Assessment Of Elemental Concentrations Of Roadside Soils In Relation To Traffic Density In Calabar, Nigeria

I.O. Akpan, E.S. William

Abstract: This study employs Particle Induced X-ray Emission (PIXE) analytical technique for the analysis of elemental concentrations in the roadside soils in Calabar, Nigeria, in order to ascertain the levels of heavy metals in relation to traffic density. Twenty one elements, viz., Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Nb and Pb with concentrations (in ppm), ranging from 9.0±3.8 (Ga) to 192560.3±789.5 (Si) respectively were detected from ten different sample locations. Significant enrichment were obtained for Mn(7.677); Cu(5.189); Zn(5.203, 5.177 and 6.554); Ti (5.723, 5.395 and 5.000); Cr (6.901, 7.323 and 14.321); P(5.683, 5.750) and Si(6.747) respectively, indicating that their concentrations were sufficient to pose environmental problems. High concentrations of Pb in areas of high traffic density and the Strong, positive and significant correlation results corroborate with results of enrichment factor, cluster analysis and counting statistics of number of vehicles plying sample locations thereby confirming heavy metals on roadside soils in Calabar to be associated with vehicular emissions.

Key words: Calabar, Elemental concentration, Heavy metal, PIXE, Roadside, Soils, Traffic density

1. INTRODUCTION

Soil is an important component of the biosphere because it is not only a geochemical sink for contaminants, but also acts as natural buffer controlling the transport of chemical elements and substances to the roadside soils. However, the most important role of soil is its productivity [1]. In Calabar, due to the rapid increase in the number of motor vehicles on Calabar roads as a boast for economic and commercial activity, considerable amount of some heavy metals are emitted to our environment. The risk posed by heavy metals to food safety and the environment are of great concern to governments and society in many countries [2], [3]. In developing countries like Nigeria, improved road accessibility most especially in urban area creates a variety of ancillary employment which range from vehicle repairs, vulcanizer, welders, battery chargers and dealers in other facilitators of motor transportation. These activities send trace metals into the air and the metals subsequently are deposited into roadside soils, which are absorbed by plants on such soils. Soil tends to accumulate metals on a relatively long term basis since many metals in the soil are so mobile. This explains the overall higher contamination level of metals in the soil [4], [5]. However, the pollution of soil by heavy metals from automobile sources is a serious environmental issue. The mechanisms of heavy metal emissions from vehicles consist of fuel and engine oil consumption, tyre and brake wear and road abrasion [6], [7]. Lead, cadmium, copper, and zinc are the major metal pollutants of the roadside environments and are released from fuel burning, wear out of tyres, leakage of oils and corrosion of batteries and car radiator.

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Apart from anthropogenic activities, heavy metals can also be found naturally with large variations in the soil. It can also be transported into the roadside soils by atmospheric precipitation or road runoff [8], [9]. It is pertinent to note that for soil to fulfill its function in agricultural production and as a habitat for numerous beneficial microorganisms, heavy metals accumulation have to be minimized to a level that is not deleterious to the ecosystem. Therefore long term accumulation of heavy metals in agricultural soils may cause serious ecological problems if tolerance levels are exceeded [10]. There is need to determine heavy metal contents in the soils to understand soil/plant uptake ratios of these toxic substances so as to monitor their pathway from soil to man [11]. Therefore this study will assess the total elemental concentration of roadside soils in relation to traffic density in Calabar and determine the levels of the contaminants.

2. MATERIALS AND METHODS

2.1 Study area

The study area is located between latitude $8^0 15^1$ E to $8^0 25^1$ E and longitude $4^0 50^1$ N to $5^0 05^1$ N as shown in Fig. 1. Ten roadside and a farmland in Eastern highway lane were chosen for this study within Calabar metropolis in Cross River State, Nigeria. Sample locations 1 to 11 represent Marian road, Ikot Ishie road, Odukpani road, Atimbo road, New Airport road, Eneobong street, Atakpa street, Edet Essien street, Home farm estate, Satellite town and Eastern Highway lane respectively. The first five locations are areas of high traffic density while the other five are of low traffic density.

2.2 Sample collection and preparation

At each location, soil sample were collected using a stainless hand trowel at 0 - 5 cm depth. As a precaution, stones and plant debris were removed before storage in a polythene bag and labeled properly. The soil was air- dried for seven days and screen with an aperture of 2 mm before it was packaged and taken to Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria for further preparation and analysis. At CERD, each of the dried sample was ground and pulverized to fine powder by SPEX mixer/mill, model S100 agate mortar. After a sample was ground into powder, the mortar and piston were properly cleaned with acetone solution before the procedure was repeated for the next sample. This was done to avoid cross - sample contaminations. Each of the samples was then mixed with 20% ultra-fine carbon in a mixer to reduce charging effects in the sample [12] and pressed into pellets of 13 mm diameter using a pelletizing machine. The pellet preparation set is a standard set that provides the needed control and integrity in sample preparation by ensuring that all samples produced from it meet the required mass and dimensional specifications [13], [14], [15].

