

Distribution of Heavy Metals in Urban Soils; A Case Study of Calabar Area, South-Eastern Nigeria

Azubuike S. Ekwere*, Solomon J. Ekwere, Bassey E. Ephraim, Anthony N. Ugbaja

Department of Geology, University of Calabar, Calabar, Nigeria

Abstract This work presents an attempt to establish the degree of anthropogenic influences of selected trace metals distribution in soils from Calabar area of south-eastern Nigeria. Fe, Mn, Pb, Cu, Zn, Cd, Co, Cr, As and Ni concentrations were determined for soils of different categories within the study area. Various geo-statistical and other techniques were used for assessment of the metal concentration in the Calabar urban soils. Geochemical data show the metal levels to be within background values and geo-accumulation index (I_{geo}) confirms that these metals are unpolluted – moderately polluted, thereby posing no significant environmental impact. The slightly elevated concentration of Pb are attributable to emissions from automobile along motored roads, waste disposal from automobile repair shops and other forms of indiscriminate dumping of effluents within the commercial areas. Principal component analyses; correlation, factor and cluster analyses indicates dominant lithogenic control and subordinate anthropogenesis. Metal speciation reveals that the trace elements are unsaturated and bound in immobile phases with some occurring as free mobile ions.

Keywords Heavy Metals, Soils, Geo-accumulation Index, Calabar, Nigeria

1. Introduction

Geochemical mapping and techniques have in recent times found diverse applications in studies of urban environment using various sampling media. This has been geared by the need to identify contaminated land and subsequent health risk assessments. Soils are considered as a very important ecological crossroad in the landscape because it constitutes a recognizable repository for the transfer, retention and domiciliation of current or potentially toxic pollutants within the geo-system. The contents of these potential pollutants may be from natural sources but increases with time are related to anthropogenesis of urbanization. Rock weathering often mobilizes elements into the soil leading to distribution and dispersion along the geochemical cycle in the secondary environment. Contents of these metals in soils govern the composition of the elements in plants and animals with an attendant influence on human and animal health. Trace element distribution in soils depends on factors such as nature of the parent material, weathering processes, human activity and climatic conditions (Martinez et al., 2003). Trace metals such as As, Pd, Cd are characterized by long residual periods, high invisibility, little transfer, high toxicity and complexity of behaviours (Alloway, 1995). Trace metals, even the most potentially toxic ones can be essential

nutrients for growth of plants and animals but exposure to elevated levels can pose threat to health and life (Nriagu and Pzcyna, 1988; Qian et al., 1996). The assessment of potentially toxic elements in soils and sediments in urbanized and industrial settings are evident in the works of Zachmann and Block, 1993; Thuy et al., 2000; Manjunatha et al., 2001; Abraham and Parker, 2002; Edet et al., 2003; Ekwere and Elueze, 2011 and Foli et al., 2012).

The Calabar area, where the present research is conducted, is an attractive socio-economic centre of the nation due to its thriving tourism potentials and fast developing sea port. Most of the lands in the metropolis are used for different purposes including residence, hospitality, industrial and commercial activities, agriculture and reserves. The influx of visitors during the annual carnival parade and the resulting rapid growth of human and industrial population in the area are bound to affect the environmental quality of surface soils in the area. This study therefore attempts to provide information on soil chemistry and possible anthropogenic impacts of environmental pollution in the metropolis. This is relevant for the management and sustainable development of this rapidly developing urban setting.

1.1. Description of Study Area

The study area spans two local administrative political units; Calabar municipality and Calabar-South local council. Both constitute the larger Calabar metropolis, which was the first administrative capital of Nigeria. Geographically the area is delimited by latitudes 4° 15' - 5° 15' North and longitudes 8° 15' - 8° 25' East (Fig. 1). The area receives an

* Corresponding author:

zerratta77@yahoo.com (Azubuike S. Ekwere)

Published online at <http://journal.sapub.org/geo>

Copyright © 2014 Scientific & Academic Publishing. All Rights Reserved

annual average rainfall of about 254mm within two distinct seasons; wet and dry. Mean annual temperature and relative humidity are 26.8°C and 84.6% respectively. The geology of Calabar area is built on the Tertiary and Quaternary sediments of the Niger Delta basin (Short and Stauble, 1967). This basin consists of alternating sequence of gravel, sand, silt, clay and alluvium which are most likely derived from the adjoining Precambrian basement (Oban Massif) complex

and Cretaceous rocks. The basement complex is made up of gneisses, granites, schists, pegmatites and host of ultra-mafic suites (Ekwueme, 2003), while The Cretaceous sedimentary unit (Calabar Flank) is built up of limestone, sandstones, shales and marls (Reijers, 1996). Topographic variations extend from less than 10m in the south to about 80m in the north of the study area.

