); Mn (192-3579, 269-963, and 302-1002); As (Below Detection Limit [BDL]-15, BDL-8, and 4-5); Cd (BDL-39, BDL-17, and 0.6-1.5); and Cr (22-93, 35-67 and 50-63). The environmental media were enriched in Pb, Cu, Zn, As and Cd especially in Bariga, Palmgroove, Ilupeju and Anthony Village areas. These locations revealed high ecological risks for all metals aforementioned except Cr, with considerable Contamination Factor and Degree for Pb, Cu and As in the environmental media. Locations along roads with heavy traffic, within the markets, along dumpsites, and automobile repair workshops revealed elevated elemental concentrations.

Keywords: Urbanization, Potentially Toxic Elements, Environmental Quality, Ecological risks

Introduction

Geochemical evaluation of Potentially Toxic Elements (PTEs) and assemblage of information about environmental media (top-soils, road dust and sediments) has become very important because of the role the media play as sink for environmental toxicants, instigating various measures of pollution in terrestrial and aquatic contexts (Papastergios *et al.,* 2009; Ajmone-Marsan *et al.,* 2019; Mokhtarzadeh *et al.,* 2020). The increase in population associated with infrastructural development without proper planning and management poses a very serious threat to the environment and the society at large. As these pollutants continue to increase in the environment, they have the eventuality of being accumulated in the different body organs leading to unpleasant consequences owing to their non-biodegradable nature and long biological half-lives (Sathawara *et al.,* 2004; Kirpichtchikova *et al.,* 2006; Olatunji and Olisa, 2014). The challenge of PTEs pollution is often recognized to be associated with industrialized areas, but the largest contributor of these elements is veritably heavy vehicular traffic (Bhattacharya *et al.,* 2013).

Lagos metropolis has grown to become a mega-city with very dense human population, road traffic congestion, and increased level of industrialization which makes it well positioned to receive pollutants from these sources. Understanding the dynamic relationship between human population and industrial activities is necessary for environmental planning and management. This study was therefore aimed at the determination of the status of soils, road dusts and drainage sediments in Shomolu, Palmgroove, Bariga,

Ojota and Oshodi areas in Lagos; by evaluating the contents of selected PTEs in them. The specific objectives were to determine the spatial distribution and concentration of PTEs of environmental significance in media, and evaluate the level of impact of the population and industrialization on them.

Study Area description

The study area, bounded by the coordinates N06^{0}31'01''- N06^{0}36'00'' and E003^{0}21'0.2''-E003^{0}25'00'', is located in the Eastern Dahomey Basin in Nigeria (Figure 1). The study centered on the Ipaja-Ikorodu traverse where the subsurface materials are characterized by lateritic clayey horizon at the topmost layer, followed by sand units of different grain sizes underlain by clayey units, sandy-clay and coarse, gravelly and conglomeratic sand and shale interbeds. The latter interbeds progressively grade into shale (Figure 2). Geologically, Lagos metropolis falls into two broad sedimentary formations in the Eastern Dahomey Basin. These are the Ilaro Formation, which borders the Basement Complex and extends along the coast of Lagos, and the Quaternary Formation of coastal plain sands (Figure 2), which is more widely spread over the area composed basically of sands, clay and thick interbeds of shale (Longe, 2011; and Adegbola *et al.,* 2016). The sandy-clay is characterized by reddish brown to pinkish color while the sand units vary from very fine silty sands to very coarse gravely sands (Olatunji, 2006).

Methods

Fifty (50) samples comprising, twenty-six (26) top-soil samples, twenty (20) road dust samples from major roads within the area and four (4) drainage sediments were collected. Composite samples of the top-soil were made from homogenizing 5 samples obtained at a depth of 0-20cm (one each from the centre together with four other points within each grid). Road dust samples were collected at preferred locations along major roads while drainage sediment samples were also collected at accessible points, from rivers flowing within the study area. The sampling locations were appropriately located using the Geographic Positioning System (GPS) and careful observations of the landforms were documented. The samples were air-dried and sieved to determine the grain size distributions. Total Dissolved Solids (TDS), pH and Electrical Conductivity (EC) of the sample-water mix were subsequently measured using digital a hand-held meter (Hach Eco model), after soaking the sample for 48 hours. 0.5g of the <75µm fraction of each sample was partially digested using Aqua Regia, prior to Inductively Coupled Plasma Emission Spectrometry (ICP-OES) for elemental composition done at the Acme Laboratories, Vancouver, Canada. **Arc-GIS software was** used to generate geochemical maps from the analytical results.

