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The Concentrations of Potentially Toxic Elements and Total Hydrocarbon in Soils of Niger Delta Region (Nigeria)

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Abstract
The present study was aimed to determine the natural background level, threshold values and evaluate the pollution status of some heavy metals and total hydrocarbon contents in soils of the Niger Delta region, NDR, (Nigeria). In order to achieve this, thirty two composite soil samples were collected and investigated for pH, EC, OC, grain size, THC, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. Analytical results show that the average concentration of total hydrocarbon contents (THC) exceeded the limit in soils for crude oil processing areas in Nigeria. The concentrations of Cd and Co in all the soils samples were higher than reported values for world soils. The average concentrations of Fe and Pb were higher than the background values. However, the concentrations of Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the soils were less than the average value for world soils. This suggests that these elements were naturally present at low concentrations. Contamination risk assessment based on the index of geoaccumulation (I-geo) values for all the samples corresponded to practically uncontaminated with the exception of THC (uncontaminated to moderately contaminated) and Cd (moderately contaminated). In addition, the pollution index (PI) values of the soil samples were low (PI < 1) indicating that on the overall the soils were not polluted. However, high values (PI > 1) in some locations reflected high concentrations of Cd, Cu and THC. The results suggests that the main source of elements in soils of the Niger delta is parent material, whereas increase in industrialization, especially, due to oil and gas related activities poses a significant impact on the distribution of some of these elements.
Keywords Heavy metals, Contamination, Soil, Niger Delta, Nigeria

1. Introduction
The Niger Delta Region (NDR) of Nigeria has witness a dramatic growth in industrialization in the last two decades due mainly to the activities of oil and gas related companies. Despite the numerous benefits from industrialization, a rapidly industrialization world faces the risk of environmental degradation (Chen, 2007). This degradation is attributed to the effects of metals and hydrocarbons. Soils are critical environmental medium and thus inevitably exposed to effects of industrialization. According to Radha et al. (1997), soil contamination by metals has become widespread and serious due to the non-biodegradable nature and their long-biological half-lives. Besides, accumulation of these elements in food chain will have significant effect on human health in long term (Alloway, 1990).
The distribution and content of these elements in soils depends on many factors including: parent material, weathering and human activity (Martinez, 2003). Some of these elements are essential nutrients for plant growth as well as human and animal health. However, at elevated concentration, some become potentially toxic (McBride, 1994). The amount of hydrocarbons and potentially toxic elements that enter the environment as a result of human activity or other sources of pollution can be evaluated on the basis of their background values in the media under consideration (LABO, 1995; Lacatusu, 1995). The values of elements and hydrocarbons in soils represent the content found in natural reserves plus atmospheric depositions (Alloway, 1995).
In the study area, data on heavy elements and total hydrocarbon contents (THC) are scanty, while background, threshold and reference values are not yet defined for the area. Therefore in this study, the levels of some potentially toxic elements and total hydrocarbon contents in soil samples collected from the Niger Delta (Nigeria) were investigated. The primary objective of the present study was therefore, to establish baseline levels for the elements and THC as a basis for assessing future soil pollution, while a secondary objective attempts to evaluate the degree of contamination by potentially toxic elements and THC in soils of the Niger Delta Region.

2. Study Area Description
The Niger Delta Region (NDR) is situated in the southern part of Nigeria (Fig. 1). The region lies between latitude 4^0 00' – 6^0 00' North and longitude 5^0 30' – 8^0 30' East. The climate of the area is tropical with wet and dry seasons. The area receives between 2073 and 4366mm of rainfall annually. The air temperature ranges from 34 to 43^0C and the relative humidity varies between 60 and 96%. (Akpokoje, 1987). Three lithostratigraphic units underlie the NDR. These include an upper Miocene–Recent Benin (sands, clays, shales), middle Eocene-Pliocene Agbada (sands, sandstones, shales) and a lower Eocene-Recent Akata (shales with minor sandstones and siltstones) Formation (Short and Stauble, 1967; Kogbe, 1976).

Soil types in Nigeria are influenced by and follow very broadly, the climatic and vegetation zones of the country. The Nigerian soils have been classified into four major groups. These groups are: (i) northern zone of sandy soils (ii) interior zone of laterite soils; (iii) southern belt of forest soils; and (iv) zone of alluvial soils (Oyenuga, 1967; Iloeje, 2001). The Niger Delta Region (NDR) lies within the southern belt of forest soils and zone of alluvial soils.

The southern belt of forest soils broadly represents those of the humid, tropical forest climate zones. Variations in local soil types in this zone depend largely on parent rock. The forest soils yield cocoa, oil palm, rubber and they are of considerable importance in Nigerian agriculture. The alluvial soils are found on the flooded plains of rivers or on deltas, or along the coastal flats. The soils found in this zone do not depend highly on climate and vegetation for their formation. The underlying parent rock is the most important factor in their formation. Soils in this zone are characteristic of fresh-water soil of grey to white sand, grey clay and sandy clay with humic topsoil. Another soil group consists of brownish to black saline mangrove soils, with a mat of rootlets.

Besides the above classification, Sobulo (1988) reported that the soils of the NDR are classified as low base saturation (Humid tropical zone) – Oxisols and Ultisols under forest vegetation. This zone is confronted with multiple nutrient problems such as soil acidity, high exchangeable Al, very low exchangeable bases, and available micronutrients. Potassium, magnesium and phosphorus are often required to maintain yields but the soils have to be moderately limed to reduce Al toxicity. Crops that are used to low base saturation and low solar radiation such as upland rice, cassava, sweet potato, some grass and pasture legumes are grown in this zone so as to achieve better utilization of the soil and inputs such as fertilizer.