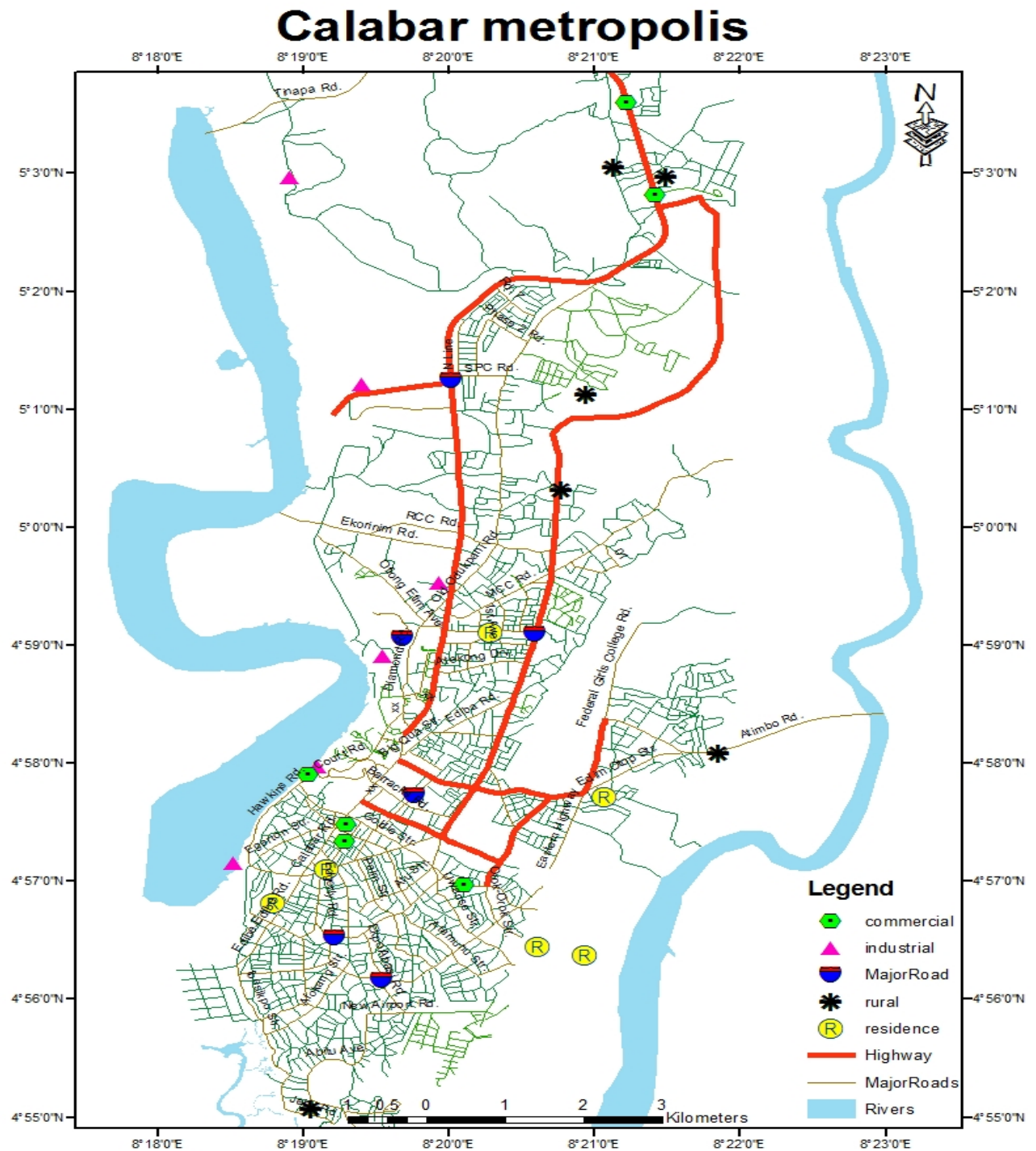


Figure 1. Map of Calabar metropolis showing sample locations

2. Methodology

Thirty soil samples were collected from locations around the study area. The samples which are described as; urban, industrial and rural soils straddled the different soil suites.