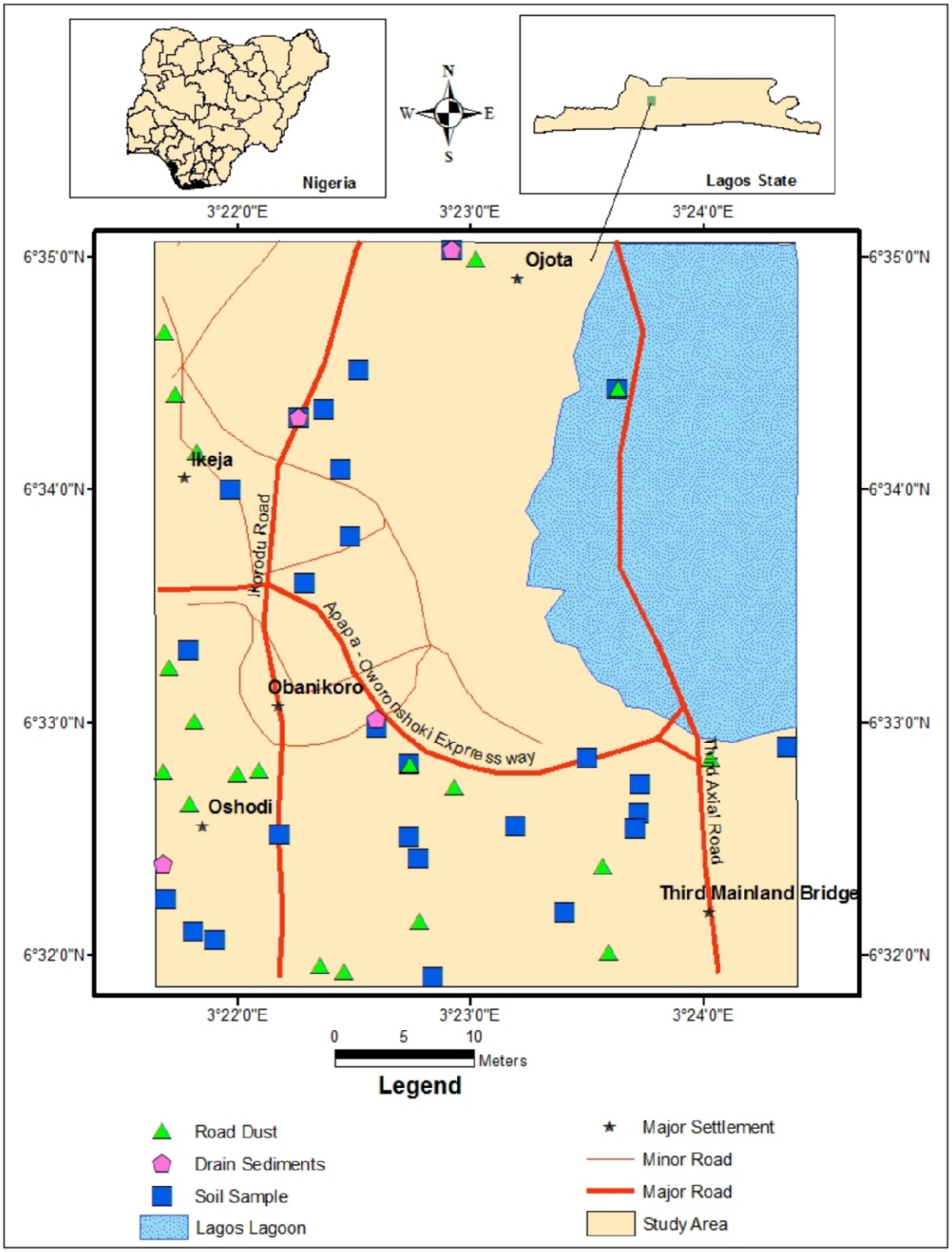


Figure 1: Location map for the Study

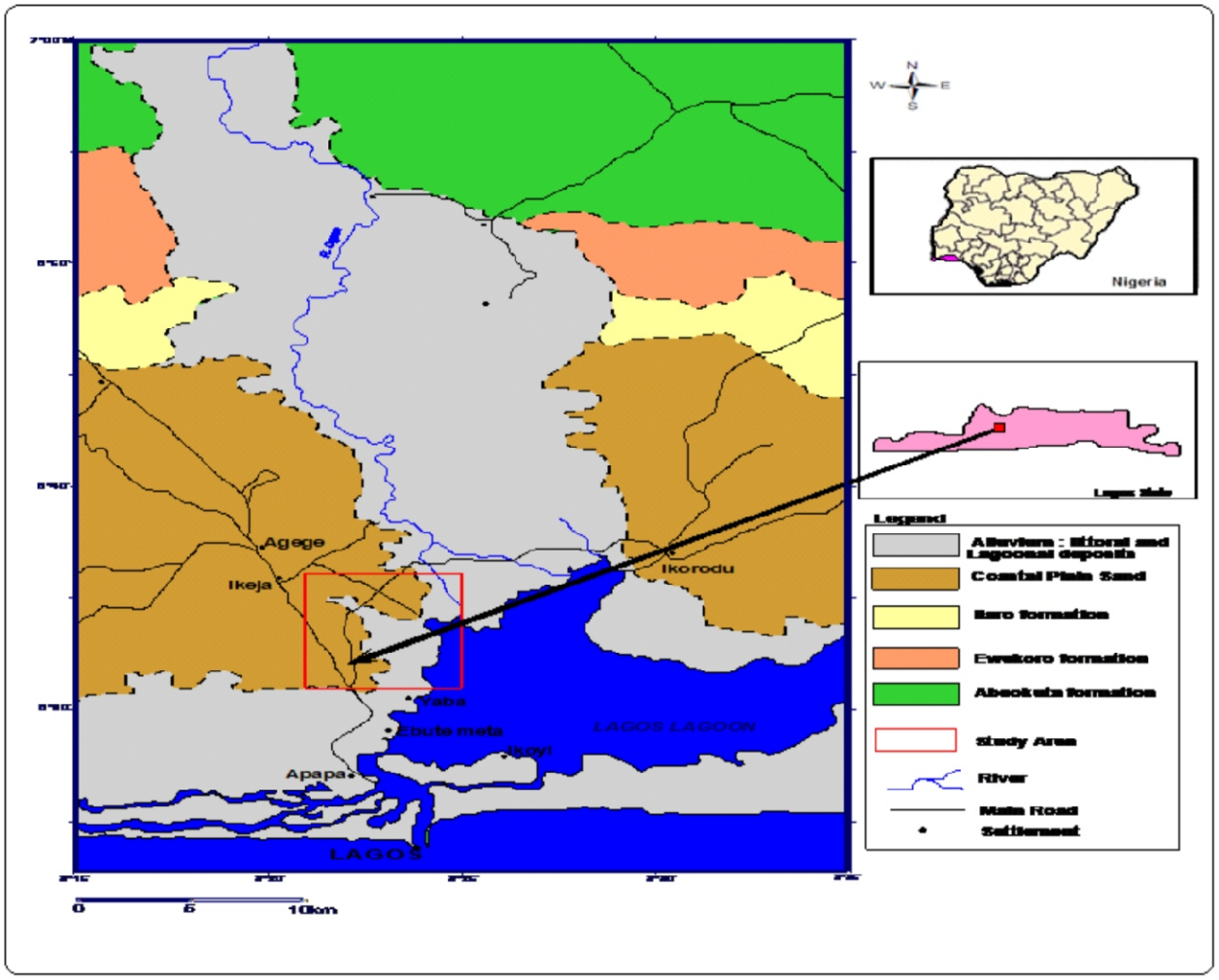


Figure 2: Geological map of Shomolu and adjoining areas (modified after NGSA, 2004)

Methods for the Evaluation of Data

Statistical analysis including the Pearson's Correlation and R-mode Factor analyses were done on the geochemical data obtained using the Statistical Package for the Social Sciences (SPSS-17) software package. The Pearson's Correlation analysis is particularly useful for testing the strength of the association between two random variables and it could be used to describe observed geochemical distribution and associations (Olatunji and Abimbola, 2010). The R-mode analysis groups related variables into principal associations known as factors on the basis of their mutual correlation coefficients (Asaah *et al.,* 2006).

An attempt was made to relate these factors to actual processes influencing the geochemistry of the sampled media. Geochemical parameters such as Metal Ratio (MR), Geo-accumulation Index (I_{geo}), Contamination Factor (CF), Contamination Degree (Cdeg) and Ecological Risk Index (RI) were determined to indicate the level of enrichment and degree of contamination in the media sampled. Several workers such as Loska *et al.,* 2004; Fakayode and Olu-Owolabi, 2007; Gbadebo, 2007; Luo *et al.,* 2007; Odewande and Abimbola, 2008; Olatunji *et al.,* 2009; Olatunji and Olisa, 2014; Odukoya, 2015; and Olatunji and Ajayi, 2016 had and are still using these contamination indices to determine significant impact of metals on the environment.