The main activities of the people of the Niger Delta include fishing, farming and exploration and exploitation for oil and gas and its related activities. The oil and gas activities have resulted in the increase in air, water and soil pollution (Fig. 2).

3. Materials and Methods

3.1 Sampling and Analysis

Composite soil samples each weighing 500g were collected from 31 locations within the study area, while one sample was collected from outside the study area as control from Obudu in the northeast of the study area (Fig. 1). Most of these samples were collected near the vicinity of oil processing facilities such as flow stations, gas recycling plants and oil terminals. All the samples were taken at depths 0.0-60.0cm. The samples were air dried and sieved through a 2mm sieve size before analysis. Soil pH was determined by pH meter with soil water ratio of 1:2.5 using glass electrode. Organic Carbon (OC) was measured with a vario EL III CHNS instrument. Effective CEC and particle distribution were determined according to ISO 11260 (1994).

Extraction was performed as proposed by ISO 11277 (1998). After digesting with a mixture of nitric acid (HNO_3) and perchloric acid ($HCLO_4$), metal concentrations were measured with Perkin Elmer Atomic Absorption Spectrophotometer (AAS) 1100 B. Quality control was done by performing duplicate analysis on all samples and by using reagent blanks and a standard reference soil (CRM 141R, BCR Brussels). The achieved precision for each sample were monitored by using the regression method (Zeien and Bruemmer, 1989) and the average precision was better than 10% (Reimann and Wurzer, 1986). The total hydrocarbon contents were determined based on ASTM D 3921.

3.2 Statistical tests

Conventional statistical analysis (mean, median, min, max, standard deviation, SD) was conducted as a first step towards an understanding of the heavy metal data. Correlation analysis was used to construct the relationship between the investigated elements. Factor analysis was used to extract latent information from multimetal data and group the measured elements into fewer groups (Bech et al., 2008) for interpretation. The statistical analyses were performed by means of the statistical package, STAISTICA (Pilz, 1993). Prior to statistical analysis, the data were standardized by means of:

$$K_{ij} = (X_{ij} - X)/S_{ic}$$

Where K_{ij} is the standardized value for X_{ij}, the *i*th variable for the *j*th sample, X is the mean of the *i*th variable and S_{ic} is the standard deviation. The adopted procedure gives equal weight to each parameter (Hussein, 2004).

3.3 Natural background level (NBL) and Threshold values (TV)

Natural background levels (NBL) and threshold values (TV) for the elements were determined based on the method as documented by Coetsiers et al. (2009). For the NBL, the method utilizes a simplified preselection defined as the 90 or 97.7 percentile of a carefully chosen dataset to approach the natural composition of the media when no national method exist for derivation of NBL. The selection of 90 or 97.9 percentile depends on the amount of data (Mueller et al., 2006). When large amount of data (≥ 60 sampling points) are available, the 97.7 percentile was preferred; while for smaller data set (< 60 sampling points), the 90 percentile was suggested (Shand and Edmunds, 2008). In this study, with sample points less than 60, the 90 percentile was used. For the determination of threshold values (TV), two cases were suggested as follows (Mueller et al., 2006):

Case 1: NBL < REF: TV = (NBL + REF)/2
Case 2: NBL ≥ REF: TV = NBL
where REF is established baseline concentration in natural or unpolluted soil (Table 1).

3.4 Contamination risk assessment

Two documented methods were employed to assess the degree of elemental enrichment in soil. These are the index of geoaccumulation (I-geo) and pollution index (PI).

3.4.1 Index of geoaccumulation

The index of geoaccumulation (I-geo) was originally defined by Mueller (1969) for quantitative measure of metal pollution in aquatic sediments. Since then, numerous studies such as Shacklette and Boerngen (1984), Loska et al. (2004), Gemici and Tarcam (2007) and Çolak (2012) have employed the I-geo to assess the contamination of soils by potentially toxic elements. The 1-geo was determined as follows: I-geo = $\log_2[C_n/(1.5 \times B_n)]$, where C_n is the measured concentration of element n in the pelitic fraction of sediment (<2μm) and B_n is the geochemical background for the element n. B_n is either directly measured or obtained from the literature (average shale value). The factor 1.5 is introduced to include possible variations of the background values that are due to lithologic variations. In the present work, the computation of I-geo was modified for the assessment of the contamination level in the soils of the study area. In the modification, C_n is the measured concentration of element n in the soil sample and B_n is the average concentration for the element n in soil obtained from literature (Goldberg, 1976; Agarwald, 2009), Table 1. According to the I-geo scheme, soils are classified as follows (Mueller, 1969; Çolak, 2012):

$I_{geo} < 0$	practically uncontaminated
$0 < I_{geo} < 1$	uncontaminated to moderately contaminated
$1 < I_{geo} < 2$	moderately contaminated
$2 < I_{geo} < 3$	moderately to heavily contaminated
$3 < I_{geo} < 4$	heavily contaminated
$4 < I_{geo} < 5$	heavily to extremely contaminated
$I_{geo} > 5$	extremely uncontaminated

3.4.2 Pollution index

The pollution index (PI) was also proposed to assess the degree of pollution in soils (Nishida et al., 1982; Sponza and Karaoğlu, 2002; Gemici and Tarcan, 2007; Gemici, 2008). The PI was computed by averaging the ratios of total concentrations of the elements to tolerable levels. In this study, the PI value for each location was calculated for 10 elements as follows:

PI = [(Cd/0.06) + (Co/8) + (Cr/100) + (Cu/20) + (Fe/38000) + (Mn/850) + (Ni/40) + (Pb/10) + (V/50) + (Zn/50)]/10

Typical concentrations of heavy metals in soils were obtained from Agarwal (2009) for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn and from Goldberg (1976) for V. Pollution index values above 1 indicated that the soils are possibly polluted by anthropogenic input (Çolak (2012)

4. Results

4.1 Physicochemical parameters

Table 1 contains descriptive statistics of the physicochemical parameters and metal concentrations for the soil samples, while Table 2 represents same data for the different soil types interms of textures. The pH ranged from 4.00 to 7.15 (mean 5.32, median 5.25) indicating that most of the samples were acidic. The dominant soil textural classes were sand (S), loamy sand (LS), silty clay loam (SCL), sandy loam (SL) and medium loam (ML). The sieve analysis of the soil samples showed that the proportion of the soil particles varied as follows: sand (34.4 – 100%), silt (2.0 – 44.0%) and clay (3.6 – 28.2%) with averages of 71.5%, 22.79% and 13.61%, respectively. The average organic carbon content (OC) in the soil samples was 2.63%. The soils have low clay-sized fraction and low organic carbon content, which can result in low adsorption capacity (Çolak, 2012) The EC values of the soil samples varied from 0.004 to 12.53 dS/m with an average value of 0.73 dS/m. High values (> 4 dS/m) were attributed to the effect of sea water. The cation exchange capacity (CEC) of the soil samples ranged from 4.05 to 159.81 meq^+/100g with a mean value of 31.43 meq^+/100g. The mean CEC value was higher than the maximum concentration in natural soils (10 meq^+/100g). The soils were rich in cations. Sodium contents ranged between 0.03 and 327.49 mg/kg, while potassium varied from 0.03 to 38.18 mg/kg. Calcium and magnesium contents varied from 0.14 to 246.5 mg/kg and 0.05 to 445.04 mg/kg. These values exceeded the average concentrations in natural soils (Table 1).

4.2 Trace elements

A descriptive summary including natural background levels and threshold values of the trace elements considered (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) are presented in Table 1. The mean concentrations of Cd, Co, Cr, Cu, Fe Mn, Ni, Pb, V and Zn were respectively 0.55, 8.12, 9.81, 5.22, 189.86, 42.92, 5.85, 8.07, 7.60 and

9.25 mg/kg. Compared to average concentration in soils, the mean values of Cr, Fe, Mn, Ni, Zn exhibited generally low level. Although some elements such as Cu and Zn, are essential nutrients for plants, it is noteworthy that once their concentrations in soil exceed specific thresholds, they will create toxicity (Zhang et al., 2009). The concentration of Fe, Pb and V exceeded their natural background levels but below the threshold values suggesting soils in parts of the NDR were possibly threatened by these elements. A comparison of the concentration of parameters considered between the study area and that of the control site at Obudu, northeast of the area showed relatively higher values for the study area, which is probably due to industrialization especially, activities of oil and gas companies.

Cadmium concentration ranged from 0.0 to 2.0 mg/kg with a mean of 0.42 mg/kg. The SCL soil type showed higher concentrations than the LS > ML > SL > S (Fig. 3). The mean Cd value exceeded the threshold value of 0.25 mg/kg, typical concentration in natural soil (Agarwal, 2009; Goldberg, 1976) and toxic limit of 0.003 mg/kg for soils, Alloway (1995), Table 1. The mean value was 140 times higher than the toxic limit. The content of cobolt ranged from 0.0 to 12.60 mg/kg with 55.6% higher than the threshold value of 9.5 mg/kg and typical concentration in natural soil of 8 mg/kg (Agarwal, 2009). The mean concentration of Co was higher in ML compared to LS > SL > S. The ML soil samples showed higher chromium contents in comparison to SL > LS > S > SCL. The mean concentration of Cr was 26.8 times higher than the toxic value of 0.25 mg/kg (Alloway, 1995). Copper contents varied from 0.15 to 60.2 mg/kg with mean of 4.57 mg/kg. The mean concentration of Cu was higher than at the control site (Fig. 3) and 68.8 times higher than the toxic limit of 0.06 mg/kg (Alloway, 1995).

High variations were observed in Fe contents, which ranged from 0.10 to 34,920 mg/kg with highest mean concentration in the sands (S). The mean concentration of Fe was lower than that from the control site (Fig. 4). This was attributed to differences in the constitution of the parent material, while the study area is underlain by sediments, the control site is underlain by metamorphic rocks. Total Mn varied from 0.0 to 211.0 mg/kg. The highest mean value of Mn was recorded for the ML and the lowest for the LS (Fig. 3). The mean concentration of Mn was lower than the normal concentration in soil of 850 mg/kg (Table 1). The study showed that nickel contents were higher in the LS compared to ML > SL > LS > SCL. The mean Ni was 47.9 times greater than toxic limit of 0.1 mg/kg.

Lead, vanadium and zinc contents varied from 0.0 to 18, 0.0 to 43.32 and 0.03 to 47.83 mg/kg, respectively. The maximum concentration of Pb was 1800 and 180 times higher than the normal concentration in soil and toxic limits of 0.1 and 0.01 mg/kg, respectively. The Pb contents in the different soil types were ML > LS > S > SCL. The average concentration of V was higher than the average concentration in soil, but lower than typical concentration in soil (Table 1). Zinc concentration for the different soil types exceeded the typical concentration in soil and toxic limit of 0.07 mg/kg, but lower than the typical value in soils (Table 1).