2.3 Calibration of detector

The detector used in the study was calibrated before the analysis to ensure accuracy and quality assurance. This was done by analyzing a standard reference material from International Atomic Energy Agency (IAEA) soil 7. The values obtained from this analysis were then compared with the certified values. It was found to be in agreement with the present study.

2.4 Analysis of samples using PIXE technique

Analysis of the samples was carried out using a Pelletron accelerator, model 5SDH, installed at the Centre for Energy Research and Development (CERD) Obafemi Awolowo University, Ile-Ife. Eleven samples of soil were loaded in a sample ladder and then placed in irradiation chamber. A 4 mm diameter beam of protons with energy of 2.5 MeV with a charge on target of 0.5 μC and a beam current which varies between 4.6 – 20.3 nA was directed on the sample. After the first pellet was analyzed, the position of the ladder was adjusted by turning a knob so that the beam will be directed to the next target until all the eleven samples were analyzed. Camberra Si(Li) detector was used in order to obtain a suitably high sensitivity characteristic X-ray emitted by each sample for each element. The signals received were processed further at a multipurpose end station to obtain PIXE spectra. The computer measures the peak intensity for each element present in the sample and converts it to concentration which was then read and recorded. After running the sample, the system takes the measurement over and over again for a reasonable number of times so that it can calculate a mean value and standard deviation of the measurements. This was used in calculating the statistical error for the measurements [16].

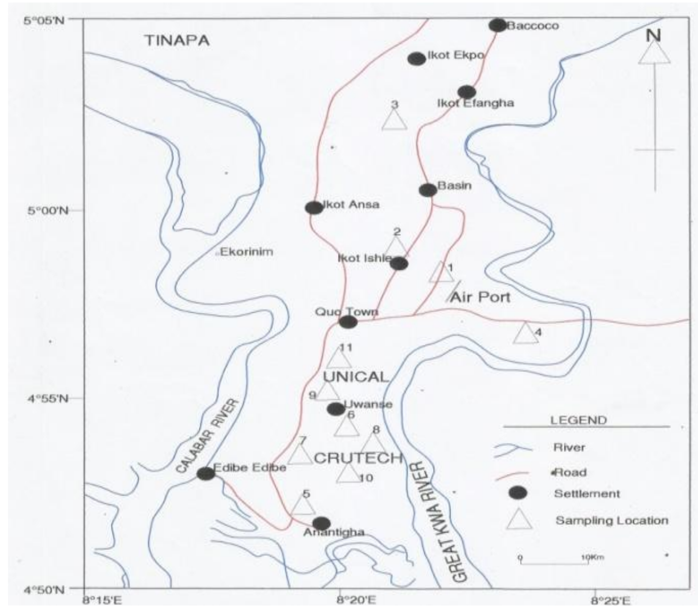

Fig. 1: Map of Calabar showing sample locations

3. RESULTS AND DISCUSSION

The results of the analysis of standard reference material for SOIL 7, together with the certified values are as shown in Table 1. These results were in good agreement with the certified values thereby leading confidence to the reliability of the data obtained in this study. The results of control used for this study is as presented in Table 2. The results of PIXE analysis of soil sample is presented in Table 3. Twenty one elements, Viz., Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Nb and Pb were detected in the roadside soils and their respective concentrations (ppm) were determined.

Table 1: Results of standard reference material for SOIL 7

Elements	Concentration (ppm) ±Error	Certified value
Mg	9,070.0 ±1176.4	9,040
Al	37,616.1 ±662.0	37,600
Si	143,985.0±835.1	144,000
K	9,678.8±66.8	9,680
Ca	130,427.8±143.5	130,400
Ti	2,442.2 ±24.9	2,400
V	68.0 ±18.6	52.8
Cr	90.5 ±11.0	[b]
Mn	525.6 ±13.3	504.8
Fe	20,568.4 ±63.8	20560
Ni	39.9 ±8.5	20.8
Zn	84.3±8.6	83.8
Ga	14.0 ±6.0	8
Rb	41.1±16.3	40.8
Sr	86.7±20.5	86.4
Pb	48.7 ±20.4	48.0

[b] Not detected.