The urban soils were collected from residential and commercial areas as well as along major motored roads. These soils are expected to exhibit elevated metal contents due to contamination by anthropogenic activities such as domestic and industrial waste disposal and vehicular exhausted fumes. The rural soils are uncultivated, expectedly less contaminated with metal contents reflecting parent material and other soil-forming factors such as climate, topography and organic matter content. The industrial soils were collected from the industrial parks within the metropolis.

Surface soil samples were taken at depths of 0 – 15cm using a shovel at each location. About 0.5kg of samples was collected at sampling points, stored in polythene bags which were transported to the laboratory.

In the laboratory the samples were air dried and disaggregated in a porcelain mortar using a rubber-end pestle. A nylon sieve was used to obtain < 63µm fraction (active fraction) of the soils for chemical analysis. Initial digestions of samples were carried out using the Heinrichs and Hermann (1990) method. This involved reaction of the samples with a combination of concentrated HF-HNO₃-HCl acids. The solution was then transferred into clean Teflon beakers and evaporated to dryness on a hot plate. To completely remove fluoride ions, 5ml concentrated HCl were added twice to the dried residue and evaporated to incipient dryness. Heavy metal analysis was carried out by

Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

3. Results and Discussion

Statistical summary of chemical analytical data of surface soils from the Calabar area are presented according to soil categories, in Table 1. Observations reveal that the industrial soils tend to be relatively higher in metal (Fe, Mn, Zn, Cd and Ni) concentrations compared to other soil categories. The average concentrations are 72.40ppm for Fe, 68.40ppm for Mn, 76.80ppm for Pb, 62.80ppm for Zn, 1.68ppm for Cd and 16.20ppm for Ni. Next to this are soils from major motored roads with mean values of 106.60ppm for Pb, 17.30ppm for Cu and 18.40ppm for Cr. Highest mean values of cobalt are recorded in the soils from the commercial urban areas and arsenic in the soils from the residential area. Generally the commercial areas exhibit high metal concentrations next to the industrial soils. Least contents of metals are generally exhibited by the soils from rural or remote areas with least anthropogenic impacts.

A general overview shows no substantial accumulations of metals in urban, industrial and rural soils except for lead (Pb). Pb shows a substantial enrichment in soils along major motored roads and the commercial sites within the study area. Pb concentrations range between 8.80 – 136.60ppm with average values of 98.50ppm and 106.60ppm from commercial and motored road soils respectively. These values are about 7 to 8 times the concentrations for the rural and residential area soils.

Table 1. Statistical summary of chemical analytical data of surface soils from the Calabar area, south-eastern Nigeria; all values in ppm