Metal Ratio (MR)

The metal ratio was employed to determine the extent of contamination by comparing the observed heavy metal concentration in the media with their respective background concentrations (in this case, average shale values and average crustal value). This was done using the formula:

$$MR = \frac{Cm}{Bn} \qquad (1)$$

Where, *Cm is the measured concentration of the metal in the sample,*

B*n is the background value, (Average shale value and Average crustal value).*

When metal ratios is >1, it is suggestive of areas with elevated metal concentration while metal ratios < 1 reveals low metal enrichment. The MR values determined using equation 1 were interpreted as indicated in Table 7.

Geoaccumulation index (I_{geo})

The degree of metal contamination in the samples was determined using the six classes of Geo-accumulation index (Table 7) proposed by Muller (1981) ranging from practically uncontaminated to extremely contaminated using the formula;

$$Igeo = Log2\left(\frac{Cn\ sample}{1.5\ x\ Bn}\right) \qquad (2)$$

Where, I_{geo} is the geo-accumulation index

Cn is the measured metal concentration in the soils and sediments,

Bn is the background value of the metal (crustal averages and average shale value),

1.5 is a constant used as a correcting factor for the variation in the lithogenic data.

The interpretation of the I_{geo} values determined using equation 2 is indicated in Table 7.

Contamination Factor (CF) and Contamination Degree (C_{Deg})

The CF represents the individual impact of each metal on the samples while the C_{Deg} index is calculated as the percentage contribution of all the metals to the contamination suffered by the soil, dusts and sediments. The two indices were calculated using the formulas in equations 3 and 4; while these indices were interpreted using the proposed classification by Hakanson, 1980 (Table 8):

$$Cf^i = \frac{C_o^i}{C_n^i} \qquad (3)$$

Where: Cf^i is contamination factor of the individual metal examined,

C_o^i is the average content of each metal (from at least 5 sampling sites),

C_n^i is the pre-industrial concentration of the respective metal in the parent materials.

$$C_{deg} = \frac{C_f^i}{\sum C_f^i} * 100 \qquad (4)$$

Where: C_{deg} is the Contamination Degree,

C^i_f is the Contamination Factor of individual elements,

$\sum C^i_f$ is the sum of contamination factors of all the elements.

Ecological Risks

The estimation of the likelihood that unfavorable ecological effects may occur under a given set of circumstances is termed ecological risk assessment (US EPA, 1998). Potential ecological risk indices of Cu, Pb, Zn, Ni, Co, Mn, As, Cd and Cr in the study locations were determined and interpreted according to Hakanson, 1980.

Ecological risk factor (E_r^i) as suggested by Hakanson (1980), is usually employed to quantitatively express the potential ecological risk of a given metal. E_r^i is calculated using:

$$E_r^i = T_r^i \times Cf^i \qquad (4)$$

Where: T_r^i is the toxic response factor for a given substance; Cf^i is the contamination factor,

T_r^i which reflects the toxic requirement (Table 9).

The sum of the individual risk factors is termed the potential Ecological Risk Index (RI).

Results and Discussion

Grain Size Distribution and Physico-chemical parameters

The grain size distribution and physico-chemical features of environmental media are important parameters in evaluating the relative mobility of heavy metals (Pasieczna and Lis, 2008). The mobility of trace metals in soils depend both on the chemical and physical parameters of the soil and speciation of elements (Kabata-Pendias and Pendias 2001; Omorogieva and Tonjoh, 2020), while the content and behavior is primarily inherited from the parent material (Kabata-Pendias 1993). The soil in the study area consists of sand, silt and clay sizes in varying proportions; but are more of silty soils than sandy soils with about 55 % falling in the silty fraction, 41% in the sandy fraction and 4% in the clayey fraction. The pH of all the samples measured ranged from 6.5 to 6.9, an indication of slight acidity (Table 1). The EC of the samples ranged from 114 µs/cm to 4961 µs/cm in soils, 261 µs/cm to 1967 µs/cm in road dusts, and 348 µs/cm to 1303 µs/cm in drainage sediments. The TDS ranged from 73 mg/l to 3168 mg/l in soils, 166 mg/l to 1259 mg/l in road dusts and 222 mg/l to 834 mg/l in drainage sediments (Table 1). Samples with high EC and TDS values were found in areas with dense population and high traffic density such as Bariga, Palmgroove, and Shomolu. The results of the pH, EC and TDS varied but it was noticed that areas with high EC values have corresponding high TDS values.

Geochemical distribution of metals

The trace elements analyzed include Cu, Pb, Zn, Ni, Co, Mn, As, Cd, and Cr. The results of elemental composition of the media is presented in Table 2. The variation of heavy metal concentration in all the sample types was observed to be in the order: Zn>Mn>Pb>Cu>Cr>Ni>Co>As>Cd.

The studied soils and road dusts have higher Cd, Pb and Zn concentrations, and slightly elevated contents of As and Cu. Ni, Co, Mn and Cr concentrations in the soils and dusts were however, observed to be within the crustal average abundance limits (Table 2). In contrast, Ni, Co, Mn, As and Cr concentrations in the sediments were observed to be within the corresponding average shale values while Cd, Pb, Zn and Cu concentrations in the sediment their corresponding levels in the average shale (Table 2). The wide trace metals concentration ranges observed in the sampled media are typical of urban environments (Alloway, 2013). The highest concentrations of metals were observed in soil samples collected around automobile mechanic workshops, open dumpsites as well as along some roads with heavy traffic in the study area.

To get a better visualization of geochemical changes in the area, the results were plotted as geochemical spatial distribution pattern (Figures 3 - 6). This aided in the assessment of the relationship between metal concentrations and is useful as an essential tool for environmental assessment (Olatunji and Olisa, 2014).

