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Pollution assessment models of surface soils in Port Harcourt city, Rivers State, Nigeria

Verla Evelyn Ngozi[1], **Verla Andrew Wirnkor**[2,*] and **Enyoh Christian Ebere**[2]

[1]Department of Environmental Technology, Federal University of Technology, Owerri, Imo State, Nigeria

[2]Group Research in Analytical Chemistry, Environment and Climate Change (GRACE&CC), Department of Chemistry, Imo State University, Owerri, Imo State, Nigeria. P.M.B 2000, Nigeria

*E-mail address: verngo@yahoo.com

ABSTRACT

Environmental pollution has resulted in several health and physiological problems in both plants and animals. This has witnessed growing number of models for assessment purposes. Some of these provide useful information, and reduce large data for easier understanding by policy-makers. In the current study of pollution, we used data from four locations: Oil Market, Trans Amadi, Borrokiri and GRA in Port Harcourt and a control taken from Federal Land Resource Umuahia (FLRU). A total of 25 composite soil samples were analyzed for physicochemical parameters and heavy metals, by means of a 969 Unicam AAS model series. The data obtained were then subjected to index models. Results showed iron (Fe) to be most abundant metal, ranging from 10.44 to 19.54 mg/kg, then Ni (8.03 to 13.6mg/kg), Cd (3.96 to 5.41 mg/kg), Pb (1.36 to 7.64 mg/kg), Zn (0.09 to 7.24 mg/kg), Cu (0.16 to 0.32) and As (0.07 to 0.11 mg/kg). All metal concentrations were below permissible limits set by NESRA. Contamination factor (C_f) and Igeo revealed moderate to heavy contamination by Cd and Zn. Anthropogenicity revealed that increasing metals in the environment are largely from anthropogenic inputs. The Pollution Index revealed that soils were unpolluted (PLI < 1) with the heavy metals. Furthermore, the Sodium absorption ratio showed that the soils are less sodic and could be good soils for plant growth. All four sites showed a linear relationship between anthropogenicity and geoaccumulation indexes, and so both indexes furnish basically the same information However, pollution from these metals in the study area should be under routine check for possible pollution in the near future, as some metals showed elevated concentrations above background values.

***Keyword*:** Anthropogenic, Contamination, Pollution indices, Residential area

1. INTRODUCTION

Man is dependent on the environment for his daily activities. Therefore, the quality of the top soil of any environment is very important to man. Over 45% of the world's total population currently resides in urban areas, and this figure is projected to surpass the majority benchmark, reaching 60% by 2030 (United Nations, 2001). This increase in population plays an important role in polluting the environment and causes severe degradation in pedosphere, hydrosphere and atmosphere. Pollution in the environment is the unfavourable alteration of our environment as a result of wastes from man's activities, changes in radiation levels, physico-chemical characteristics and abundance of organisms in a harmful way (Miller, 1988; Adewoyin et al, 2013). However, a pollutant is a substance that occurs in the environment, at least in part, as a result of human activities, and which has deleterious effect on the environment (Bayero, 2004; Adewoyin *et al*, 2013).

Soil is the loose material that covers the land surfaces of earth and supports growth of plants (Enyoh *et al*, 2017) and human activities. Over the past few decades environmental quality of urban soil has been closely related to human health and so people have become more concerned about the potential pollution of soil around them (Annao et al, 2008; Zakir et al, 2008 and Verla et al, 2015). Soil pollution arising from socioeconomic activities of man may threaten human health if not properly checked (Verla et al, 2015). It is also a natural reservoir of metals whose concentrations are associated with several factors such as biological and biogeochemical cycling, parent material and mineralogy, soil age, organic matter, soil pH, redox concentrations and microbial activities (Obasi et al, 2012). Knowledge of soil characteristics and heavy metal levels is important for safety policy formulation and awareness in urban soils.

However, as a result of the increasing rate of industrialization in Nigeria, a lot of harmful substances are now being discharged into the environment. Port Harcourt is an example of an industrialized location in Nigeria**,** where population and traffic densities tend to be high, and also housed two oil refineries, two major airports, sea ports and major industrial estates, amongst others**.** These has resulted to increased anthropogenic activities such as agricultural practices, industrial activities, energy consumption and waste disposal methods which lead to large release of heavy metals into soil, thus leading to the contamination of the soils (Ndiokwere and Ezehe, 1990; Eja et al., 2003; Ololade et al., 2007; Ebong et al., 2007, 2008 and Obasi et al, 2012). The poor management of waste or effluents could create a number of adverse environmental impacts, including wind-blow litter, attraction of mice and pollutants such as leachate, which can pollute underground soil bed, and / or aquifer (Abdulssalam, 2009; Osazee et al, 2013). Therefore, the need to understand urban environmental quality and its associated implications for the environment and human health is important.

Several studies reported on Port Harcourt soil have been mostly on the effects of dumpsites (Ogbonna et al, 2002; Ogbonna et al, 2009 and Ukpaka and Pele, 2012). However, no study, as far as it could be established, have been reported on the general pollution status of soils from the city. Godson (2004) studied the quality of soil near a chemical fertilizer industry at Port Harcourt, Nigeria and showed that the soil environment around was the most affected with the highest mean phosphate and potash levels of 494.5mg/kg and 32.3mg/kg respectively. The presence of metals and other mineral elements at various concentrations revealed that the industrial wastes contaminated the soils. The author also remarked that the impact of the pollutants as assessed appear to be more on the soil. Ukpaka and Pele (2012) performed elemental analysis of soil characteristics due to municipal solid waste in Port Harcourt City and were found to contain significant amount of toxic and essential elements**.** Edori and Kpee (2017) did an index models assessment of heavy metals in soils within selected abattoir and reported that the soil showed high abundance of iron (Fe) and slight contamination by copper (Cu). However, the general view of pollution index (PI), geo-accumulation and enrichment factor showed that the soil were free from pollution (Edori and Kpee, 2017). The present distribution of metals in the soil can serve as an indication of time, history, and extent of pollutants discharged in the area. Assessing the problems caused by contaminated soils typically involves soil chemistry as well as laboratory and field studies to fully assess the extent and significance of any adverse environment effects (Osakwe et al., 2003**;** Akpoveta et al, 2010) of industrialization. Therefore, the aim of this study was to examine the physicochemical properties and heavy metal levels in soils of Port Harcourt city with a view to establish the pollution or contamination status of the soils as a result of anthropogenic input. This study will build on past works conducted in various part/area of Port Harcourt city by presenting concrete and reliable data from the analysis of soil samples in selected sites that will serve as a benchmark for future studies on soils in Port Harcourt city.