Element		Residential (n=6)	Motor roads (n=6)	Commercial (n=6)	Industrial (n=6)	Rural (n=6)
Fe	Mean	23.25	32.00	38.00	72.40	35.30
	Range	9.00 - 34.00	18.00 - 46.00	28.00 - 48.00	36.00 - 116.00	12.00 - 46.00
Mn	Mean	57.00	36.70	59.00	68.40	55.76
	Range	42.00 - 77.00	22.00 - 42.00	36.00 - 74.00	28.00 - 108.00	40.00 - 85.00
Pb	Mean	13.20	106.60	98.50	76.80	12.70
	Range	8.80 - 18.00	78.00 - 136.60	75.00 - 136.00	16.00 - 114.00	12.00 - 16.80
Zn	Mean	19.50	49.70	52.00	62.80	20.30
	Range	9.00 - 25.00	24.00 - 94.00	16.00 - 78.00	14.40 - 122.00	14.80 - 28.00
Cu	Mean	12.25	17.30	16.50	13.50	11.70
	Range	8.00 - 16.00	12.80 - 22.00	14.00 - 22.60	9.60 - 36.00	10.50 - 12.60
Cd	Mean	0.85	1.35	1.04	1.68	0.72
	Range	0.20 - 1.80	1.06 - 1.80	0.80 - 1.88	0.60 - 2.46	0.64 - 0.80
Cr	Mean	16.45	18.40	16.80	14.20	17.40
	Range	9.80 - 26.00	10.00 - 32.40	14.00 - 26.60	12.00 - 18.60	14.80 - 22.00
Co	Mean	5.45	6.44	10.40	5.86	3.30
	Range	4.80 - 6.20	5.80 - 7.84	7.60 - 11.80	4.00 - 7.40	0.80 - 6.40
As	Mean	5.65	4.86	4.20	3.72	3.80
	Range	4.60 - 6.00	4.38 - 5.40	3.80 - 5.40	3.60 - 6.78	0.44 - 8.00
Ni	Mean	12.00	10.46	9.40	16.20	13.70
	Range	10.00 - 15.00	8.40 - 14.80	8.00 - 12.40	12.00 - 18.00	10.00 - 20.40

Table 2. Correlation matrix for the soils within the study area

	Fe	Mn	Pb	Zn	Cu	Cd	Cr	Co	As	Ni
Fe	1.00									
Mn	0.55	1.00								
Pb	0.42	-0.10	1.00							
Zn	0.75	0.29	0.67	1.00						
Cu	0.80	0.48	0.62	0.93	1.00					
Cd	0.57	0.30	0.66	0.82	0.83	1.00				
Cr	0.04	0.11	-0.13	-0.27	-0.12	-0.33	1.00			
Co	-0.08	-0.15	0.36	0.03	0.00	0.11	0.33	1.00		
As	0.45	0.45	0.18	0.32	0.30	0.18	-0.15	-0.19	1.00	
Ni	0.36	0.25	-0.26	0.18	0.04	-0.01	-0.11	-0.26	0.49	1.00

3.1. Geo-statistical Methods

Correlation trend between metals across the various soil categories is shown in the correlation matrix table (Table 2). Observation shows a moderate positive correlation (0.50-0.70) of Fe with Mn (0.55) and Cd (0.57). A strong positive correlation (>0.70) exists for Fe with Zn (0.75) and Cu (0.80). Pb exhibits moderate positive correlation with Zn (0.67), Cu (0.62) and Cd (0.66). The strongest correlations are exhibited between Zn: Cu (0.93), Cd (0.82) and Cu: Cd (0.83). The correlation of Fe to Mn, Cd, Zn and Cu are reflective of background associations of these metals as concentrations of sediments derived from the ferromagnesian and related rocks most likely sourced from the adjoining Precambrian basement (Oban Massif) terrain. The correlations between Pb, Zn, Cu and Cd may be attributed to sediments from chalcophile progenitor rocks which are within the catchment region. The Lower Benue Trough is a typical example.

Factor analysis statistical technique was applied for the refinement observed correlations among the metals and environmental factors. The rotated factor matrix is given in Table 3. Only factor loadings greater than 0.50, were considered significant for interpretation. Three explicable factor groupings accounting for about 77% of total data variance, reveals a dominant lithogenic control on metal concentration in the soils. Factor 1 (Fe, Mn, Pb, Zn, Cu, Cd) accounts for about 43% of total data variance. This factor is related to geogenic sourcing of metals in sediments from the rocks of the basement complex. Factor 2 (Pb, Cr, Co, As, Ni) accounts for 20% of data variance. This factor is also a petrologic factor from the metal association, which can be attributed to soil chemistry related to sediments derived from the ultra-mafic/mafic rock suites of the Oban Massif. Imprints of metal complexing from exchange and replacement reactions may also be established. Factor 3 (Cr and Co) accounts for 13% of data variance and can be of geogenic or anthropogenic control.

Similarly cluster analysis reveals three significant factor loadings of; F1 (Fe, Pb, Zn, Cu, Cd), F2 (Fe, Mn, As, Ni) and F3 (Cr, Co). These clusters determine the oblique factors for hierarchical analysis.