Table 2: Results of control soil sample at eastern Highway

Elements	Concentration ±Error (ppm)
Al	18,078.4 ±379.7
Si	63,820.2 ±523.3
P	378.1 ±154.4
Cl	202.4±47.2
K	2,238.6±31.6
Ca	5,867.4±34.0
Ti	1,030.0 ±26.1
V	40.4±20.5
Cr	27.1 ±7.2
Mn	100.1 ±9.3
Fe	26,042.6±65.1
Ni	11.8±6.2
Cu	21.4±6.3
Zn	127.9±12.9
Ga	12.8 ±7.1
As	9.6 ±6.7
Rb	21.2 ±13.8
Sr	33.4±16.4
Zr	227.0±48.3

.**Table 3:** Sample locations and concentrations (ppm) of elements in the soil

Locations	Al	Si	P	Cl	K
Atimbo	13,029.6 ±444.9	157,780.5 ±725.8	893.0 ±173.8	226.3±46.9	15,28.3 ±27.5
Atakpa	7,302.7±342.9	107,652.3±592.1	645.0 ±158.9	[b]	3,000.6 ±34.5
Edet Essien	16,134.6±371.1	91,884.2±588.1	663.3 ±159.3	177.6 ±47.9	3,175.7 ±35.3
Eneobong	12,305.4±443.8	165,505.4±744.8	610.2±194.8	187.9 ±50.1	1,942.7 ±31.5
Home Farm	8,123.6±497.8	192,560.3±789.5	961.0±196.3	311.4 ±49.9	1,584.3 ±28.9
Ikot Ishie	14,800.2±361.1	97,478.0±584.8	1,308.2±177.3	185.1 ±51.7	1,654.2±29.9
Marian	17,213.5±428.7	124,604.8±672.8	870.6 ±179.6	242.9±50.5	3,187.5±36.9
New Airport	8,002.9±307.5	95,029.4±551.2	464.5±149.9	111.9±44.0	2,464.6±31.8
Odukpani	18,557.8±398.9	103,280.1±630.0	1,438.0 ±215.9	149.5±56.3	2,542.5±35.3
Satellite T.	13,517.8 ±463.4	136,055.6±693.9	385.6 ±172.8	303.8 ±52.5	2,160.0 ±32.2

Locations	Ca	Ti	V	Cr	Mn	Fe
Atimbo	478.6 ±15.8	2,348.1±18.8	43.7±13.5	51.7±6.6	49.8±6.8	14,034.7±47.7
Atakpa	3,244.0±28.6	1,758.2±16.5	[b]	70.9±6.2	69.5 ±6.6	9,872.8±39.5
Edet Essien	3,355.8 ±29.2	2,110.8±17.9	[b]	90.9±7.0	133.1±8.5	24,770.2±61.9
Eneobong	4,527.2±31.7	2,659.1±20.2	52.9±14.9	110.5±7.3	89.6 ±7.7	14,501.2±47.9
Home Farm	1,710.6 ±21.9	2,636.2±20.0	44.0±14.6	43.5 ±6.7	54.4 ±6.8	11,646.7±43.1
Ikot Ishie	4,379.6 ±31.1	3,343.8±22.1	62.2±17.3	46.9±8.1	178.3±9.6	15,670.2±50.1
Marian	3,542.9±30.1	3,832.0±23.4	61.7±18.1	293.5±9.3	124.3±8.9	19,694.5±57.1
New Airport	1,869.3 ±22.9	1,561.2±15.6	[b]	54.7 ±5.8	319.7±9.0	10,834.1±42.3
Odukpani	14,873.5±52.1	2,553.7±20.7	87.6±15.1	71.5 ±7.8	216.6±9.6	20,820.8±58.3
Satellite T.	1,027.2±20.5	2,794.3±20.9	78.5±15.9	44.2 ±8.1	56.3 ±8.4	15,922.5±50.9

Locations	Ni	Cu	Zn	Ga	Br	Rb
Atimbo	[b]	49.2 ±7.5	300.2 ±6.1	[b]	19.1 ±7.7	[b]
Atakpa	6.3 ±4.7	39.1 ±6.1	152.8 ±8.3	9.0 ±3.8	[b]	29.3 ±12.2
Edet Essien	23.8±7.0	29.8 ±9.7	633.0±16.3	[b]	[b]	[b]
Eneobong	[b]	37.9 ±6.9	319.6±11.9	16.9±5.4	15.0±6.8	28.4±12.3
Home Farm	[b]	17.9±6.5	46.6±5.9	[b]	[b]	30.8±11.5
Ikot Ishie	26.5±8.9	38.1±54.3	398.4±15.3	[b]	[b]	[b]
Marian	18.4±6.5	52.4 ±7.8	218.1±10.7	18.3±7.0	[b]	[b]
New Airport	[b]	46.2 ±6.2	129.0 ±8.1	[b]	[b]	[b]
Odukpani	44.6±6.9	81.7 ±8.9	670.2±13.4	[b]	[b]	[b]
Satellite T.	[b]	[b]	[b]	[b]	[b]	[b]

Locations	Sr	Zr	Nb	Pb
Atimbo	47.4 ±14.1	133.2 ±36.9	[b]	25.1 ± 32.2
Atakpa	29.6±12.8	150.9 ±28.7	[b]	[b]
Edet Essien	42.3 ±17.9	206.7 ±34.0	[b]	23.7±12.8
Eneobong	67.8 ±18.1	505.8 ±49.8	56.8 ±22.8	33.8 ±14.7
Home Farm	42.6 ±13.9	193.8±36.5	[b]	[b]
Ikot Ishie	56.2 ± 27.1	140.5 ±37.5	[b]	37.5± 23.6
Marian	43.6 ± 37.1	372.5 ±50.0	59.4 ±24.2	39.2 ± 65.1
New Airport	57.3±12.2	417.8 ±43.6	[b]	39.0 ±13.2
Odukpani	59.7±14.7	300.7±37.9	[b]	43.5± 13.6
Satellite T.	[b]	314.6 ±41.5	[b]	[b]

[b] Not detected.