Table 1: Summary of the Physico-Chemical Parameters

Parameter	Range in Soils	Range in Road Dust	Range in Drainage Sediments
PH	6.5-6.9	6.5-6.9	6.5-6.9
Electrical Conductivity (EC) (µs/cm)	114 4961	261 - 1967	348 1303
Total Dissolved Solids (TDS) (mg/l)	73 3168	166 - 1259	222 834

Table 2: Summary of Trace Elemental Composition in the Soil, Dust and Drainage Sediments

	Soils		Road Dusts		Drainage Sediments	
Metal	Range	Mean ±Std. Dev	Range	Mean ±Std. Dev	Range	Mean ±Std. Dev
Cu	29-543	86.63 ±77.83	47-222	93.50 ±43.7	34-109	79.5 ±32.11
Pb	23-1891	185.89 ±278.46	62-687	181.30 ±147.3	83-236	170.5 ±76.81
Zn	100-2201	601.39 ±404.72	245-1256	497.55 ±241.89	291-677	512 ±162.26
Ni	9-65	20.24 ±9.07	12-45	21.50 ±6.87	14-24	20 ±4.32
Co	3-18	6.91 ±2.61	3-9	6.20 ±1.58	5-11	8 ±2.45
Mn	192-3579	587 ±495.13	269-963	455.85 ±146.84	302-1002	557.5 ±314.22
As	bdl-15	3.96 ±3.21	bdl-8	3.25 ±2.10	4-5	4.33 ±0.58
Cd	bdl-39	0.88 ±0.67	bdl-17	0.79 ±0.41	0.60-1.5	1.05 ±0.39
Cr	22-93	48.93 ±11.75	35-67	51.95 ±9.58	50-63	57.5 ±5.45

***bdl - below detection limit;**

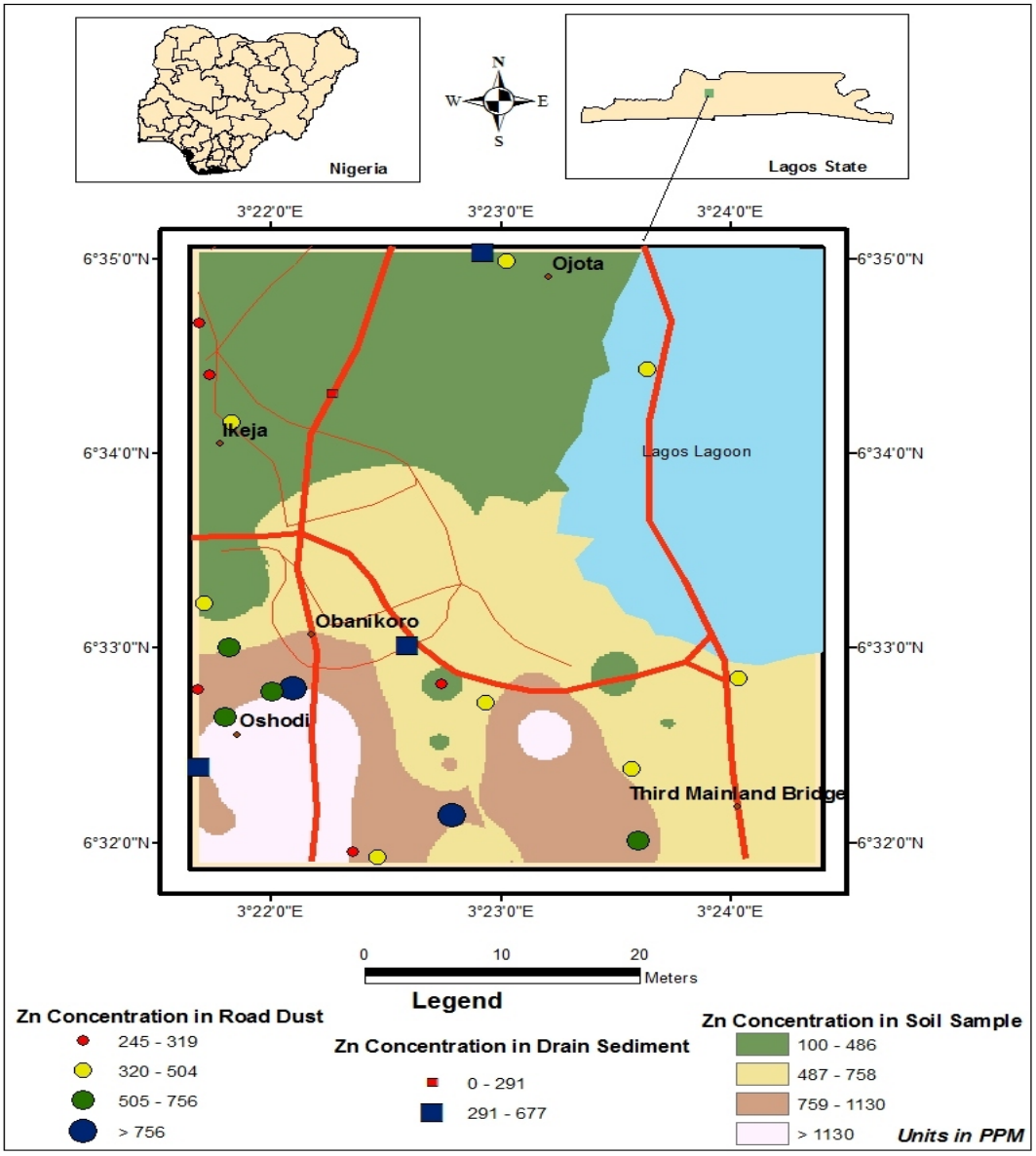


Figure 3: Spatial distribution of Zn in soils, dusts and sediments of the study area