Though, influence of anthropogenesis may be evident in geochemical characteristics of some soil categories,

principal component analysis shows that geologic control is more dominant.

Table 3. Factor loadings for analysed metals

Elements	Factor 1	Factor 2	Factor 3
Fe	0.8556	0.2046	0.2500
Mn	0.5038	0.4925	0.4231
Pb	0.6572	0.6061	0.0752
Zn	0.9403	0.1361	0.1112
Cu	0.9494	0.1232	0.0570
Cd	0.8531	0.2817	0.1718
Cr	0.2264	0.0883	0.8990
Co	0.0019	0.6418	0.5790
As	0.4937	0.5515	0.0490
Ni	0.2240	0.7448	0.0015
% total variance	42.7627	20.4347	13.3312
Cumul. %	42.7627	63.1975	76.5287

3.2. Metal Speciation

Speciations of extractable aqueous phases of metals were assessed by means of geochemical modelling using the visual MINTEQ modelling program. Results shows that lead (Pb) is primarily bound in oxide and hydroxide phases (litharge and massicot). Pb also occurs bound with arsenate [$\text{Pb}_3(\text{AsO}_4)_2$] and as free mobile ions. These extractable fractions of Pb account for about 93% of total concentration.

Fe occurs mainly as amorphous Fe-oxides and in organic bounded phases. Associated with these Fe-oxides are metals such as Ni, Co and Cu.

Copper occurs as amorphous tenorite accounting for about 46% of total concentration and also as free mobile ions. Manganese (Mn) is primarily bound entirely as pyrochroite (82%) and a fraction to amorphous Fe-oxide. Zinc (Zn) is bound in multiple soluble hydroxide phases, arsenate [$\text{Zn}_3(\text{AsO}_4)_2$] and zincite accounting for about 72% total concentration. Cadmium exists almost entirely as free mobile ions. Cr exists as free mobile ions constituting about 73% of total extractable fraction and about 20% occurring as hydroxide bound phase.

All the metals generally occur at concentration levels below equilibrium i.e. they are unsaturated within the soil media. Elements can accumulate or be depreciated during erosion episodes depending on the soil type and soil pH (acidity). The depletion of metals such as Co, Cu, As and Ni

could be due to the assumption that, monovalent or divalent element are lost during long periods of weathering. This is because these metals cannot be incorporated into the structures of clay mineral fractions without producing charge imbalances (Martinez, 2003). Pb though divalent, showed enhanced concentration for some of the soil categories suggesting mobilization from anthropogenesis. Pb as well as Zn is capable of forming strong complexes with soil organic matter (Martinez, 2003), probably within the hydromorphic soil zones.

3.3. Geo-accumulation Index (I_{geo})

As a means of quantifying metal accumulation related to contamination, data for the different soil categories were subjected to computation of geo-accumulation index (I_{geo}). This index has been applied widely for evaluation of degree of metal pollution in different environments (Manjunatha et al., 2001; Tijani et al., 2004 and Elueze et al., 2009). The geo-accumulation index is expressed as;

$$I_{geo} = \log_2 (A_n/B_n \times 1.5)$$

Where: A_n = concentration of element A in a sample

B_n = background value of element A (average shale composition, Wedepohl, 1971)

1.5 = factor for possible variations in background data due to lithologic effects.

Results from computation are as shown in Table 4(a) and interpretation is based on the seven grade classification scheme of Muller (1979) in Table 4(b). From Table 4(a), it is obvious that the investigated soils are unpolluted for most of the metals. Pb exhibits enrichment in soils with values within the moderately polluted level, while soils from the motored roads show levels within moderately – highly polluted range. Fe, Mn, Zn, Cu and Cd fall within the unpolluted - moderately polluted range for soils from the commercial and industrial areas. Cadmium ranges from unpolluted to moderately polluted for all the soils except the rural soils and the same trend exist for Cu with exception of residential area soils. All other metals are within the background levels, implying no significant contributions from anthropogenesis, earlier noted with geo-statistical methods.

