

## Determination of Pollution Intensity in the Soils of Stubbs Creek Forest Reserve, Akwa Ibom State, Nigeria

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**Abstract:** *The soils of Stubbs Creek Forest Reserve were collected and analyzed. The aim was to determine the intensity of its pollution. Soil samples were collected in 14 locations in bush fallow/farmland, (BF/F) 11 locations in secondary forest (SF), 8 locations in freshwater swamp, (FWS), 6 locations in mangrove swamp forest (MSF) and 3 locations in Gmelina plantation (GP) making a total of 42 locations. Samples were collected using stratified random technique at two depths (0-15cm-surface) and (15-30cm-subsurface) which amounted to 84 samples with the aid of soil auger. Samples were processed in the laboratory. Metal contents were assessed using atomic absorption spectroscopy (AAS); soil samples were extracted and measured using spectrophotometer after which THC was calculated. Also, Contamination factor (CF) of the metals was determined by finding the ratio of the mean concentration of these metals in the soil to their tolerable level. Pollution load index (PLI) was computed as the concentration factor of each heavy metal with respect to the tolerable level. For Igeo, indices of the metals were computed using the formular:  $I_{geo} = \log_2 (C/1.5B)$ . Results revealed that Fe values in BF/F, GP and MSF were above the permissible limit for agricultural soils due to human factor. For THC, GP had the highest value compared to others but within the permissible limit for agricultural soils. In terms of CF, Cr value, was >1 in BF/F while Fe value was >1 in MSF indicating pollution state. For Pollution load index, GP and MSF values were >1 indicating high levels of pollution while Igeo values for the five metals were < 0 ( $I_{geo} < 0$ ) which could be natural with little human factor. Besides, the stated and tested hypothesis with ANOVA revealed that there were significant variations in soil properties among the land use types. Therefore, phytoremediation method is recommended for its sustainability.*

**Keywords:** Heavy Metal, Phytoremediation Method, Pollution, Total Hydrocarbon Content

### 1. Introduction

Environmental, economic, and other health issues have been brought on by pollution from a variety of anthropogenic activities from industrial and agricultural sources on a global scale (Xiao-yong *et al.*, 2007). One of the major global issues is soil contamination with metals and semi-metals, and organic pollutants (Nasehi *et al.*, 2008). Lin *et al.*, 2012; Lokeshwari *et al.*, 2006; reported that when pollutants are transported by groundwater, drainage, and other sources and enter the food chain, it is extremely hazardous. However, significant efforts have been made to clean up the environment, and various techniques have been developed and used appropriately (Tajziehchi *et al.*, 2013). Pollution with heavy metal is significantly considered as a potential ecological risk (Siegel, 2002; Lin *et al.*, 2012). More so, human activities and their contaminating agents globally are very complicated and they have serious impact on the various environmental components (Karbassi *et al.*, 2007). According to Akpomuvie (2011), the oil and gas exploration and exploitation, industrial production, and urbanization have had significant impact on the ecological systems for many years now and have caused extensive environmental pollution in the Niger Delta Region of Nigeria, including heavy metal and hydrocarbon contamination. Oil spills, gas flares, industrial discharges, agricultural runoff, domestic effluents, and leachates have all been reported to have negative effects in this area (Jamabo and Chinda, 2010). Moreso, several researchers have investigated the concentration of heavy metals, and hydrocarbon contaminations in the coastal rivers with tidal effect in Nigeria. A good account of such studies in the Niger Delta Region is given in the work of Asonye *et al.* (2007). Equally, heavy metal load of several rivers in Nigeria, mostly in sediments have been reported by Obiere *et al.* (2003) and Davies *et al.* (2006) on Elechi creek, Chindah *et al.* (2004) on Bonny river, Omoigberale and Ogbeibu (2005) on Ase river and Babatunde *et al.* (2013) on Bonny/New Calabar river estuary in which they advised on how most of the industrial activities should be conducted in this area.