2. MATERIAL AND METHODS

2. 1. Study area

The study area is Port Harcourt metropolitan city in Nigeria. Call the oil city, it is well known with sea port and lots of goods imported through the Port Harcourt Warf. Many industries exist in Port Harcourt ranging from small sized industries to multinational companies such as Shell Petroleum Development Corporation (SPDC) with its numerous activities involving oil exploration and refining of oil products, cement, glass, and agro industrial companies. Four sampling sites include Trans Amadi (TA) and Oil Mill market (OM) for the industrial road area and GRA Diobu (GRA) and Borokiri (BO) for the residential areas. The control was taken from Federal Land Resource, Umuahia (FLRU). Three composite samples were collected from five different sites. At each site, a W-shaped line was drawn on a 2×2 m surface and the top (0 – 10 cm depths) soil samples were collected using a hand held auger (Verla et al, 2015; Enyoh et al, 2017). The soils were pooled, treated to coning and quartering to obtain a composite sample of each site. The soil samples were air dried, sieved with a 2 mm mesh size, and stored in black polythene bags in triplicate, until analysis (Udo and Fagbami, 1979; Taofeek and Tolulope, 2012).

2. 2. Soil analysis

pH measurements were carried out in deionized water (50 mL), after stirring (with a hand held polypropylene rod for 15 mins) the air dried sample portion of 2.0 g for an hour. Using the same solution the electrical conductivity was measured by means of Yokogawa conductance Sc. 82 conductivity meter. The organic matter content was determined as a weight loss by weighing the sample before and after heating at 500 °C for 2 hours (Ano, 1994; Sezgin et al, 2003; Enyoh et al, 2017). Particle size distribution was determined by the sedimentation method (Mustapha, 2003;Abechi et al,2010). 2 g of each sample were mixed with 20 mL of 4 M HNO_3 at 90 °C for 4 hours. The mixtures were filtered into 25 mL standard flask and solution made up to mark with ionized water. Appropriate standard solutions were made and concentrations of Pb, Cd, Cr, Fe, Zn, Ni, and Cu and As in the digest were determined using 969 Unicam ASS.