Table 4: Enrichment factor of elements in the roadside soil

Sample Locations	Al	Si	P	Cl	K	Ca	Ti	V	Cr	Mn	Ni	Cu	Zn	Sr	Zr
Atakpa	1.066	4.448	4.499	b	3.536	1.458	4.503	b	6.901	1.831	3.644	4.266	4.355	2.338	1.754
Edet E.	0.938	1.514	1.844	0.923	1.491	0.601	2.155	b	3.527	1.398	2.121	1.464	5.203	b	b
SatelliteT.	1.223	3.487	1.668	2.455	1.578	0.286	4.437	3.178	2.668	0.92	b	b	b	b	2.267
Home F.	1.005	6.747	5.683	3.44	1.582	0.652	5.723	2.435	3.589	1.215	b	1.87	0.815	2.852	1.909
Ikot Ishie	1.361	2.538	5.75	1.52	1.228	1.241	5.395	2.559	2.876	2.96	3.732	2.959	5.177	2.796	1.029
Eneobong	1.222	0.227	2.898	1.667	1.559	1.386	4.636	2.352	7.323	1.608	b	3.181	4.488	3.646	4.002
Odukpani	1.284	2.024	4.757	0.924	1.421	3.171	3.101	2.712	3.3	2.707	4.728	4.775	6.554	2.236	1.657
New A.	1.064	3.579	2.953	1.329	2.646	1.766	3.643	b	4.852	7.677	b	5.189	2.424	4.124	4.424
Marian	1.259	2.582	3.045	1.587	1.883	0.798	5	2.019	14.321	1.642	2.062	3.238	2.255	1.726	2.17
Atimbo	1.337	4.588	4.383	2.05	1.267	0.151	4.23	2.007	3.54	0.923	b	2.48	0.435	2.633	1.089

[b] not detected

Table 5: Number of elements detected and their concentration (ppm) ranges in the roadside soils

Sample locations	Number of elements	Concentration (ppm) range	Least element	Highest element
Atimbo	17	30.0 – 157,780.5	Zn	Si
Atakpa	16	9.0 – 107,652.3	Ga	Si
Edet Essien	16	23.7 – 91,884.2	Pb	Si
Eneobong	20	15.0 – 165,505.4	Br	Si
Home farm	17	17.9 – 192,560.3	Cu	Si
Ikot Ishie	17	26.5 – 97,478.0	Ni	Si
Marian	19	18.3 – 124,604.8	Ga	Si
New Airpot	17	33.0 – 95,029.4	Cu	Si
Odukpani	17	43.5 – 103,280.1	Pb	Si
Satellites T.	12	44.2 – 136,055.6	Cr	Si