Table 4(a). Geo-accumulation index of soils types from study area

Element/Soil type	RA	MR	CA	IA	RUA
Fe	-2.96	-1.26	0.14	0.56	-1.72
Mn	-0.21	-0.43	0.14	0.49	-0.19
Pb	1.96	2.06	1.86	1.44	1.04
Zn	-0.78	-0.24	1.36	0.96	-0.46
Cu	-0.95	0.22	0.87	1.06	0.48
Cd	0.34	0.42	0.68	0.16	-0.26
Cr	-1.82	-1.54	-0.62	-0.55	-1.74
Co	-1.15	-0.72	-0.16	-1.05	-0.78
As	-0.44	-0.54	-0.20	-0.12	-1.02
Ni	-1.88	-1.05	-0.96	-1.02	-1.86

NB: RA-residential area; MR-motored roads; CA-commercial area; IA-industrial area; RUA-rural area

Table 4(b). I_{geo} classification grade (after Muller, 1979)

I_{geo} Class	Sediment quality
< 0	Unpolluted
0 - 1	Unpolluted – moderately polluted
1 - 2	Moderately polluted
2 - 3	Moderately – highly polluted
3 - 4	Highly polluted
4 - 5	Very highly polluted
5 - 6	Extremely polluted

3.4. Environmental Implications

Elevated concentrations and exposure of trace metals in the environment can pose a serious health concern for plants, animals and humans. The element Pb is ubiquitous in natural environment and is considered a non-essential element (Merian, 1991). Guagliardi et al., (2010) observed that many urban soils are contaminated with high concentrations of lead and exposure to it disrupts the development of the nervous system, causing delays in growth and learning disabilities. However in the study area this element is relatively low in concentration though I_{geo} indicates moderate pollution levels. Its elevated concentration is basically in soils in the vicinity of motored roads. It is therefore reasonable to attribute its accumulation as resulting from automobile exhaust fumes along motored roads, waste disposal from automobile repair shops and other forms of indiscriminate dumping of effluents within commercial areas. Vehicular emission is commonly known to be a significant and increasing source of soil pollution in urban environment (Rossini and Fernández, 2007). These are evident from the observed dotting of numerous automobile repairs and spare parts retail shops within the metropolis.

Cadmium (Cd) is another non-essential element for biota growth and development and potentially toxic. Though existing almost entirely as free mobile ions in the studied soils, concentration indicates levels that are within background with a considerably small environmental impact.

Cr contents vary for the different soil categories within background levels. Content of extractable fraction (> 90%) exists as free mobile ions and as hydroxide bound complexes. The concentration poses no significant environmental concern.

Other metals; Fe, Mn, Co, As, Ni, Cu and Zn, as revealed from I_{geo} , are generally depleted for all soil categories, probably due to weathering episodes and mineralogical variations in the catchment geology. These metals exist in low concentrations bound largely in immobile phases as revealed from metal speciation modelling, thus posing minimal environmental impact.

4. Conclusions

Results and interpretation show that the surface soils in Calabar metropolis are affected by anthropogenic activities but at very low degrees of possible environmental impact. Geogenic sourcing appears to be the dominant controlling

factor on metal levels in soils within the study area. The enrichment of Pb is noticeable in soils of major motored roads and areas of increased human activities (commercial and industrial layouts). The other metals are depleted below expected levels of pedogenic origin. This may result from weathering episodes and some form of organo-metallic complexing. However mean concentrations are within acceptable range and bound in phases of no serious hazard potency.

The study has provided background information for vulnerability assessment of sampled areas for future investigation and development planning. A complete and detailed mapping of trace metal distribution in each of the urban soil groups especially along profiles may be recommended. This will provide information to vector the trend of these metals over time.