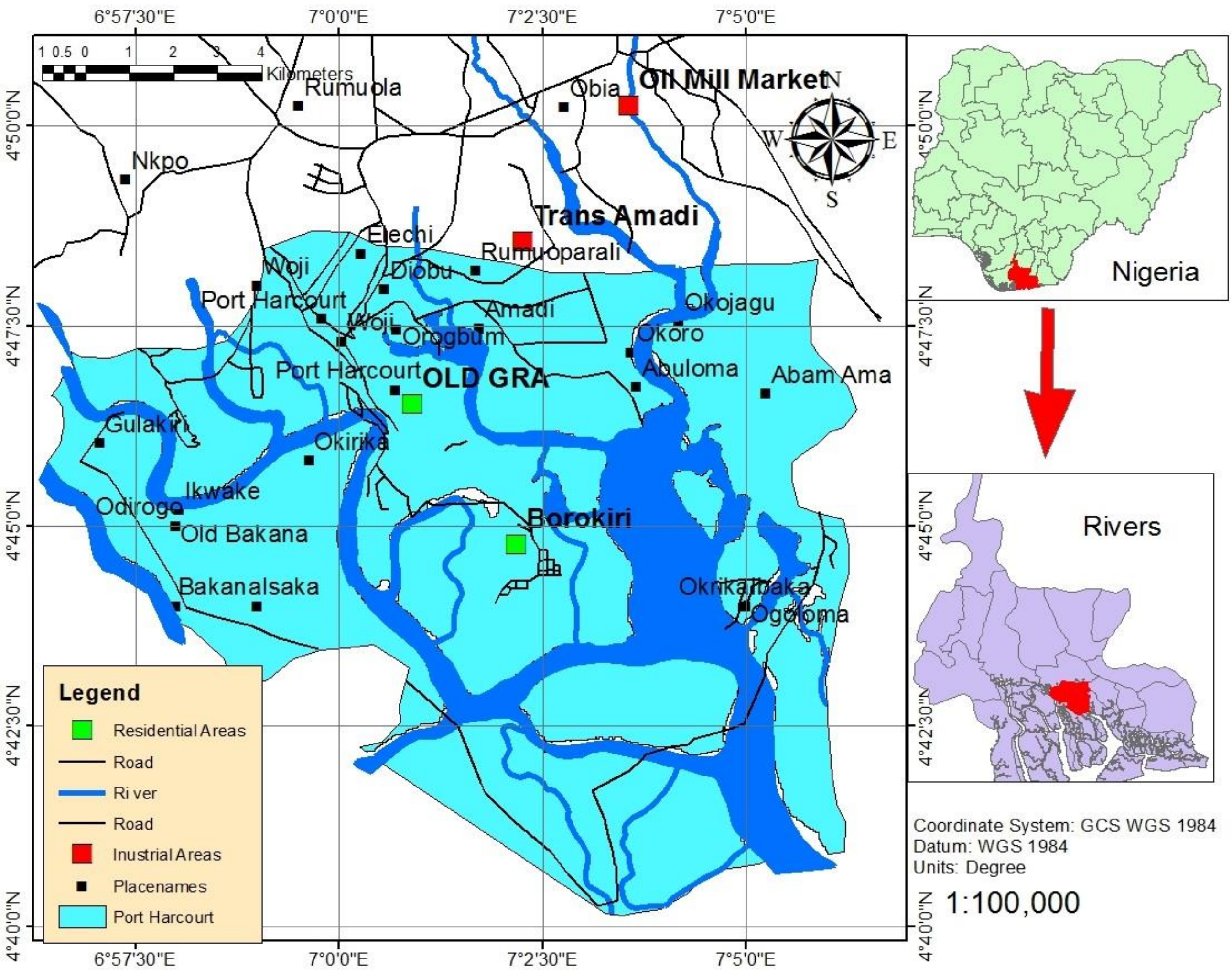


Figure 1. Map of Port Harcourt area showing sampling location

2. 3. Data analysis

The data was analysed using LSD at 5% level of probability according to the Michigan State University software program for the design and analysis of agronomic research experiment (MSTACC) statistical package. A two tailed Pearson correlation coefficient was determined for heavy metals and heavy metals.

2. 4. Pollution index models

In order to assess the heavy metal pollution levels and extent of contamination in the soil samples, the data obtained for the heavy metal concentrations were used to calculate the

Contamination Factor (CF), the Pollution Load Index (PLI), Geoaccumulation Index (Igeo), and the Anthropogenicity (Apn).

Assessment of the extent of soil contamination or enrichment with heavy metals was carried out using the contamination factor (CF) estimation as proposed by Forstner and Calmano (1993). CF is obtained by dividing the concentration of the elements by their background concentration as presented in following:

$$CF = \frac{C_m}{C_b} \quad (1)$$

where Cm is the concentration of the metal in the soil and Cb is the concentration of the metal in the background. The background concentrations were taken as the target value (mg/kg) of the Department of Petroleum Resources. These values are: Fe - 38000, Zn - 140, Pb - 85, Co - 20, Cu - 36, Cr - 100, Ni - 35, Mn - 850, As - 1.0 and Cd - 0.8 (DPR, 2002).

The Pollution Load Index (PLI**)**, as proposed by Thomilson et al. (1980), was used to assess the quality of soil in a polluted site. PLI is obtained as a product of the measured contamination factors of the different metals in the soil samples. Generally, the PLI is estimated using the following:

$$PLI = (CF_1 X\ CF_2 X\ CF_3 \ldots \ldots CF_n)^{1/n} \quad (2)$$

where n is the number of metals considered in the study and CFi is the contamination factor for each individual metal. The PLI provides a comparative means for assessing a site quality.

The Geoaccumulation Index (Igeo) was introduced by Müller (1981) to assess the extent of metal pollution in soil samples. The Igeo was estimated using the following Eq. (3):

$$\text{Igeo} = \log 2 \left(\frac{C_m}{1.5 C_b}\right) \quad (3)$$

where Cm is the concentration of the metal in the sample, C_b is the background value of the metal, 1.5 is the background matrix correction factor due to lithogenic effects; hence, this index is used to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. The background value taken is considered from world average value in shale (mg/kg) of the metals determined in the study.

The values are Fe = 47200, Zn = 95, Pb = 20, Co = 19, Cu = 45, Cr = 90, Ni = 68, Mn = 850, As = 13 and Cd = 0.3 (Edori and Kpee, 2017).

Anthropogenicity (Apn) measures directly the anthropogenic influence on the metal concentrations in the soil.

$$\text{Apn} = \frac{\mu}{\text{Cb}} \times 100 \quad (4)$$

The μ is current or measured concentrations of metals in the soil, while Cb is the background value is considered from world average value in shale (mg/kg) stated above.

Sodium absorption ratio (SAR) was calculated according to Verla et al, 2015, Mmolawa et al., 2011).

$$SAR = \frac{Na}{\frac{\sqrt{(Ca+Mg)}}{2}} \qquad (5)$$

3. RESULT AND DISCUSSION

3. 1. Physico chemical properties

The results for the Physico chemical properties in soil samples taken from Port Harcourt areas during January 2014 are presented in Table 1 below.

Table 1. Physicochemical properties of soil samples.

Parameter	Location					Arithmetic mean	Geometric mean	FLRU
	OM Market	Trans Amadi	Borokiri	GRA	SDV			
pH	6.00	6.30	5.63	6.47	0.37	6.10	6.09	6.13
H^+	2.73	0.79	1.43	3.06	1.07	2.00	1.75	0.84
EC (S/cm)	0.51	0.82	0.09	0. 31	0.50	0.47	0.34	0.32
AP	10.5	16.31	14.65	13.57	0.37	13.76	13.58	20.10
NO_3^- (mg/kg)	0.42	0.33	0.61	0.57	0.33	0.48	0.47	0.28
SO_4^{2-} (mg/kg)	1.96	5.84	4.36	5.81	0.31	4.49	4.13	3.22
TN	0.23	0. 35	0.22	0.18	0.29	0.21	0.21	0.19
B.Sat (%)	34.30	27.41	43.01	50.31	0.28	38.76	37.77	17.81
OC (%)	3.98	3.52	1.73	2.05	0.26	2.82	2.65	1.01
Sand (%)	22. 87	6.057	91.53	85.03	0.25	60.87	36.12	13.00
Silt (%)	68.27	26.60	6.70	10.63	0.25	28.05	18.96	57.27
Clay (%)	8.90	6.70	1.73	4.30	0.24	5.41	4.59	29.73
THC (%)	7.57	6.77	4.70	7.27	0.23	6.58	6.47	6.73

EC = Electrical conductivity, AP = Available Phosphorus, TN = Total Nitrogen, B.Sat = Base Saturation, OC = Organic Carbon, THC = Total Hydrocarbon