4.2 Total hydrocarbon contents

The total hydrocarbon contents (THC) ranged between 0.52 and 2591.65 mg/kg with an average value of 317.43 mg/kg. The concentration of total hydrocarbons in sixty six percent of the soil samples considered exceeded the EGASPIN (2002) limit of 10 mg/kg. The high concentration of THC was attributed to the activities of oil and oil-related companies (Fig. 2). A comparison between the study results with that of the control site at Obudu alongside data from literature (FPDD, 1990; Goldberg, 1976; Agarwal, 2009) revealed a normal global average of potentially toxic elements in soils of the Niger Delta (Table 1, Figure 4).

4.3 Multivariate Analysis

4.4.1 Pearson correlation

The Pearson correlation coefficients between the soil basic properties and heavy metals are listed in Table 3. In the study, pH and EC correlated positively with Cd. The OC correlated with Cd and Co indicating that this soil component is an important sink for these elements. The CEC showed a positive linear relationship with Cd, Co Cr and Pb.

The clay content exhibited a positive relationship with Cu, Fe, Ni, Pb, V and Zn. The correlations between elements and clay contents have been attributed to the high affinities of heavy metals to clay (Ravikovitch et al., 1961; Adriano, 1986; Wang and Chen 1994; Kabata-Pendias and Mukherjee, 2007). These results suggested that the adsorption and retention of elements in soils of the NDR are influence by several factors including pH, EC, OC, CEC and clay content. Copper had a significant correlation with Fe, Mn, Ni, Pb, and V ($r = 0.53 – 0.89$) at 0.01 significance level, which could indicate common influential factors for these elements (Zhang et al., 2009). Lead also presented relatively significant correlation with Cd ($r = 0.50$, $p < 0.01$), Co ($r = 0.74$, $p<0.01$), Cr ($r = 0.70$, $p<0.01$). In addition, manganese had significant correlation with V ($r = 0.73$, $p<0.01$), and Zn ($r = 0.76$, $p<0.01$). Significant correlation was also evident between vanadium and Fe ($r = 0.85$, $p<0.01$) and Ni ($r = 0.91$, $p<0.01$). This indicates that high correlations among heavy metals in soils suggest that similar processes control the element associations in soil (Bradford et al., 1996).

4.4.2 Principal component analysis

To better understand the relationships among the soil parameters and heavy elements, principal component analysis based on factor analysis (PCA/FA) was applied. Five varimax factors (VFs) were identified, which explained a total variance of 85.35% with eigen values >1. VF coefficients with correlation > 0.50 were considered significant. VF 1, 2, 3, 4 and 5 accounted respectively for 35.96, 15.98, 14.67, 11.10 and 7.64% of total variance (Table 4). VF 1 was positively correlated with CEC, Total N, Na, K, Ca and Mg having values of 0.87, 0.74, 0.82, 0.85, 0.93 and 0.94, whereas VF 2 showed positive correlation with Co, Cr and Pb (r = 0.90, r = 0.80, r = 0.84). The parameters pH, THC, sand, silt and Cd were significantly correlated (r = 0.86, r = 0.77, r = 0.69, r = -0.88, r= 0.51) with VF 3. VF 4 was negatively correlated with clay, Cu, Fe and Zn with values of -0.92, -0.79, -0.72 and -0.83, while VF 5 showed positive correlation with OC (r = 0.75) and negative correlation with Mn (-0.77), Ni (r = -92) and V (r = -84).

5. Discussion

5.1 Sources of potentially toxic elements

The Niger delta comprises of three geomorphological units including freshwater, transition zone and coastal zone. The drainage system consists of an upper braided belt and meander belt region with tributaries (Amadi et al., 1989). These tributaries drain and criss cross the delta through a network of rivers and creeks with at least 18 major river systems. During the rainy season, flood occurs. These flood water are loaded with eroded materials from the different geomorphologic zones including impacted sites from activities of oil and gas industries, thus resulting in the pollution of the soils. However, organic matter and clay contents in soils have significant influence on element accumulation and retention (Wang and Qin, 2006), which could have effects on metal mobility and bioavailability (Rejuwerts et al., 1998; Manta et al., 2008).

Significant correlation of Na, K, Ca and Mg with more than one soil properties (OC, CEC, and Total N) highlighted their common origin in the area. This observation has also been documented by Malik et al. (2010). According to Chen et al. (1999) and Qadir et al. (2006) metals of significant correlations with soil properties such as pH, OC, CEC, Total N and soil texture were of natural source. However, Biptista-Neto et al. (2006) reported that metal concentration is much more influenced by the source area rather than their correlation among each other and with soil properties. Thus metals such as Co, Cu, Fe, Ni, Pb, V and Zn, which did not show correlation with pH, EC and OC indicated that their sources were not related to parent materials. According to Zhang (2005), metals such as Na, K, Ca and Mg are abundant in the earth crust, mobile in the environment, highly reactive, do not exist in free form, soluble in water and have similar mode of deposition and depletion in soils. The mean concentrations of these metals were higher than the toxic limits in soils indicating abundance (Table 1).

Significant correlation between Na and K, Ca, Mg; K and Ca, Mg; and Ca with Mg indicated their origin from parent material. Na, K, Ca and Mg were also highly correlated with CEC, total N and OC in factor 1 and to an extent indicated their common source which could be attributed to natural source. The area as earlier mentioned at times is flooded with seawater into the coastal and transitional zones. This indicates another source for these metals which is seawater. Na and K were negatively correlated with Pb, which indicated that some proportion of their accumulation in soil was due to processes depleting Pb or increasing Na and K.