Table 5 shows number of elements and their concentration ranges for 10 different sample locations. Highest number of elements was detected at Eneobong street with 20 elements followed by Marian road with 19 elements etc. Silicon has the highest concentration in all the sample locations followed by Iron and Aluminum respectively. Aluminum concentration ranges from 7,302.7 – 18,557.8 ppm. Aluminum was detected in all locations. Odukpani road recorded highest concentration while Atakpa street recorded the least concentration. Both WHO/FAO and EFSA has set a Provisional Tolerable Weekly Intake (PTWI) respective Tolerable weekly intake (TWI) to 1 mg/ kg (1 ppm) body weight per week [17]. Aluminium toxicity is associated with the development of bone disorders. Titanium concentration ranges from 1,561.2 – 3,832.0 ppm. The highest concentration was detected at Marian road while the least concentration was at New Airport road. Ti was found in all the sample locations. Titanium average concentration in soil appears to be below 5 g/kg. However, some soils contain titanium dioxide at a concentration of about 10-100 g/kg. The mean titanium dioxide content in the soils ranged from 6 to 12 g/kg [18]. Vanadium concentration ranges from 43.7 – 87.6 ppm. The highest concentration was detected at Odukpani road while the least concentration was at Atimbo road. It was not detected in Edet Essien street, New Airport road and Atakpa street. Dietary intake of vanadium is generally in the range of 10-30 µg/day [18]. Chromium is important for glucose tolerance in human body. The food and nutrition board of the NAS/NRC states that a safe, adequate intake of Chromium for an adult is 18.3g/year [19]. In this study, Chromium concentration ranges from 43.5 – 293.5ppm. The highest concentration was found at Marian road location site while the least concentration was at Home farm estate. It was detected in all the sample locations. Manganese concentration ranges from 49.8 – 319.7 ppm. The highest concentration was recorded in New Airport road while the least concentration was found at Atimbo road. Manganese was detected in all the sample locations. WHO recommended 2–9 mg per day of Mn for an adult [18]. Manganese is known to block calcium channels and with chronic exposure results in CNS dopamine depletion. Iron is an important component of heamoglobin. In this study, Fe concentration ranges from 9,872.8 – 24,770.2 ppm. The highest concentration was recorded at Edet Essien street while the least concentration was at Atakpa street. The maximum iron level permitted for food is 15 mg/ kg (15 ppm) according to Nirmal et al [20]. Nickel concentration ranges from 16.3 – 26.5 ppm. The highest concentration was detected at Ikot Ishie road while the least concentration was at Atakpa street. Nickel was not detected at Atimbo road, Home farm estate, Eneobong street, New Airport road and Satellite town. The prescribed WHO safe limit of Nickel is 3 to 7 mg/day in humans [20]. Excess intake leads to asthma, nausea, headache, and epidemiological symptoms like cancer of nasal cavity and lungs. Copper is an essential substance to human life. Excess Cu causes hypertension, sporadic fever, coma etc [20]. In this study, Cu concentration ranges from 17.9 – 81.7 ppm. The highest concentration was detected at Odukpani road while the least concentration was found at Home farm estate. Copper was not detected at Ikot Ishie road and Satellite town. The acceptable limit for human consumption of Cu is 10.00 mg/kg (10 ppm) [18]. Zinc concentration ranges from 30.0 – 633.0 ppm. The highest concentration was found at Edet Essien street while the least concentration was at Atimbo Road. Zn was found in all sample locations except Satellite town. The acceptable WHO save limit for human consumption of Zn is 150 ppm [20]. Although the average daily intake of Zinc is 7-16.3 mg Zn/day, the recommended dietary allowance is 15 mg Zn/day for men and 12 mg Zn/day for women [21]. Zn is an essential component/cofactor for more than 300 enzymes involved in the synthesis and metabolism of carbohydrates, lipids, proteins, nucleic acids and other micro-nutrients. It is also involved in DNA synthesis and process of genetic expression [21]. Lead concentration ranges from 23.7 – 43.5 ppm. WHO save limit of Pb is 2mg/kg (2 ppm) [18]. Nirmal et al [20] emphasized that most of the accumulated Lead is sequestered in the bones and teeth. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can re-enter the blood stream during periods of increased bone mineral recycling (pregnancy, lactation, menopause, advancing age, etc). Mobilized lead can be re-deposited in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive, and developmental effects [22]. Concentration of Potassium in this study ranges from 1,528.3 – 3,187.5ppm. Marian road recorded highest concentration while the least concentration was detected at Atimbo road. Potassium was detected in all the sample locations. Calcium concentration ranges from 478.6 – 14,873.5ppm. The highest concentration was recorded at Odukpani road while the least concentration was recorded at Atimbo road. Calcium was detected in all the sample locations. Metals such as K, Ca and Ga do not pose any danger to the environment even at high concentration levels although K in the presence of P and N may enhance eutrophication of water bodies. Calcium is needed in the body to build and maintain strong bones. Our heart, muscles and nerves also needs Calcium to function properly. However too little of Calcium in the body may result in health problems related to weak bones, children may not reach their full potential adult height and adults may have low bone mass which is a risk factor for osteoporosis [23]. Phosphorus concentration ranges from 385.6 – 1,438.0 ppm. The highest concentration was recorded at Odukpani road while the least concentration was recorded at Satellite town. Excess phosphorus in the blood can lead to hyperphosphatemia; a condition found in people with damage kidney.The ingestion of heavy metals in the study areas may either come from polluted air from exhaust fumes or the food crop cultivated along these roads as most houses in Calabar are located along roadside and in cluster mode. Generally, concentration of heavy metals in this study are all above the values reported for these metals in soil samples on heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria [5] and studies by Hassan and Basahi [24] in assessing roadside conditions and vehicular emissions using roadside lettuce plants. Also concentrations of heavy metals in this study were found to be higher than studies by Onder et al [25]. Though Co and Cd found in their studies were not detected in the present study. Although the concentration of heavy metals in this study were found to be lower than studies by Arslan and Gizir [26] on heavy metal content of roadside soil in Mersin, Turkey with very high traffic volume in Mersin town compared to the present study, implies that the higher the traffic density, the more the accumulation of heavy metals in the soil. Results of enrichment factor show significant enrichment at Home farm Estate for Si (6.747); P (5.683 and 5.750) at Home farm and Ikot Ishie road; Ti (5.723, 5.395 and 5.000) at Home farm, Ikot Ishie and Marian roads; Cr (6.901, 7.323 and 14.321) at Atakpa street, Eneobong street and Marian road; Mn (7.677) at New Airport road; Cu (5.189) at New Airport road; Zn (5.203, 5.177 and 6.554) at Edet Essien street, Ikot Ishie and Odukpani roads as presented in Table 4.