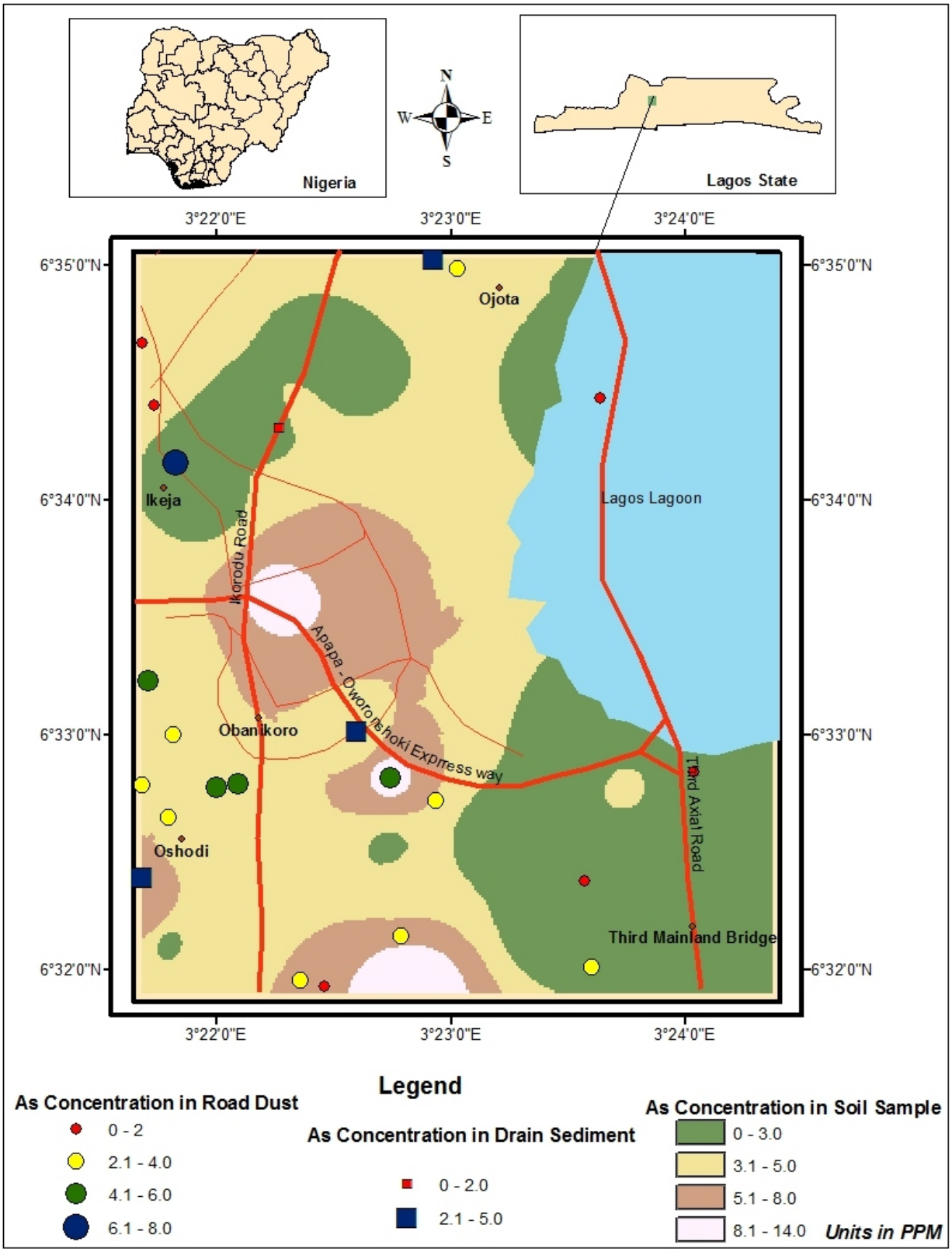


Figure 4: Spatial distribution of As in the studied soils, dusts and sediments

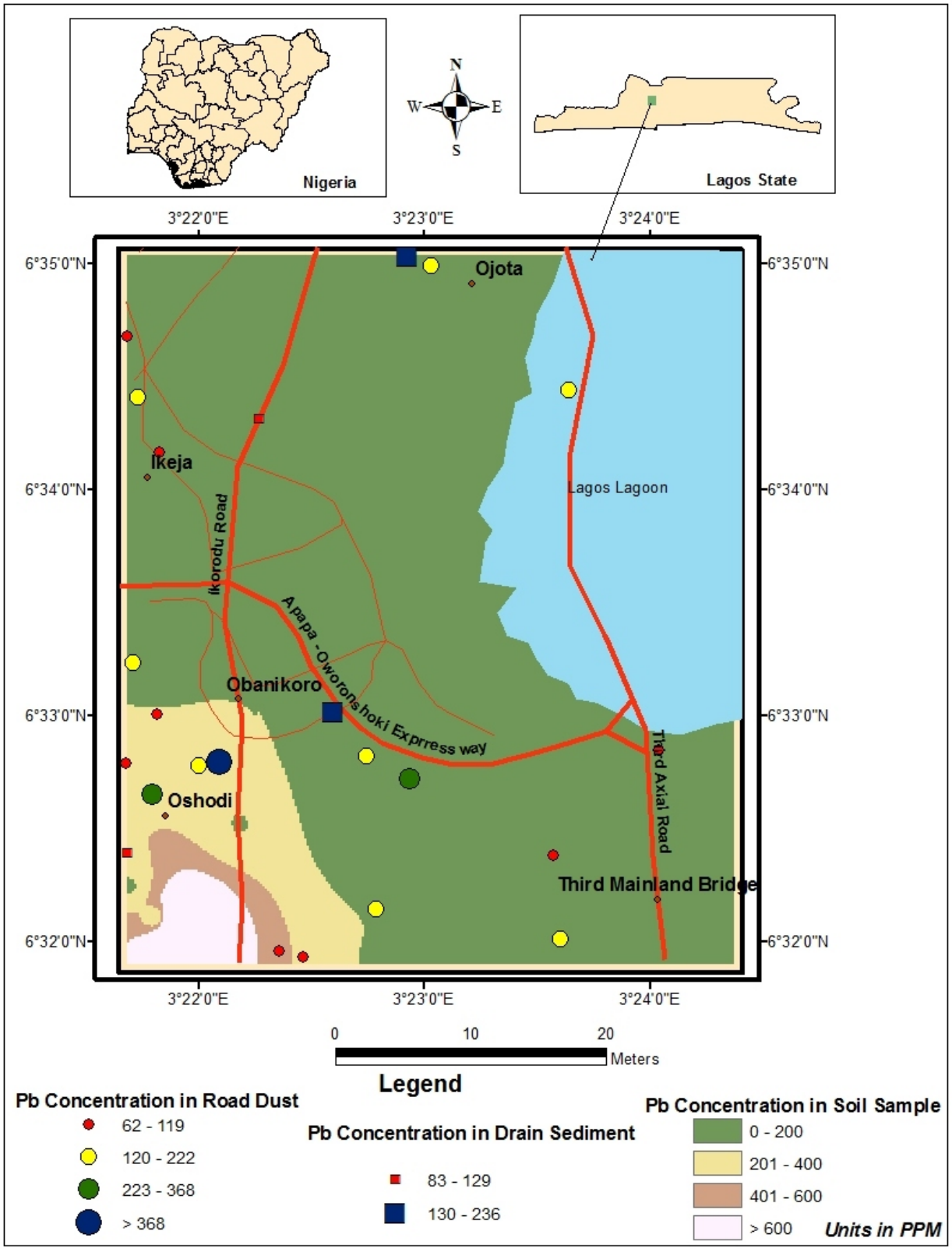


Figure 5: Spatial distribution of Pb in the sampled media

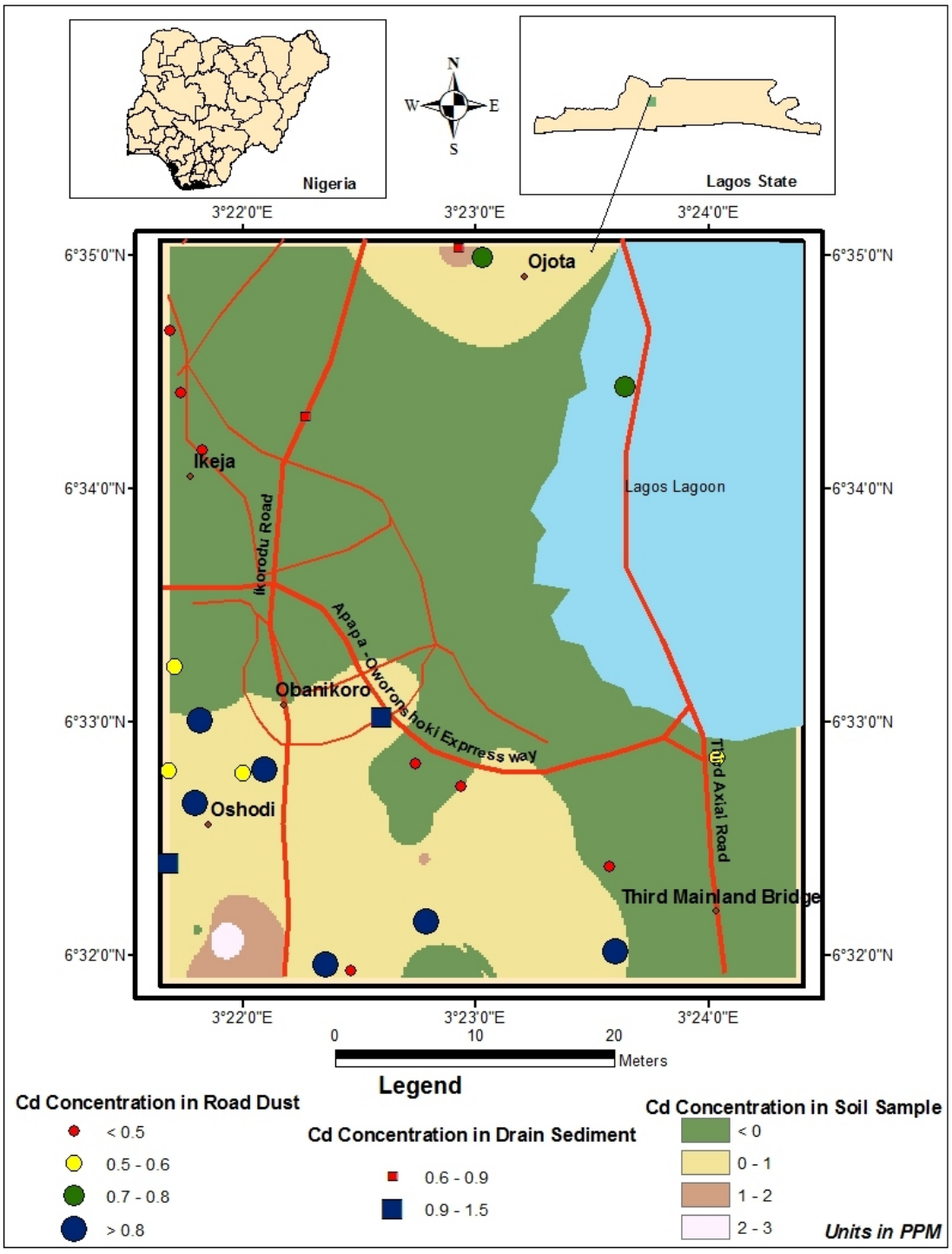


Figure 6: Spatial distribution of Cd in soils, dusts and sediments of the study area

Metal Associations and Quantification of Sources

Statistical analysis of the analytical results including the Pearson's Correlation and R-mode Factor analyses were done to determine the inter-elemental relationships. For the soil and road dust samples, As displayed very low correlation with every other metal which implies a different pathway for its introduction in the soil and road dust of the study locations (Tables 3 and 4). However, significant positive correlation (with correlation coefficient >0.5) exists among Cu, Pb, Zn, Ni, Co, Cd and Cr in the soil and Cu, Pb, Zn and Mn in the road dust (Tables 3 and 4). This is an indication that these metals in the respective sample types have been introduced from similar sources.

R-mode Factor Analysis

Three factor models were identified from the Principal Component Analysis (PCA) for soil with factor 1 made up of Cu, Pb, Zn, Ni, Co, Cd, Cr; and Factor 2 made up of Mn accounting for 64.34% and 11.94% (of total variance), respectively (Table 5). It is primarily adjudged that some metals in principal component 1 such as Cu, Pb, Zn, and Cd (owing to their exceedances relative to their corresponding respective background values) in the soil of the study area are influenced by human activities (Fig. 7). However, it was observed that Ni, Co and Cr (having values less than the background values) show varying degrees of correlation with Cu, Pb, Zn and Cd in the same component (Table 3). This indicates that their sources are different (Figure 7a). Mn was observed to having poor correlations with other metals except Zn (Table 3). The separation of Mn from other metals in factor 2 could however suggest