Most of the soil samples collected near DE 1, DE 2, RV 1 and RV 7 within the transitional zone had high concentrations of Co, Cr and Pb were grouped in factor 2, which indicated their common source. Contamination of Co, Cr and Pb has been related to anthropogenic activities such automobiles, sewage sludge. Besides, about 95% of Pb emitted to the environment is associated with human activities (Abraham and Parker, 2002) and added to the environment from automobiles (Newsome et al., 1997; Li and Huang, 2007). The contents of Cd and Co were also related to traffic activities including fuel combustion (Zhang, 2005).

PCA/FA classified Cd in factor 3, which also highlighted anthrogenic sources such as combustion of fuel, wear-and-tear of tyres (Adachia and Tainoshob, 2004). Copper, Fe and Zn were grouped into factor 4 and were also attributed to anthropogenic sources related with vehicular emissions and industrial activities. Cu and Zn showed strong positive correlation indicating same origin. Fe showed negative correlation with OC, CEC and total N indicating that the depletion of Fe is as a result decrease in these parameters due to natural processes. Factor 5 includes Mn, Ni and V. OC belongs to this factor (5) with 0.75, thus an increase in OC led to a decrease in Mn, Ni and V.

5.2 Contamination Risk

The indices of geoaccumulation (I-geo) were calculated for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn and THC. Cd concentrations corresponded variously to moderately contaminated (DE 6), moderately to heavily contaminated (IM 1, RV 1, RV 2); heavily contaminated (BA 1, DE 1, DE 2) and heavily to extremely contaminated (BA 4). Lead (IM 1, DE 1, RV 6) corresponded uncontaminated to moderately contaminated. THC varied from practically uncontaminated through heavily to extremely contaminated at BA 3, BA 5, and DE 1 to extremely

contaminated at RV 1, RV 2, RV 3, BA 1 and BA 2. These locations constitute the area of main activities of oil industries. On the average, the I-geo values for all the samples from the different sampled locations corresponded to practically uncontaminated with the exception of THC (uncontaminated to moderately contaminated) and Cd which corresponded to moderately contaminated (Fig. 5)

The pollution index values of the soil samples varied between 0.001 (AK 11) and 3.67 (BA 4) with an average of 0.63. The low average value indicated that the area of study on the overall was not polluted. High PI (> 1) obtained at BA 1, BA 4, DE 1, DE 2, IM 1, RV 1 and RV 6 reflected high Cd, Cu and THC. Considering the fact that the area is characterized by oil and gas related activities the source of these potentially toxic elements and hydrocarbon were attributed spilled crude oil, lubricating oil, diesel oil, tyres, sewage sludge and oil combustion (Sutherland, 2000).

6. Conclusions

The study has documented for the first time average concentrations, natural background levels and threshold values for some potentially toxic elements in soils of the Niger Delta region of Nigeria. Compared to the average concentration in global soils, the mean values of Cr, Fe, Mn, Ni and Zn exhibited concentration low level. However, the concentration of Fe, Pb and V exceeded their natural background levels but below the threshold values suggesting soils in parts of the study area were possibly threatened by these elements.

Correlation analysis indicated that the soil components are important sink for these elements. This suggested that the adsorption and retention of elements in soils of the area are influence by several factors including pH, EC, OC, CEC and clay contents. Principal component analysis based on factor analysis (PCA/FA) showed that the possible sources of the elements under consideration in the Niger Delta region include: natural, parent materials, oil and gas related activities such as spills, leakages, high volume of traffic and combustion of fuel and indiscriminate disposal of waste.

In terms of pollution assessment, the soils of the Niger Delta region are not severely polluted with respect to all the metals under consideration and are safe considering the metals, Co, Cr, Cu, Fe, Mn, Ni, and Zn.

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Table 1 Descriptive statistics of soil parameters and elements including concentration in soils of the control area (Obudu), background levels and threshold values. *Values below analytical detection limit were reported as 0 for statistical computations*

Parameter	Unit	n	Mean	Med	Min	Max	SD	Control (Obudu)	Background value	Threshold value	Average concentration in soil FPDD (1990)	Typical concentration in soil (Agarwal, 2009)	Typical concentration in oil (Goldberg, 1976)	Toxic limits (Alloway, 1995)
pH		32	5.32	5.25	4.00	7.15	0.75	6.05	6.10		5.1-6.0			
EC	ds/m	19	0.73	0.05	0.004	12.53	2.86	0.09	0.09		4			
OC	%	30	2.81	1.56	0.08	23.71	4.77	2.05	2.40		0.2			
CEC	mg/kg	18	31.43	9.79	4.05	159.81	51.39	5.04	15.00		10			
Total N	%	18	0.14	0.12	0.00	0.61	0.14	0.05			0.2			
Na	mg/kg	30	13.60	0.11	0.03	327.49	59.76	0.06			0-7 - 2.0			
K	mg/kg	31	6.04	0.11	0.03	38.18	12.43	0.10			0.6 - 1.2			
Ca	mg/kg	31	22.82	2.28	0.14	246.50	61.00	3.52			10.0 - 25.0			
Mg	mg/kg	31	21.84	1.20	0.05	445.04	80.16	1.36			3.0 - 8.0			
Sand	%	18	68.28	72.35	25.00	100.00	21.65	75.24						
Silt	%	18	16.47	15.65	0.00	41.40	14.73	6.68						
Clay	%	18	15.02	16.80	0.00	45.00	10.90	18.06						
THC	mg/kg	28	317.43	14.60	0.52	2591.65	669.00		950	950				
Cd	ppm	18	0.52	0.39	0.00	2.00	0.50	0.42	0.9	0.9		0.06	0.01	0.003
Co	ppm	10	7.31	8.00	0.00	12.60	5.22	0.00	10	10		8		
Cr	ppm	15	9.81	7.50	0.06	33.30	10.16	0.00	10.20	5.1		100		0.25
Cu	ppm	28	5.22	1.92	0.15	60.20	11.63	0.00	6.5	3.25		20	0.14	0.06
Fe	ppm	30	1897.86	55.10	0.10	34920.00	6439.10	2272.75	100.5	50.25		38000		
Mn	ppm	27	41.36	10.10	0.00	211.10	61.06	6.20	98	49		850	0.10	
Ni	ppm	18	5.85	5.00	0.02	22.80	6.28	2.02	6.5	3.28		40	10.00	0.1
Pb	ppm	21	7.30	3.09	0.00	18.00	7.59	1.98	6.05	7.025		10	0.30	0.01
V	ppm	13	7.01	0.42	0.00	43.32	14.74	0.19	6.8	6.8	0.19		50.00	
Zn	ppm	30	9.25	1.98	0.03	47.83	13.72	0.00	21.5	20.75		50	0.25	0.07