The soil pH obtained in this study generally hovers around the slightly acidic to neutral range, which ranges from 5.63 at Borrokiri to 6.47 at GRA with arithmetic and geometric mean of 6.10 and 6.09 respectively**,** these values are expected as most soils in the tropics have their ranging from acidic to slightly neutral (alloway, 1997 and Okoro et al, 2015)**.** In comparison, with the control soil (FLRU) the soil have lower pH. Although, all soils showed acidity, this is in conformity with soil pH reported in other studies conducted in other areas in Nigeria (Verla et al, 2015; Ahukaemere et al, 2016; Enyoh et al, 2017). Ahukaemere et al (2016) reported that the soil acidity could be due to the parent material from which the soils are derived. However, only Trans Amadi and GRA showed higher acidity to the control soil. Ranking in decreasing order of soil acidity; GRA > Trans Amadi > FLRU (control) > OM Market > Borrokiri. The soil pH is a function of H^+ and plays an important role in metals availability for uptake by plants and animals.

The electrical conductivity (EC) is a measurement of the dissolved material in an aqueous solution, which relates to the ability of the material to conduct electrical current through it (Enyoh et al, 2017).The (EC) measurements show that samples from Trans Amadi recorded highest (0.82 S/cm) and GRA (0.31 S/cm) recorded lowest. However, in comparison with the control soil (0.32 S/cm), arithmetic (0.47 S/cm) and geometric values (0.34 S/cm) were higher. The observed EC in this study could have been due to the textural class of the soil. EC usually correlates strongly to soil texture and Cation exchange capacity (CEC) (Verla et al, 2015). This is in conformity with the concentrations of cations obtained in this study (Table 2).

Table 2. Mean total metal concentrations (mg/kg dry matter)

Metal Symbol	Location					Arithmetic mean	Geometric mean	FLRU	NESRA Standard
	Oil Mill Market	Trans Amadi	Borokiri	GRA	SDV				
K	9.11	7.81	8.36	4.37	2.10	7.41	7.14	4.02	-
Na	13.01	10.33	10.26	11.25	1.28	11.21	11.16	10.27	-
Ca	28.05	20.11	26.31	27.80	3.72	25.57	25.34	52.30	-
Mg	9.30	8.31	9.36	13.61	2.36	10.15	9.96	11.6	-
Al	0.30	2.30	1.40	1.21	0.82	1.3	1.04	0.84	-
Cd	5.41	4.43	3.96	4.06	0.66	4.47	4.43	1.32	3
Cr	0.73	0.21	0.11	0.46	0.27	0.38	0.30	0.24	100
Fe	10.44	19.54	13.06	18.15	4.27	15.3	14.83	9.87	20

Cu	0.32	0.11	0.21	0.16	0.09	0.20	0.19	0.11	100
Ni	9.46	13.6	9.11	8.03	2.44	10.05	9.85	8.74	68
Zn	0.09	7.24	0.46	4.71	3.45	3.13	1.09	3.11	421
As	0.11	0.11	0.11	0.07	0.02	0.10	0.10	0.03	20
Pb	7.64	5.34	1.36	6.48	2.73	5.21	4.35	1.10	-

Organic carbon (OC), total nitrogen (TN) and Available phosphorus (AP) were 2.82%, 0.21% and 13.76 % respectively. Organic carbon (OC) content of the soil was rated moderate (> 2%); while TN value was rated medium (Osakwe, 2014), AP was rated high. The OC, TN and AP obtained in Port Harcourt soils were higher (OC and TN) and lower respectively, when compared with the control soil (1.01 %, 0.19 % and 20.10 %) from Umuahia, Abia state. The presence of Nitrogen and Phosphorus are indicators of agrochemical usage on the soil. This is similar to earlier study conducted near a chemical fertilizer industry at Port Harcourt, Nigeria by Godson (2004).

Nitrate and sulphate level obtained in the study ranges from 0.33 at Trans Amadi to 0.61 mg/kg at Borokirri and 1.96 at OM Market to 5.84 mg/kg at Trans Amadi respectively. In comparison with the control soil, the arithmetic mean is higher 0.48 mg/kg > 0.28 mg/kg for nitrate and 4.49 mg/kg > 3.22 mg/kg for sulphate in the soils respectively. Burning of fossil fuels in power plants and cars, and all internal combustion engines that usually result in the production of nitric acid ammonia as air pollution is source of nitrate in the environment. Industrial applications of nitrate as an oxidizing agent, in the production of explosives and as purified potassium nitrate for glass making are also potential sources of environmental nitrate (Morgan et al., 1989). When nitrogen undergoes natural processes of photochemical oxidation during lightening and thunderstorm, it gives oxides of nitrogen, which is a source of nitrate in the environment (Udofia, 2005). When in excess in the environment, it can be hazardous to health, especially for children and pregnant human.

The sulphate concentration in the soil solution is a good indicator of sulphur availability to plants. Sulphur is an essential micronutrient required by plants and animals. Under normal agricultural conditions, the quantity of sulphur released from organic matter and oxidized to the plant–available sulphate form depends to a great extent on the amount and sulphur status of the organic matter present and on satisfactory microbial environment including soil pH, temperature and water status (Isirimah et al, 2003). Deficiency of sulpur in the soil causes initial yellowing of young leaves spreading to whole plant while excess of sulphur in the soil may cause premature dropping of leaves in plants (Osakwe, 2014).

The base saturation obtained in this study ranged from 27.41 % at Trans Amadi to 50.31 % at GRA and is consistent with the mean pH value recorded in the study, since percentage base saturation means the amount of the cation exchange capacity not holding potential acidity. This is similar to values obtained by Osakwe (2014). The percentage base saturation expresses the relative contribution of the exchangeable bases to the overall exchange capacity and it is an important property of soil acidity useful for soil fertility evaluation because a high percentage base saturation implies desirable nutrient levels and low soil acidity. The base saturation was generally higher than control soil (17.81 %).