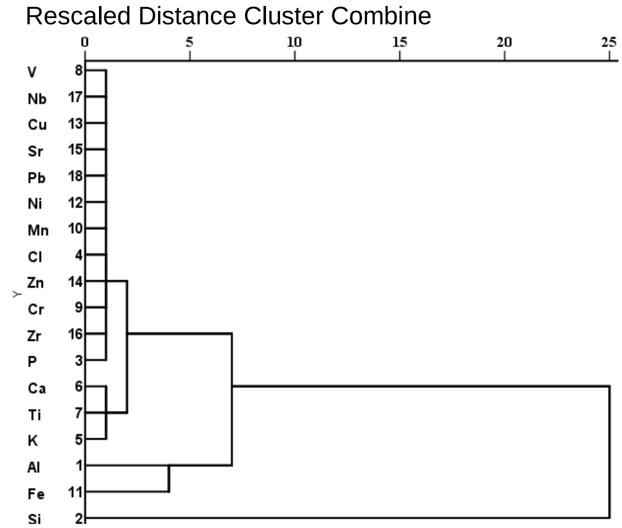

Fig. 2: Cluster analysis of elements in the roadside soils

Fig 2 shows cluster analysis results for the analyzed elements. On the x-axis of the dendrogram is the similarity matrix rescaled distance cluster combine, while on the y- axis are listed number of clusters corresponding to analyzed elements. From the clustering analysis results, the gross elemental associations for all the elements detected in the soils of roadside indicated two major groups, viz., Si as a group which is crustal- type elements and other elements as a group. The last group showed three sup-groups, viz., Al/Fe, Zn/Cr/Zr/P/Ca/Ti/K, and V/Nb/Cu/Sr/Pb/Ni/Mn/ Cl/Zn/Cr/Zr/P. It is observed that heavy metals showed closest inter-elemental clustering indicating that they are from the same source. Table 6 shows the result of Pearson correlation matrices of the soil samples using analyzed elements as variables. The results show that some of the elements were positively correlated while some were negatively correlated. It is noted that elements that are associated with vehicular emission and traffic related cases such as V/Fe (r = 0.784), V/Cu (r = 0.839), V/Zn (r = 0.854), V/Pb (r = 0.907), Mn/Ni (r = 0.899), Fe/Zn (r = 0.832), Al/Fe (r = 0.891), Al/Zn (0.800), Si/Cl (r = 0.696), Ca/Ni (r = 0.952), Ca/Cu (r = 0.765), Ca/Zn (r = 0.673) and P/Ca (r = 0.670) had strong, positive and significant correlation. Similar conclusions were also obtained from studies by Yan et al [27]. While Si/Mn (r = 0.663) and Cl/Mn (r = 0.839) show negative correlations.

3.1 Vehicular movement along sample locations

In studying the rate of traffic density around sample locations, counting statistics was carried out on the number of vehicles plying each sample location per week. Two field assistants were with me mounting at a particular sample location by 6 am with food and a ludo game, with one person counting at a time for an hour before interchanging with the other person. The procedure continued until 6 pm where the exercise closed for the day. This went on for one week before relocating to another sample location to repeat the same procedure till the counting was successfully carried out in all the sample locations. This was done in order to study if there is a relationship between the number of vehicles plying these routes and their influence on the roadside soils. The result show that Marian road recorded 88,020 count number of vehicles followed by Odukpani road with a total of 71,203;

New Airport road recorded 59,259 as Ikot Ishie road and Atimbo road recorded 35,842 and 30,254 respectively while Eneobong street (14,858), Atakpa street (12,706), Satellite town (9,636), Edet Essien street (4,767) and Home farm estate recorded 4,185 count of vehicles as presented in Fig. 3. Major roads like Odukpani, Marian, Ikot Ishie, New Airport and Atimbo had higher traffic densities compared to streets such as Edet Essien, Atakpa, Eneobong, Home Farm and Satellite town. This might be due to commercial activities and transportation of persons and goods within and outside the State. Besides, the major roads serve as link roads to different places in Calabar. This implies that emission from vehicles contributed to heavy metal concentrations in the soils along roadside.