Table 2 Average concentration of parameters in different soil textures

Parameter	Unit	Texture					
		S	LS	SCL	SL	ML	Control
pH		6.42	6.20	4.90	4.37	4.50	6.05
EC	ds/m	0.06	0.22	0.00	3.16	0.07	0.09
OC	%	1.08	2.72	1.20	3.27	1.51	2.05
CEC	mg/kg	9.94	5.15	10.13	10.15	9.79	5.04
Total N	%	0.07	0.17	0.09	0.25	0.10	0.05
Na	mg/kg	109.20	0.07	0.06	0.88	0.05	0.06
K	mg/kg	8.24	0.05	0.07	0.32	0.06	0.10
Ca	mg/kg	83.42	2.16	1.80	2.74	3.44	3.52
Mg	mg/kg	149.08	1.20	1.00	26.09	1.08	1.36
Sand	%	97.17	84.20	74.90	67.02	38.85	75.24
Silt	%	0.67	2.00	4.00	24.25	38.35	6.68
Clay	%	2.17	13.80	21.10	7.62	22.95	18.06
THC	mg/kg	766.41	1400.00	780.00	1080.55	127.50	
Cd	ppm	0.34	0.69	0.70	0.52	0.63	0.42
Co	ppm	4.13	7.40	0.70	5.53	8.00	0.00
Cr	ppm	9.26	10.35	0.00	12.33	14.00	0.00
Cu	ppm	3.60	2.40		18.34	6.50	0.00
Fe	ppm	2854.60	52.20		1263.46	155.25	2272.75
Mn	ppm	92.10	15.50	20.90	96.54	131.00	6.20
Ni	ppm	10.40	4.60	0.80	5.63	6.50	2.02
Pb	ppm	7.90	14.30	0.00	7.78	17.50	1.98
V	ppm	12.06	0.00	0.00	0.63	4.25	0.19
Zn	ppm	4.65	23.35	4.70	8.64	17.75	0.00

Table 3 Pearson correlation coefficient between soil parameters and heavy metals
(Bold correlations are significant at p < 0.05)

Parameter	THC	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
pH	**0.557**	**0.584**	**-0.415**	**-0.575**	-0.314	-0.013	**-0.651**	-0.284	-0.299	-0.092	-0.032
EC	0.008	0.380	-0.200	-0.113	-0.217	-0.215	-0.336	-0.322	-0.111	-0.314	-0.106
OC	**0.514**	**0.506**	**0.500**	0.334	**-0.561**	**-0.627**	**-0.691**	**-0.777**	-0.102	**-0.796**	-0.056
CEC	0.028	**0.549**	0.253	0.305	-0.290	**-0.495**	-0.123	-0.398	0.018	**-0.470**	-0.366
Total N	0.113	**0.552**	0.210	0.266	-0.396	**-0.459**	**-0.643**	**-0.637**	-0.268	**-0.603**	-0.344
Na	-0.164	0.382	-0.271	-0.279	-0.263	-0.236	-0.375	-0.411	**-0.688**	-0.273	-0.294
K	-0.258	0.316	-0.277	-0.277	-0.280	-0.262	-0.125	-0.216	**-0.665**	-0.152	-0.382
Ca	0.070	**0.650**	0.047	0.005	-0.303	**-0.407**	-0.212	-0.382	-0.206	-0.363	-0.296
Mg	0.068	**0.503**	0.114	0.098	-0.289	-0.371	-0.281	-0.362	-0.292	-0.369	-0.287
Sand	**0.519**	0.289	-0.079	-0.108	**-0.690**	**-0.460**	-0.257	-0.085	-0.214	-0.189	-0.514
Silt	**-0.620**	-0.360	0.194	0.316	**0.472**	0.167	**0.403**	0.032	0.235	0.017	0.216
Clay	-0.243	-0.120	-0.092	-0.187	**0.779**	**0.707**	0.001	0.131	0.127	0.358	**0.753**
THC	1.000	**0.430**	0.346	0.083	-0.314	-0.261	-0.397	-0.295	0.354	-0.347	0.269
Cd		1.000	0.103	-0.131	-0.363	-0.358	**-0.542**	**-0.561**	0.097	**-0.491**	-0.048
Co			1.000	**0.860**	-0.080	-0.332	-0.010	-0.167	**0.635**	-0.391	0.233
Cr				1.000	-0.035	-0.321	0.035	-0.131	**0.569**	-0.361	-0.038
Cu					1.000	**0.907**	0.380	**0.594**	0.352	**0.694**	**0.699**
Fe						1.000	0.245	**0.664**	0.111	**0.838**	**0.607**
Mn							1.000	**0.762**	0.256	**0.570**	0.129
Ni								1.000	0.167	**0.928**	0.267
Pb									1.000	-0.009	**0.481**
V										1.000	0.326
Zn											1.000