that its concentration in the samples analyzed may have been sourced from an origin different from others as its presence in factors 2 and 3 is an indication of possible multiple sources. It may have been introduced through anthropogenic means such as industrial waste water, e-waste, batteries, and paints (Su and Liu, 2014; and Barzegar *et al.,* 2019). Factor 3 comprised Mn and As accounting for 11.20% of observed variance (Table 5). The indicated similar sources are presumably more of anthropogenic processes (Fig. 7a). In general, the cluster of metals in the soil for Factors 1 to 3 shows a combination of both geogenic and anthropogenic sources, with preponderance of anthropogenic sources believed to be lubricating oils and grease, batteries, industrial waste water, vulcanizing activities, and refuse incineration.

Similarly, a three-component model was also established for the analysis of the results for the road dust samples. Factor 1 comprised Cu, Pb, Zn, Ni, Co, Mn, Cd, and Cr; accounting for 56.30% of the observed variance (Table 6). The average values of Ni, Co, Mn and Cr are less or similar to the average crustal values (Table 2). This suggests that they are not or only slightly influenced by man and are thus mainly affected by natural leaching and absorption of geologically introduced metals in soils and from the bedrock (Olatunji *et al.,* 2020). The varied correlation shown by Ni, Co, Mn and Cr with Cu, Pb, Zn, and Cd (Table 4) in group 1(Table 6), is indicative of both varying sources (Figure 7b). Most of these metals in principal component 1 are derived mainly from industrial emission and metallurgical processes because they are mainly used as alloys, fillers or anti-wear agents. Factors 2 and 3 consist of As accounting for 14.67% and 9.60% respectively of total variance (Table 6). The presence of As in both factors is indicative of possible multiple sources of the metal input into the environment which is presumably more of anthropogenic processes rather than geogenic.