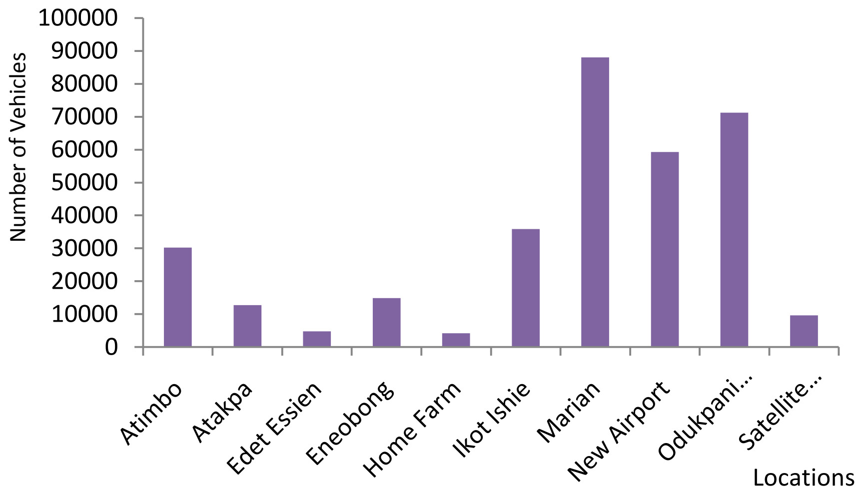

Fig. 3: Number of vehicles plying sample locations per week

Table 6: Pearson correlation matrix of the analyzed elements in the soil

	Al	Si	P	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Zr	Pb
Al	1.000																
Si	-.301	1.000															
P	.490	-.088	1.000														
Cl	-.143	**.696***	-.149	1.000													
K	.236	-.611	-.230	-.300	1.000												
Ca	.552	-.334	**.670***	-.443	.215	1.000											
Ti	.594	.195	.419	.450	-.115	.104	1.000										
V	.729	-.731	.204	-.312	.553	.686	.118	1.000									
Cr	.424	-.049	.002	.053	.562	.060	.585	.016	1.000								
Mn	.096	**-.663***	.160	**-.839****	.230	.391	-.230	.633	-.021	1.000							
Fe	**.891****	-.365	.282	-.158	.448	.439	.359	**.784***	.381	.093	1.000						
Ni	.613	-.331	.801	-.842	-.365	**.952***	-.031	.958	-.378	**.899***	.415	1.000					
Cu	.566	-.385	.466	-.501	.224	**.765***	.096	**.839***	.190	.434	.314	.786	1.000				
Zn	**.800****	-.479	.456	-.463	.236	**.673***	.078	**.854***	-.051	.207	**.832****	.797	.491	1.000			
Sr	.297	.054	.207	-.579	-.404	.401	.173	.409	-.101	.461	.105	.820	.355	.302	1.000		
Zr	.073	.072	-.378	-.270	.181	.148	.076	.242	.390	.343	.042	.229	.229	-.061	.638	1.000	
Pb	.129	-.296	.435	-.358	.098	.618	.305	**.907***	.192	621	-.168	.499	.630	-.099	.510	.425	1.000

*Correlation is significant at the 0.05 level (2-tailed)
**Correlation is significant at the 0.01 level (2-tailed)

4. CONCLUSION

Particle Induced X-ray emission (PIXE) spectrometry was employed for the analysis of elemental contents in roadside soils in Calabar metropolis. Twenty one elements: Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Nb and Pb were detected in roadside soils in ten different sample locations. Their concentrations, enrichment factors, cluster analysis and correlation pattern among the elements were determined using appropriate statistical package. Results of counting statistics of number of vehicles plying sample locations corroborate with enrichment factor results, cross plot results and correlation matrices among the elements, hence heavy metals in this study were found to be associated with vehicular emissions along traffic routes. Heavy metal toxicity represents an uncommon, yet clinically significant, medical condition. Therefore, if unrecognized, it can result in significant morbidity and mortality [28].

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REFERENCES

[1] E.P. Inyang, I. Akpan, and E. Obiajunwa, Investigation of soils affected by burnt hospital waste in Nigeria using PIXE. A Springer Open Journal, vol.2, no. 208, pp.1 – 4, 2013.

[2] B. Wei, and L. Yang, A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemistry Journal, vol. 94, pp. 99 - 107, 2010.

[3] F. Zhang, X. Yan, C. Zeng, M. Zhang, S. Shrestha, L. Devkota, and T. Yao, Influence of Traffic Activity on Heavy Metal Concentrations of Roadside Farmland Soil in Mountainous Areas, International Journal of Environmental Research and Public Health, vol. 9, no. 5, pp. 1715–1731, 2012.

[4] E.S. Abechi, O.J. Okunola, S.M.J Zubairu, A.A. Usman, and E. Apene, Evaluation of heavy metals in roadside soils of major streets in Jos metropolis, Nigeria, Journal of Environmental Chemistry and Ecotoxicology, vol. 2 no. 6, pp. 98-102, 2010.

[5] O.D. Opaluwa, M.O. Aremu, L.O. Ogbo, K.A. Abiola, I.E. Odiba, M.M. Abubakar, and N.O Nweze, Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria, Advances in Applied Science Research., vol. 3, no. 2, pp.780-784, 2012.

[6] J.A. Markus, and A.B. McBratney, An urban soil study: Heavy metals in Glebe, Australia. Australian Journal of Soil Research, vol. 34, pp. 453–465, 1996.