Table 4 Varimax factor loadings for the soil parameters and heavy metals heavy metals
(Bold correlations are significant at p < 0.05)

Parametr	Factor					Commu
	1	2	3	4	5	nalities
pH	0.06	-0.39	**0.85**	-0.04	0.25	0.93
EC	0.09	-0.25	0.21	0.03	0.41	0.65
OC	0.36	0.26	0.23	0.11	0.75	0.93
CEC	**0.87**	0.27	-0.07	0.21	0.14	0.93
Total N	**0.74**	0.03	0.10	0.13	0.52	0.93
Na	**0.82**	-0.44	-0.01	0.01	0.25	0.94
K	**0.85**	-0.41	-0.05	0.16	0.03	0.93
Ca	**0.93**	0.03	0.11	0.10	0.13	0.92
Mg	**0.94**	0.03	0.10	0.13	0.15	0.93
Sand	0.10	-0.05	0.69	0.68	-0.03	0.93
Silt	-0.05	0.16	-0.88	-0.34	0.02	0.93
Clay	-0.13	-0.12	-0.24	**-0.92**	0.04	0.92
THC	-0.08	0.43	**0.77**	0.03	0.25	0.90
Cd	0.47	0.09	0.51	-0.07	0.43	0.87
Co	0.05	**0.90**	-0.10	0.03	0.22	0.91
Cr	0.03	**0.80**	-0.33	0.18	0.17	0.91
Cu	-0.11	0.06	-0.22	**-0.79**	-0.47	0.93
Fe	-0.21	-0.21	0.02	**-0.72**	-0.52	0.93
Mn	-0.12	0.16	-0.40	0.07	**-0.77**	0.91
Ni	-0.21	0.00	-0.03	-0.13	**-0.92**	0.93
Pb	-0.24	**0.84**	0.06	-0.25	-0.11	0.92
V	-0.19	-0.24	0.02	-0.34	**-0.84**	0.93
Zn	-0.20	0.29	0.15	**-0.83**	-0.10	0.91
Eigenval	8.27	3.68	3.37	2.55	1.76	
% Total variance	35.96	15.98	14.67	11.10	7.64	
Cumul Eigenval	8.27	11.95	15.32	17.87	19.63	
% Cumul Eigenval	35.96	51.94	66.61	77.71	85.35	

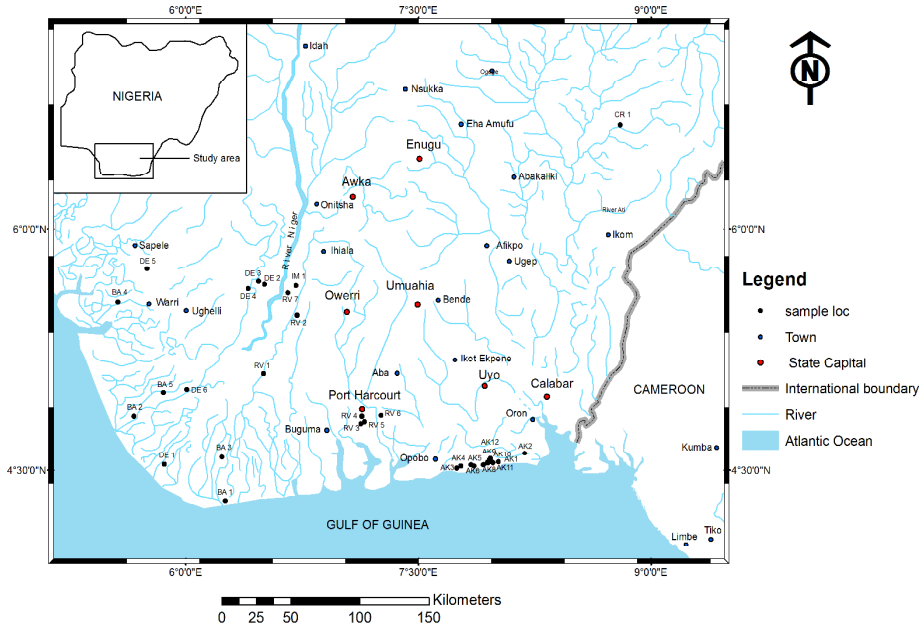

Fig. 1 Map of Niger Delta showing sample locations (The sample point in the NE outside the study area is the control point, Obudu, CR 1)

Fig. 2 Typical spill of crude oil in parts of the study area.