The textural class of the soil obtained using the USDA soil textural triangle showed that the soils were sandy in nature (table 1) from the arithmetic and geometric means. This phenomenon is in agreement with reports by Oyedele *et al.*, (2008), Ideriah *et al.*, (2010), Eneje and Lemoha (2013), and Osazee et al, (2013), However, OM Market and Borrokiri were silty in nature, which are in support of earlier report by Ogbonna *et al.*, (2009), who indicated that majority of top soil samples collected from waste dump sites in Port Harcourt, Rivers State, Nigeria were silty in nature. Silt is granular material of a size between sand and clay, whose mineral origin is quartz and feldspar and may occur as a soil (often mixed with sand or clay).

3. 2. Total heavy metal contents

Arithmetic and geometric mean concentration of cations and heavy metals in Portharcourt soils was calculated from the mean values of each element determined for every studied site. The calculated arithmetic mean concentration of K, Na, Ca, Mg, Al, Cd, Cr, Fe, Cu, Ni, Zn, As, and Pb were 7.41, 11.21, 25.57, 10.15, 1.3, 4.47, 0.38, 15.30, 0.20, 10.05, 3.13, 0.10, and 5.21mg/kg respectively. For comparison, in the control soil (i.e Federal Land Resource, Umuahia, FLRU) analyzed, the arithmetic mean concentrations of K, Na, Ca, Mg, Al, Cd, Cr, Fe, Cu, Ni, Zn, As, and Pb were 4.02, 10.27, 52.30, 11.60, 0.84, 1.32, 0.24, 9.87, 0.11, 8.74, 3.11, 0.03 and 1.10 mg/kg respectively, which are similar with those in the obtained from Portharcourt soils studied.

Furthermore, it is observed that the concentrations of heavy metals in studied soils are within permissible limits for heavy metals in soil, as compared to National Environmental Standard and Regulation Agency, NESRA, (2011).

According to Ure and Berrow (1982) the geometric mean concentration of Zn, Cu, Cd and Pb in world soils was 50, 25, 0.62 and 29 mg/kg, respectively. In comparison with the mean geometric concentration of Zn, Cu, Cd and Pb obtained here (1.09, 0.19, 4.43 and 4.45 mg/kg, respectively), these indicates that the examined soils have not been contaminated. Comparison with literature data also revealed that our data for urban area are much lower than those presented in Czech Republic (Strnad et. al., 1994) and Italy (Imperato et. al., 2003) indicating that soils of PortHarcourt are not polluted by heavy metals.

However, a critical look at table 2 showed elevated mean concentrations of cations and heavy metals of Na, Ca, Mg, Fe, and Ni at various locations in the study. However, they are below permissible values and always in the range of the determined contents of heavy metals for agricultural soil in Spain (Zurero-Cosano et. al., 1989) and USA (Holmgren et. al, 2003).

The low contents of metals in the soil could be attributed to the Organic Carbon (OC %) contents in the soil obtained in this study (Table 1), as soil OC contents is known to form complexes with metals (Enyoh et. al, 2017) and impedes bioavailablity of metals (Verla et al, 2015). In addition, soil pH (5.30 to 6.47) Ttable 1) could have effect on the solubility of metals retention in soil; the greater retention and lower solubility of metal occurs at high soil pH (Škrbić and Miljević, 2002)

Table 3. Spearman's correlation coefficient between metal concentrations at 5% significance level.

Metal	K	Na	Ca	Mg	Al	Cd	Cr	Fe	Cu	Ni	Zn	As	Pb
K	1												
Na	0.801	1											
Ca	0.722	0.967	1										
Mg	0.407	0.850	0.910	1									
Al	0.126	0.077	0.012	0.136	1								
Cd	0.862	0.986	0.917	0.757	0.089	1							
Cr	0.165	0.422	0.362	0.297	-0.705	0.437	1						
Fe	0.400	0.685	0.639	0.770	0.703	0.651	-0.106	1					
Cu	0.696	0.687	0.694	0.405	-0.596	0.699	0.675	-0.057	1				
Ni	0.793	0.778	0.649	0.543	0.602	0.826	-0.016	0.824	0.238	1			
Zn	-0.342	-0.165	-0.277	0.012	0.744	-0.153	-0.321	0.539	-0.774	0.285	1		
As	0.971	0.871	0.800	0.560	0.293	0.910	0.092	0.604	0.590	0.891	-0.176	1	
Pb	0.230	0.578	0.452	0.487	-0.238	0.600	0.853	0.354	0.425	0.362	0.153	0.258	1

The spearman's correlation coefficient model was used to show relationship or association between metals in Port Harcourt soil and the coefficient are shown in table 3 above. The inter-relationship or association between the metals showed close association between Cd and Na (0.99), Cd and Ca (0.92), As and K (0.97) and Cd and As (0.91) which showed strong correlation significance. Most metal pairs were positively correlated which is an indication that most metals have common contamination source. However, Zn showed negative correlation with K, Na, Ca, Cd, Cr and Cu. Positive correlation indicates similar source of contamination while negative indicates dissimilar source of contamination.

3. 3. Pollution assessment models

Contamination factor (CF) and Geoaccumulation Index (Igeo) are indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil. These indexes of potential contamination are calculated by the normalization of one metal concentration in the topsoil respect to the concentration of a reference element (Barbieri, 2016).