[7] W. Wilcke, M. Silke, K. Nualsri, and Z. Wolfgang, Urban soil contamination in Bangkok: Heavymetal and aluminium portioning in top soils. Geoderma, vol. 86, pp. 211–228, 1998.

[8] B. Viard, F. Pihan, S. Promeyrat, J.C. Pihan, Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: Bioaccumulation in soil, graminaceae and land snails. Journal of Chemosphere vol. 55, pp.1349–1359, 2004.

[9] G. Nabuloa, H. Oryem-Origa and M. Diamond, Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala city, Uganda. Journal of Environmental Research, vol.101, pp. 42–52, 2006.

[10] A.S. Ekop, I.J. Williams, and T.C. Daiko, Effects of poultry droppings in soil on some heavy metals uptake potential of water leaf (Talinum triangulare) and fluted pumpkin (Telfairia occidentalis). African Journal of Agriculture Research, vol.6, no.16, 3729 – 3732, 2011.

[11] E.P. Inyang, Assessment of Effect of Anthropogenic Activities on Soil Elemental Composition in Ile-Ife Using Beam Analysis (IBA) Techniques and the Health Implications, Unpublished Ph.D Qualifying Examination, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria, 2009.

[12] M.A.Chaudnuri and A.Crawford, Nuclear instrumentation method. New York: Macmillan, pp.133-141, 1981.

[13] E.I. Obiajunwa, and J.I. Nwachukwu, Simultaneous PIXE and PIGME analysis of a Nigerian tar sand sample from a deep borehole. Journal of Radioanalytical and Nuclear Chemistry, vol. 245 no.3, pp. 659 – 661, 2000b.

[14] E.I. Obiajunwa, A.C. Adebajo, and O.R. Omobuwajo, Essential and trace element contents of some Nigerian medicinal plants.Journal of Radioanalytical and Nuclear Chemistry, vol. 252, pp. 473–476, 2002.

[15] I.O. Akpan, A.E Amodu, and A.E. Akpan, Elemental analysis of limestone samples from Obajana and Mfamosing limestone deposits, Nigeria, using nuclear techniques. Journal of Applied Radiation and Isotopes, vol. 69, pp.1355-1358, 2011.

[16] S.N. Ghoshal, Nuclear physics. New Delhi: S. Chand, 1-44, 1994.

[17] European Food Safety Authority, Safety of aluminium from dietary intake. Scientific Opinion of the Panel on Food Additives, Flavourings, processing Aids and Food Contact Materials (AFC), The EFSA Journal, vol. 754, pp. 1-34, 2008.

[18] World Health Organisation (WHO), Quality directive of potable water 2nd ed. Geneva: World Health Organisation, 1994.

[19] E. Zahir, I. Imam, Naqvi and S.M. Uddin, S. M. (2009). Market basket survey of selected metals in fruits from Karachi City (Pakistan). Journal of Basic and Applied Sciences, vol.5 no.2, pp.47 – 52, 2009.

[20] J.I.K. Nirmal, H. Soni, R.N. Kumar, Characterization of heavy metals in vegetables using inductive coupled plasma analyzer (ICPA). Journal of Applied Science Environmental Management, vol.11, no.3, 75 – 79, 2007.

[21] Agency for Toxic Substances and Disease Registry (ATSDR), “Toxicological profile for zinc and cobalt” New York: US Department of Health and Human Services, pp. 501-502, 1994a.

[22] C.I. Adamu and T.N. Nganje, Heavy metal contamination of surface soil in relationship to land use patterns: A case

study of Benue State, Nigeria. Materials Sciences and Applications, vol.1, pp. 127 –134, 2010.

[23] C.S. Mayo, “Calcium supplements,” Available on http//:www. Mayoclinic.org/ health-living/Calcium Supplement, May 13, 2014.

[24] Hassan and J.M. Basahi, Assessing roadside conditions and vehicular emissions using roadside lettuce plants, Pol. J. Environ Stud.vol. 22, no. 2, 287-293, 2012.

[25] S. Onder, S. Dursun, S. Gezgin, and A. Demirbas, Determination of heavy metal pollution in grass and soil of city centre green areas, Turkey: Konya, Polish J. of Environ. Stud. vol.16, no.1, pp. 145- 154, 2007.

[26] H. Arslan and A.M. Gizir, Heavy- metal content of roadside soil in Turkey: Mersin, Fresenius Environmental Bulletin, vol.15, no.1, pp. 1-6, 2006.

[27] X. Yan, F. Zhang, D. Gao, C. Zeng, W. Xiang, and M. Zhang, Accumulations of Heavy Metals in Roadside Soils Close to Zhaling, Eling and Nam Co Lakes in the Tibetan Plateau, Int J Environ Res Public Health,10(6), 2384–2400, 2013.

[28] Osumex, “Heavy metal test kids,” Available at http://www.heavymetalstest.com, August 13, 2013.