Table 3: Correlation matrix for selected metals in the soil samples

Correlations									
	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Cr
Cu	1								
Pb	**.988****	1							
Zn	**.730****	**.717****	1						
Ni	**.943****	**.929****	**.830****	1					
Co	**.723****	**.727****	**.545****	**.728****	1				
Mn	0.188	0.188	**.543****	0.266	0.298	1			
As	0.17	0.092	0.093	0.148	0.196	0.068	1		
Cd	**.810****	**.788****	**.781****	**.855****	**.700****	0.277	0.118	1	
Cr	**.762****	**.754****	**.545** ***	**.772****	**.746****	0.21	0.32	**.782****	1

Table 4: Correlation matrix for selected metals in road dust samples

Correlations									
	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Cr
Cu	1								
Pb	**.902****	1							
Zn	**.727****	**.733****	1						
Ni	**.564****	0.372	**.666****	1					
Co	.471*	.505*	**.585****	.481*	1				
Mn	**.683****	**.764****	**.870****	**.510***	**.716****	1			
As	0.265	0.312	0.31	0.173	-0.111	0.42	1		
Cd	0.37	0.299	**.671****	**.586****	**.720****	**.599****	0.084	1	
Cr	**.551***	.474*	0.291	.461*	0.398	0.399	0.283	0.209	1

Table 5: Principal Component Analysis of soils

Trace Elements	Factor 1	Factor 2	Factor 3
Cu	**.944**	-.117	-.162
Pb	**.933**	-.079	-.221
Zn	**.834**	.376	.080
Ni	**.962**	-.009	-.117
Co	**.822**	-.090	.051
Mn	.366	**.731**	**.535**
As	.216	-.551	**.781**
Cd	**.907**	.027	-.081
Cr	**.853**	-.258	.084
Percentage of Variance	64.339	11.938	11.195
Cumulative Percentage (%)	64.339	76.277	87.472

Table 6: Principal Component Analysis of dusts

Trace Elements	Factor 1	Factor 2	Factor 3
Cu	**.849**	.256	-.252
Pb	**.826**	.310	-.174
Zn	**.904**	-.056	.255
Ni	**.724**	-.173	-.010
Co	**.747**	-.501	-.156
Mn	**.909**	.034	.206
As	.346	**.707**	**.511**
Cd	**.695**	-.534	.289
Cr	**.580**	.297	-.542
Percentage of Variance	56.302	14.668	9.603
Cumulative Percentage (%)	56.302	70.970	80.573

Quantification of Anthropogenic and Geogenic input

The proportion of anthropogenic input was determined for each metal using the formula of Asaah, 2006 (Figure 7):

$$\textit{Anthropogenic metal} = \frac{X - Xc}{Xc} \times 100$$

Where: X = Average concentration of the metal in the soil,

X_c = Crustal average/ Average shale content.

There is very little or no anthropogenic input for metals such as Ni, Co, and Cr for soils in the study area; Ni, Co, and Mn for road dusts; and Ni, Co, and As for drainage sediments in the study area.

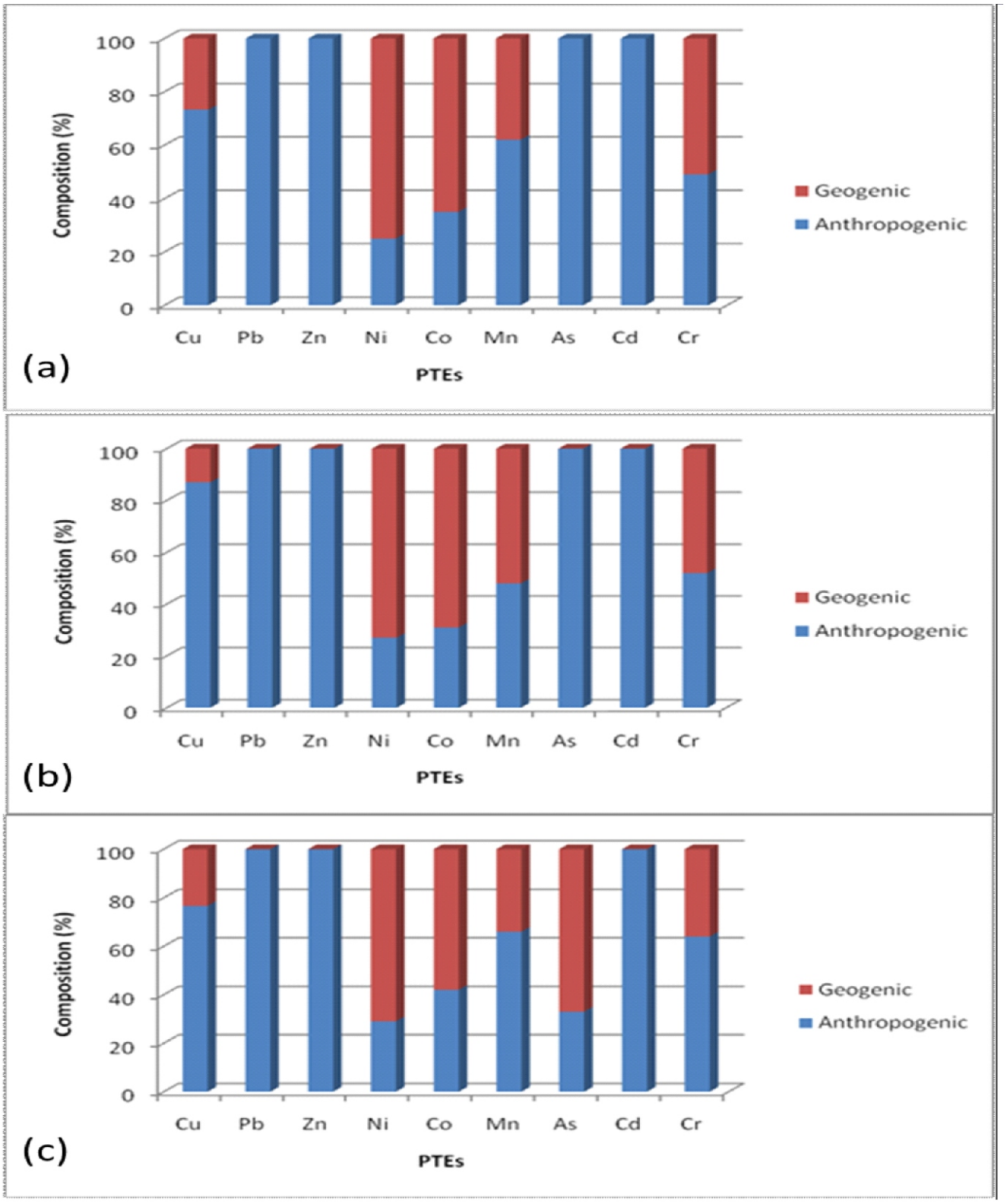
Environmental Assessment of Potentially Toxic Elements

Metal ratio

The metal ratio calculated for the metals revealed that the level of enrichment is highest in the soils of the study area (Table 7). Areas with metal enrichment, when greater than 1 (Pb, Zn, Cu, Mn, As and Cd) are considered to be where there has been considerable accumulation of these metals and such metals are of environmental significance. The areas are characterized by dense population and high traffic density.