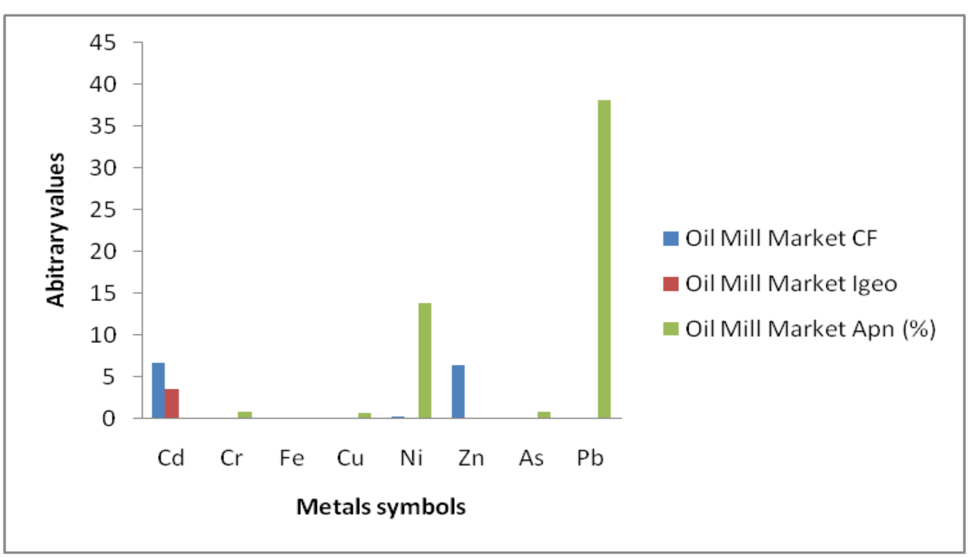
Table 4. Showing assessment models result for Port Harcourt soils.

Metals	Oil Mill Market			Trans Amadi			Borrokiri			GRA		
	CF	Igeo	Apn (%)	CF	Igeo	Apn (%)	CF	Igeo	Apn (%)	CF	Igeo	Apn (%)
Cd	6.76	3.62	1803	5.54	2.96	1476	4.95	2.65	1320	5.075	2.72	1353
Cr	0.0073	0.00163	0.81	0.0021	0.000046	0.23	0.0011	0.000241	0.12	0.0046	0.00102	0.51
Fe	0.00027	0.00004	0.02	0.0005	0.000080	0.04	0.00034	0.000060	0.03	0.00048	0.000080	0.04
Cu	0.0089	0.00142	0.71	0.0031	0.000482	0.24	0.0058	0.000944	0.47	0.0044	0.000723	0.36
Ni	0.27	0.028	13.91	0.39	0.000402	0.20	0.26	0.027	13.40	0.23	0.024	11.81
Zn	6.42	0.00018	0.09	0.052	0.02	7.62	0.0033	0.000964	0.48	0.034	0.0099	4.96

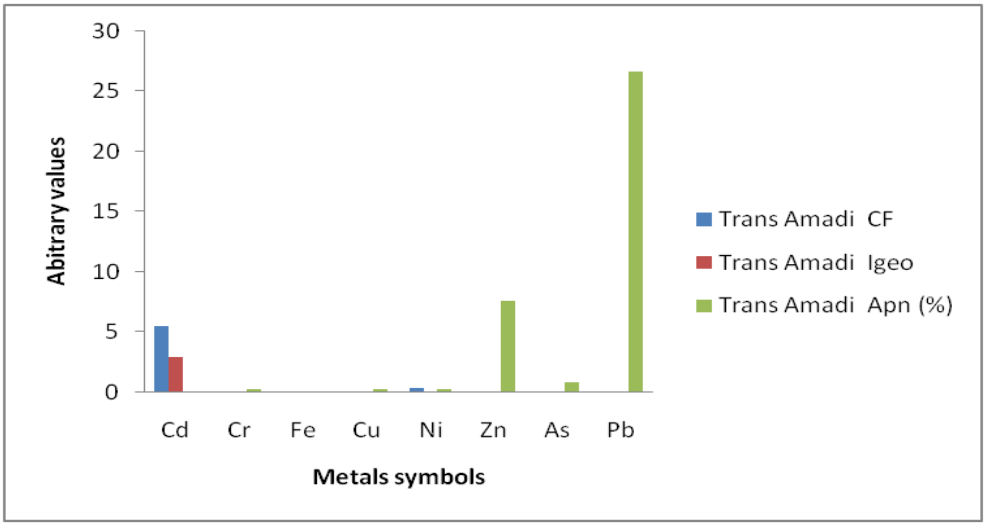
As	0.11	0.00171	0.85	0.11	0.00171	0.85	0.11	0.00171	0.85	0.07	0.0011	0.54
Pb	0.089	0.077	38.20	0.062	0.054	26.70	0.016	0.014	6.80	0.08	0.065	32.40
PLI	0.082			0.036			0.019			0.035		
SAR $(Cmol/kg)^{05}$	4.25			3.02			3.41			3.49		

*CF = Contamination factor, Igeo = Geo accumulation Index, Apn = Anprogenicity, PLI = Pollution index, SAR = Sodium Absorption Ration.

The contamination factors were categorized according to Mathias and Stephen (2016). Values < 1 are low contamination, 1≤CF<3 are moderately contaminated, 3≤ CF ≤ 6 are considerably contaminated and ≥ 6 very highly contaminated. Therefore, from the study, Oil Market is highly contaminated with Cd (6.76) and Zn (6.42), Trans Amadi, Borrokiri and GRA were all considerably contaminated with cadmium showing high values of 5.54, 4.95 and 5.08 respectively. Cadmium (Cd) is one of the most toxic elements to which man can be exposed at work or in the environment. Once absorbed, Cd is efficiently retained in the human body, in which it accumulates throughout life. It is primarily toxic to the kidney, especially to the proximal tubular cells, the main site of accumulation. Cd can also cause bone demineralization, either through direct bone damage or indirectly as a result of renal dysfunction (Bernard, 2008).