REFERENCES

- [1] Martinez, (2003). Distribution of some selected major and trace elements in four Italian soils developed from the deposits of the Gauro and Vico volcanoes. *Geo-Derme*, 117(3-4): 215-224.
- [2] Alloway, B. J., (1995). Heavy metals in soils. Blackie Academic and Professional, London, pp. 38-57.
- [3] Nriagu, J. O. and Pzcyna, J. M., (1988). Quantitative assessment of worldwide contamination of air, water and soil trace metals. *Nature*, 333: 134-139.
- [4] Qian, S., Wang, Z and Tu, Q., (1996). Distribution and plant availability of heavy metals in different particle-size fractions of soils. *Sci. Total Environ.*, 187 (2): 131-141.
- [5] Zachmann, D.W., and Block, R., (1993). Studies of availability of toxic elements in soils and stream sediments in the vicinity of a lead smelting site (Germany).
- [6] Thuy, H. H. T., Tobschall, H. J., and An, P. V., (200). Distribution of heavy metals in urban soils – a case study of Danang-Hoian area, Vietnam. *Environ. Geol.* 39(6) pp.603-610.
- [7] Manjunatha, B. R., Balakrishna, K., Shankar, R., and Mahalingam, T. R., (2001). Geochemistry and assessment of metal pollution in soils and river components of a monsoon-dominated environment near Karwar, southwest coast of India. *Environmental Geology* 40: pp.1462-1470.
- [8] Abraham, G and Parker, R., (2002). Heavy metal contaminants in Tamaki estuary: impact of city development and growth, Auckland, New Zealand. *Environmental Geology* 42: pp. 883-890.
- [9] Edet, A. E., Merkel, B. J., and Offiong, O. E., (2003). Trace element hydrochemical assessment of the Calabar coastal plain aquifer, south-eastern Nigeria, using statistical methods. *Environmental Geology* 44: pp. 137-149.
- [10] Ekwere, A. S. and Elueze, A. A., (2011) Trace Element Assessment of Stream Sediments around the Aluminium Smelting Company in Ikot-Abasi, South-Eastern Nigeria. *Res. Jour. Applied Sci. Engr. & Tech.* vol. 4(4) pp. 256-261.
- [11] Foli, G., Nude, P. M. and Apea, O. B., (2012). Geochemical characteristics of soils from selected districts in the upper east region, Ghana: Implication for trace element pollution and enrichment. *Res. Journ. Environ. Earth Sci.* 4(2): 186-195.
- [12] Short, K. C., and Stauble, A. J., (1967). Outline of geology of Niger Delta. *AAPG Bulletin* 52, pp.761-779.
- [13] Ekwueme, B. N., (2003). The Precambrian geology and evolution of the south-eastern Nigerian basement complex. University of Calabar Press 135p.
- [14] Reijers, T. J. A., (1996). Selected Chapters on Geology, Sedimentary Geology and Sequence Stratigraphy and three case studies and field guide, SPDC Publications, Warri, Nigeria, 197p.
- [15] Heinrichs, H. and Hermann, A. G., (1990). Practical Geochemical Analysis. Springer Verlag, Berlin, Heidelberg, New York 355p.
- [16] Tijani, M. N., Jinno, K., and Hiroshiro, Y., (2004). Trace element distribution in aquatic sediments of Ogunpa River, Ibadan area, south-western Nigeria. *Jour. Min. Geol.* vol. 40(1) pp.73-83.
- [17] Elueze, A. A., Ekwere, A. S., and Nton, M. E., (2009). Geoenvironmental assessment of the environs of the Aluminium Smelting Company in Ikot Abasi, south-eastern Nigeria. *Journal of Geology and Mining.* Vol.45. No.2: pp. 115-128.
- [18] Wedepohl, K. H., (1971). Environmental influences on chemical composition of shales and clays, in Ahrens, L. H., Press, F., Runcom, S. K., and Urey, H. C., eds., *Physics and Chemistry of the Earth*, v.8: Oxford, Pergamon Press, p. 305 – 335.
- [19] Muller, G., (1979). Schwermetalle in der sedimenten de Rheins Veranderungen Seit 1971. *Um shau* 79: pp. 778-783.
- [20] Merian, E., (1991). Metals and their compounds in the environment. Occurrence , analysis and biological relevance. VCH, Weinheim.
- [21] Guagliardi, I., Buttafuoco, G., Cicchella, D., and De-Rosa, R. (2010). Assessment of lead contamination in urban soils in an area of southern Italy. 19th World Congress of Soil Science, Soil Solutions for a Changing World. August 2010, Brisbane, Australia
- [22] Rossini, O. S and Fernández, E. A. J. (2007) Monitoring of heavy metals in topsoils, atmospheric particles and plant leaves to identify possible contamination sources. *Microchemical Journal* 86, 131-139.