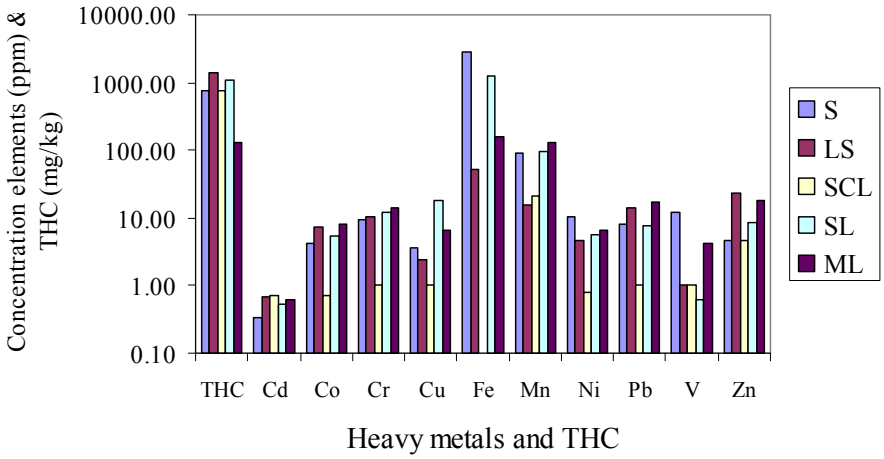

Fig. 3 Average concentration of elements in different soil types

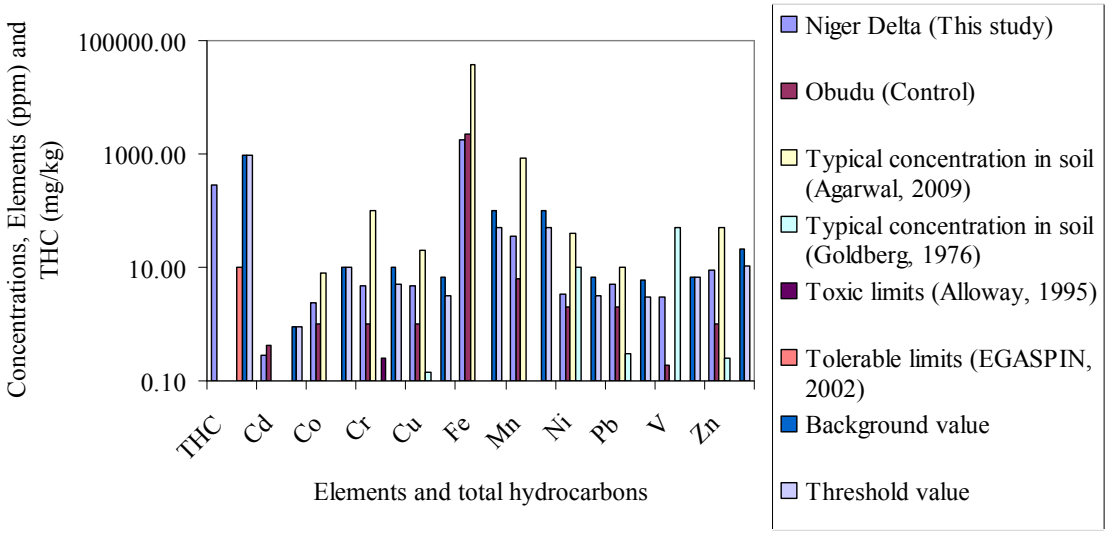

Fig. 4 Average contents of potentially toxic elements for the study area relative to the control area and standards.

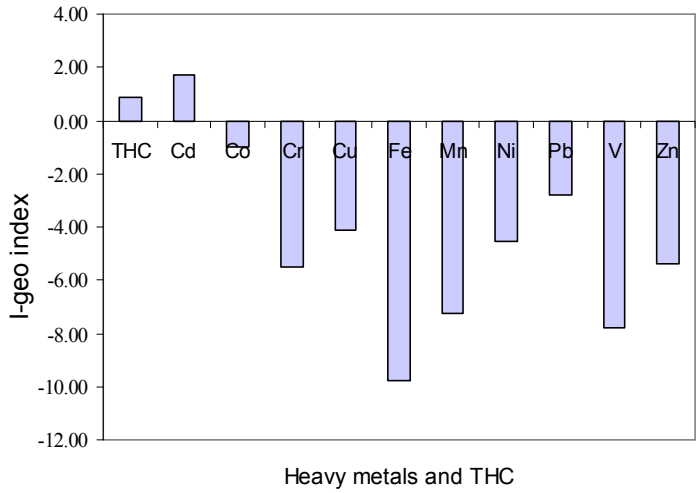

Fig. 5 Average concentration of indices of geoaccumulation (I-geo) for different trace metals and THC

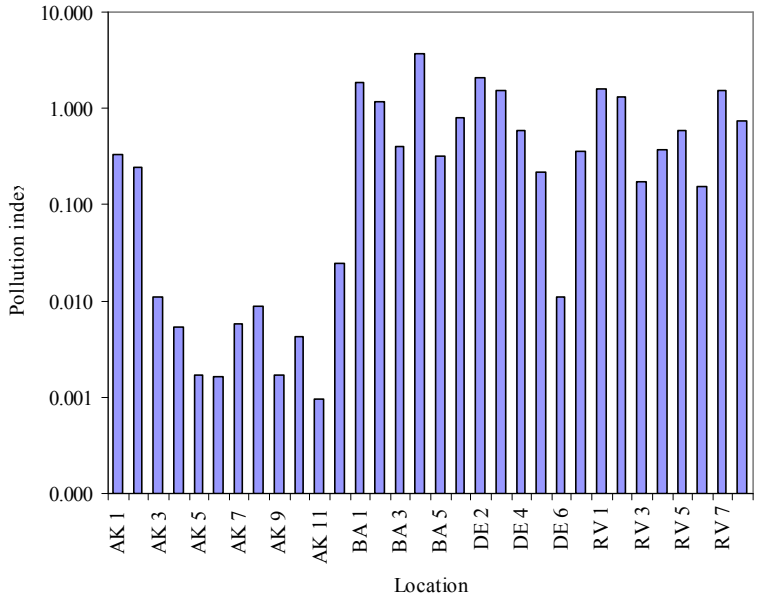

Fig. 6 Distribution of pollution indices for the different locations within the study area