(a)



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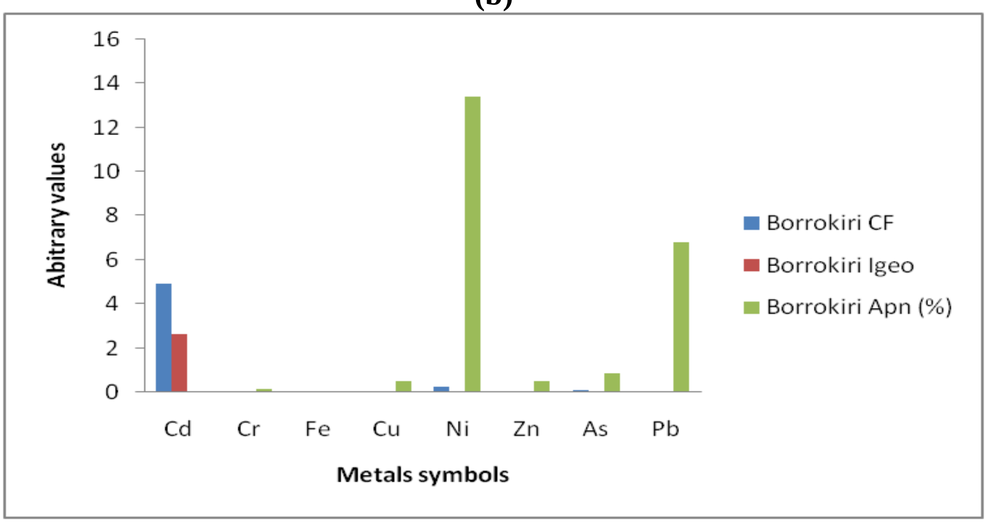
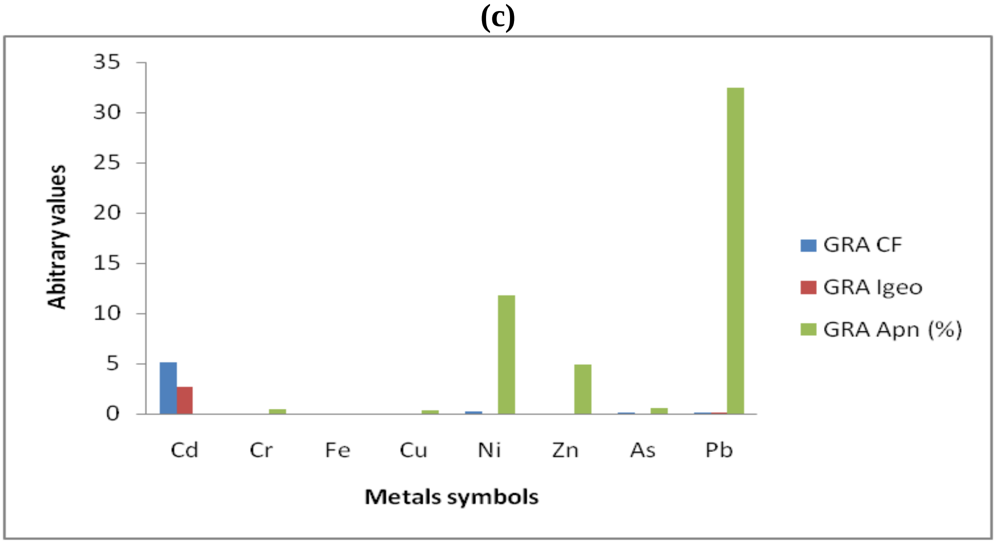


(c)



(d)

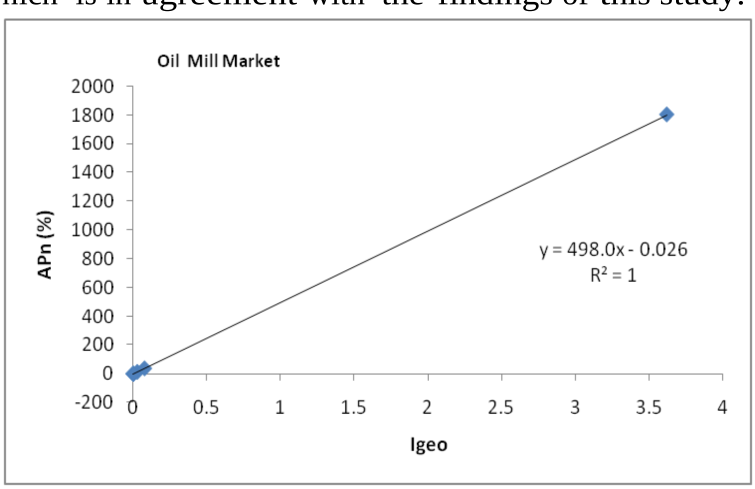
Figure 1(a-d). Bar charts of values for comparing CF, I_{geo} and Apn of the four sampling sites

Generally, the pollution index obtained in this study was less than 1. The contamination level maybe classified based on their intensities on a scale ranging from 1 to 5 (0 = none, 1 = medium, 2 = moderate, 3 = strong, 4 = strongly polluted, 5 = very strongly polluted). The overall pollution status indicates the total pollution of the individual pollution indexes. The result obtained from this study signifies that the top soils from the Port Harcourt are not contaminated with heavy metals. However, the values obtained were significant.