Geoaccumulation index (I_{geo})

The calculated Igeo based on the crustal averages and average shale value revealed no contamination moderate contamination of Ni, Co, Cr and Mn in all the sample types; while heavy to extreme contamination (Igeo of 3 to 6) of Cu, Pb, Zn and Cd were detected (Table 7). As had greater level of contamination in soil and road dust compared to drainage sediments. The evaluation of the geo-accumulation index for these metals revealed that they have accumulated in most especially the road and dust samples, in such quantity that they impair the quality of the samples in the study area.



Figures 7a, b and c: Stacked bar charts with percentage composition of geogenic and anthropogenic fractions of heavy metals in the (a) soils [n=26], (b) road dusts [n=20] and (c) drainage sediments [n=4]of the study

Table 7: Summary of the calculated MR and I_{geo} for elements

	Soils and Road Dusts (Using Crustal Average*)		Sediments (Using Average Shale values**)	
Elements	MR Range	Igeo range	MR Range	Igeo range
Cu	, , ,	-1 3	1 11	4 6
Pb	2 135	1 7	4 12	2 4
Zn	1 29	0 5	3 8	2 3
Ni	<1 1	-3 0	<1	-3 2
Co	<1 1	-3 0	<1 1	-2 1
Mn	<1 4	-2 2	<1 1	-1 0
As	<1 10	0 3	<1 1	-1 0
Cd	<1 13	0 4	2 5	2 3
Cr	<1 1	-2 0	1	-1

* Taylor, 1964; **Turekian and Wedepohl, 1961

Keys:

MR ≤ 1 = low contamination, 1 ≤ MR < 3 = moderate contamination, 3 ≤ MR < 6 = considerable contamination, MR > 6 = very high contamination.

Igeo≤0= Uncontaminated, 0<Igeo<1= Uncontaminated to moderately contaminated, 1<Igeo<2= Moderately contaminated, 2<Igeo<3=Moderately to heavily contaminated, 3<Igeo<4= Heavily contaminated, 4<Igeo<5= Heavily to extremely contaminated, Igeo≥5= Extremely contaminated

Contamination factor and Contamination Degree

The extent of contamination in the soils and dusts in the study area can revealed that Pb, Zn, As and Cd have the highest impact on contamination of the samples collected (Table 8).

Ecological risk associated with heavy metals in soils, road dust and drainage sediments

The ecological risk factor of Cu, Zn Ni, Co, Mn, and Cr in all the sample reflects a low risk while Pb and Cd concentrations in soil, road dust and drainage sediment present moderate and considerable risk, respectively (Table 9). Cd posed the greatest risk even though Cd concentrations were very low in the samples. The ecological risk for Cd was high because of the higher toxic response value (T_r) of Cd relative to other metals (Table 9). $E^i_r$of As in soil was observed to be within moderate level while it was low for drainage sediment and road dust samples. The risk factors of the metals for all the sample types were summed in order to determine the overall potential risk. The risk index for all the sample types fell within the moderate risk class (Table 9).

Table 8: Summary of trace element contamination levels in soils, dusts and sediments of the study

Metals	Contamination Factor			Contamination Degree		
	Soils	Road Dust	Drainage Sediments	Soils	Road Dust	Drainage Sediments
Cu	2	2	2	4	5	6
Pb	14	13	9	36	35	34
Zn	9	8	6	24	21	22
Ni	0	0	0	1	1	1
Co	0	0	0	1	1	2
Mn	1	1	1	2	2	3
As	4	3	0	10	9	2
Cr	0	0	1	1	1	2

Keys: Cf<1= low contamination, 1<Cf<3 = moderate contamination, 3<Cf<6 = considerable contamination, 6<Cf = very high contamination. Cdeg<8 = low degree, 8≤Cdeg<16 = moderate degree, 16≤Cdeg<32 = considerable degree, 32≤Cdeg = very high degree

Table 9: Summary of the results of Ecological risk assessment in the study locations

Elements	Contamination Factor (Cf)			Toxic response factor (T_r^i)	Ecological risk factor (E_r^i)		
	Soil	Road dust	Drainage sediment		Soil	Road dust	Drainage sediment
Cu	2	2	2	5	10	10	10
Pb	14	13	9	5	70	65	45
Zn	9	8	6	1	9	8	6
Ni	0	0	0	5	0	0	0
Co	0	0	0	5	0	0	0
Mn	1	1	1	1	1	1	1
As	4	3	0	10	40	30	0
Cd	4	4	4	30	120	120	120
Cr	0	0	1	2	0	0	2
RI					250	234	184

Keys: E_r^i<40 = low risk, 40≤ E_r^i<80 + moderate risk, 80≤ E_r^i<160 = considerable risk, 160≤ E_r^i<320 = high risk, E_r^i ≥320 = very high risk. RI <150 = low risk, 150≤RI≤300 = moderate risk, 300≤RI≤600 = considerable risk, RI>600 = high risk.

Conclusion

This study presented data on the concentrations of selected metals in the top-soils, road dust and sediments in Shomolu and adjoining areas of Lagos Metropolis. The relationship has been established between the concentration and distribution of the metals in the sampled media. The elevated concentrations of Cu, Pb, Cd, As, and Zn in soils, dusts, and sediment samples are attributable to indiscriminate discharge of urban wastes, erosion, activities at mechanic workshops and market places;

traffic emissions, population density and release of effluents. Ni, Co and Cr concentrations in all the sample types were mainly from natural sources such as parent materials and geologic processes. Comparatively, some metals like Mn, As and Cr were derived from mixed sources. The potential ecological risk index showed that individuals in the study areas are at a moderate risk of developing health-related complications. However, this risk varies with the heavy metal in question, as Cd presented the highest ecological risk.

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