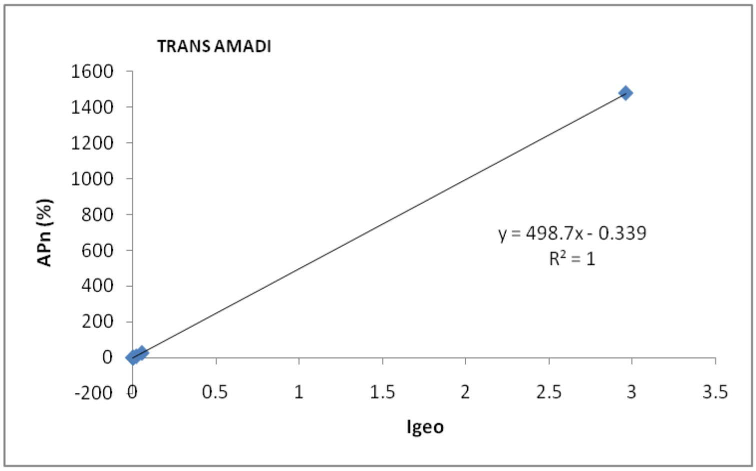
SAR is a widely accepted index for characterizing soil sodicity, which describes the proportion of sodium to calcium and magnesium in soil solution. SAR values obtained ranged from 3.02 $(Cmolkg^{-1})^{05}$ at Trans Amadi to 4.25 $(Cmolkg^{-1})^{05}$ at OM Market. The mean of SAR for all Port Harcourt soil was 3.54. This value falls within the typical range of 2.17-8.0 $(Cmolkg^{-1})^{05}$. Higher values of SAR indicate loamy sand, clay loam and clay soil (Alloway, 2002). However, values of adsorption ratios showed in table 4 indicate that the textural class was neither of the above class. This agrees with the textual class established through particle size distribution. Sodium adsorption ratio is of increasing importance as an index for measuring salinity. Threshold value reported in literature is 12 $(Cmolkg^{-1})^{05}$ (Mohsen et al, 2009). In comparison with the threshold, it showed that Port Harcourt soils have low SAR. These suggest that the soils are less sodic. Sodic soils tend to have poor structure with unfavourable physical properties such as poor water infiltration and air exchange, which can reduce plant growth.

3. 4. Chemometric assessment of APn and Geoaccumulation index

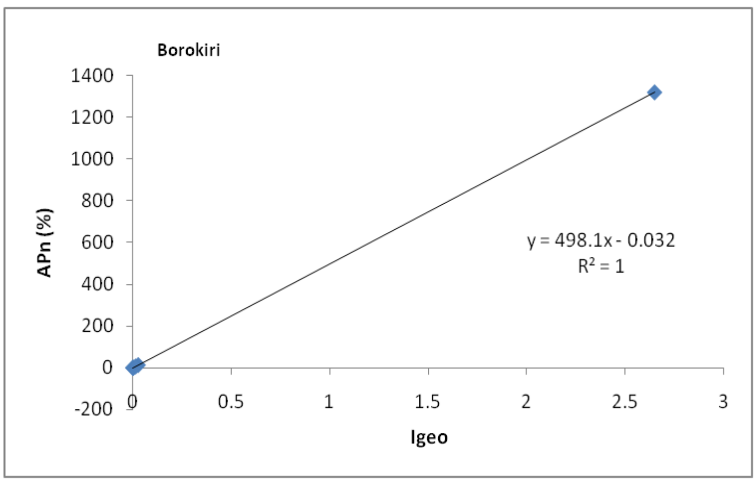
Anthropogenicity (APn), although, similar to Igeo, measures the percentage or extent of anthropogenic input on the environment. The Igeo value obtained in this study were all below zero (0) which indicate uncontamination of the soil, except for, Cd which showed moderate contamination at Borrokiri (2.65) to heavy contamination at Trans Amadi (3.62), as categorized by Edori and Kpee (2017). These suggest that Port Harcourt soils are contaminated by Cd, which is confirmed by the high anthropogenic input (1320 % to 1803 %) as shown in table 4. Pb, Ni and Zn were also significant. Ranking in order of decreasing contributions showed Cd>Pb>Ni>Zn>As>Cu>Cr>Fe. Edori and Kpee (2017) observed that certain metals (Cadmium, arsenic, and lead etc.) are always found in low concentration in the upper layer of the soil except when there is anthropogenic interference which is in agreement with the findings of this study.



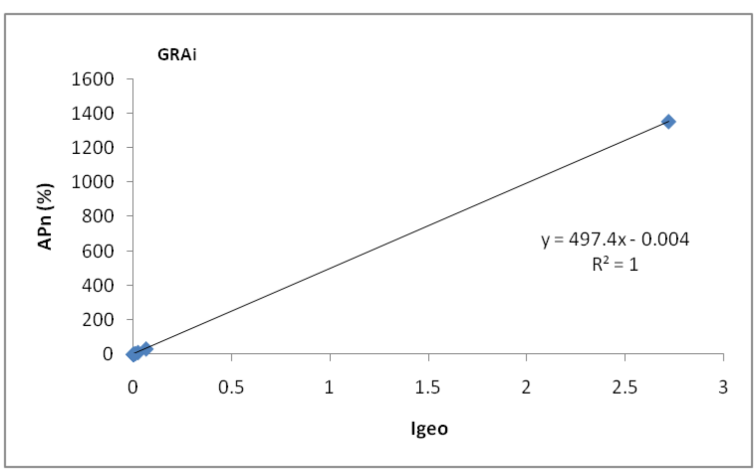
(a)



(b)



(c)



(d)

Figure 2(a-d). Scatter plot showing relationship between I_{geo} and APn in soils of Port Harcourt

The accumulation of these metals in the environment to a large extent is directly caused by anthropogenic activities with (+1) R-value as shown in Figure 2 above. Increasing anthropogenic activities will cause increasing geo accumulation of these metals in the soil. Therefore, there is need to reduce anthropogenic activities, because, these metals are very detrimental to health of plants and animals when in high concentrations or due to their bio-accumulation tendencies.

4. CONCLUSIONS

The results obtained for the heavy metals in the soils of Port Harcourt indicated that the soil is uncontaminated by these metals, except for Cd and Zn, which showed moderate to heavy contamination. Index models applied to the result of the heavy metals revealed that the source of the metals in the soils were largely from anthropogenic sources. Pearson's correlation analysis revealed that Cd/Na, Cd/Ca, As/K, and Cd/As strongly correlated to each other, which revealed that contamination could be from similar anthropogenic source. Also, the PLI index models confirmed that the soils were unpolluted, they were of no significance. SAR also showed that Port Harcourt soils are less sodic and could be a good soil for plant growth. However, the problem of pollution from these metals in these areas should be under routine check for possible pollution in the near future as some metals showed elevated concentrations above background values.

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