Soil contamination by heavy metals is of most important apprehension throughout the industrialized world (Hinojosa *et al.*, 2004). The adverse effects of heavy metals on soil biological and biochemical properties are well documented. The soil properties i.e organic matter, clay contents and pH have major influences on the

extent of the effects of metals on biological and biochemical properties (Spiera *et al.* 1999). Heavy metals indirectly affect soil enzymatic activities by shifting the microbial community which synthesizes enzymes (Shun-hong *et al.*, 2009). Conversely, long-term heavy metal effects can increase bacterial community tolerance as well as the tolerance of fungi such as *Arbuscular mycorrhizal* (AM) fungi, which can play an important role in the restoration of contaminated ecosystems (Mora *et al.*, 2005) hereby supported by Chen *et al.* (2010) who suggested that heavy metals cause a decrease in bacterial species richness and a relative increase in soil actinomycetes or even decreases in both the biomass and diversity of the bacterial communities in contaminated soil while Karaca *et al.* (2010) reported that the enzyme activities are influenced in different ways by different metals due to the different chemical affinities of the enzymes in the soil system. As observed by Wang *et al.* (2007), it is important to investigate the functioning of soil microorganisms in ecosystems exposed to long term contamination by heavy metals. This is necessary in order to decide on the kind of treatment that should be given to such soil. Again, some of these heavy metals such as As, Cd, Hg, Pb or Se are not essential for plants growth, since they do not perform any known physiological function in plants. Others such as Co, Cu, Fe, Mn, Mo, Ni and Zn are essential required elements required for normal growth and metabolism of plants, but these elements can easily lead to poisoning when their concentrations are greater than optimal values (Garrido *et al.*, 2002; Rascio and Izzo, 2011; Yan *et al.*, 2016).

In recent years, it has become possible to gauge the level of pollution within a system by using sediment and soil geochemistry (Nouri *et al.*, 2008). One of the indices for determining the level of soil pollution is the index of geo accumulation (Igeo) (Muller, 1979). Fe, Zn, and Ni have natural origins in wetlands sediments, according to a study on the amount of heavy metal pollution in Bamdezh wetlands sediments (Vaezi *et al.*, 2015). In a different study, the concentrations of heavy metals in the sediments of the Shavoor River in Khuzestan Province, Iran, showed that the geochemical indicators Enrichment factor (EF) and Igeo were used to quantitatively assess the severity of contamination in the sediments. The experiment's findings revealed that the organic matter content ranged from 1.95% to 3.43%, with a mean value of 2.49%. The elements' EFs were calculated, and the results showed that heavy metals were categorized as non-polluted ones. Similar outcomes were shown by the geo-accumulation index and the enrichment factor (EF) (Karbassi and Pazoki, 2015a).

It is worthy to note that, apart from index of geo-accumulation (Igeo) and Enrichment factor (EF), there are other methods such as “Contamination factor (CF) and Pollution load index (PLI)” that could be used to estimate the extent of pollution within a system (USEPA, 1999; Agarwal, 2009). Metal ions can cause serious issues and contaminate soils, because of its toxicity and bioaccumulation in the biota (Morillo *et al.*, 2002). Since remediation of soils contaminated with metals through engineering and other methods is very expensive (Persans and Salt, 2013), special attention has been paid to phytoremediation method as an emerging, affordable, and practical technology to clean-up soil pollutants, especially when the local plants are used (Gerhardt *et al.*, 2009; Hassani *et al.*, 2015).

Accordingly, having noticed the various anthropogenic activities and their potential effects on the soils of Stubbs Creek Forest Reserve, soil samples were obtained and analyzed in order to determine the concentrations of some heavy metals, total hydrocarbon content and proffer clean-up measure for this area, which prompted the need of carrying out this research based on the following objectives:

- i) To determine the various land use types in SCFR.
- ii) To obtain soil samples from each of them and analyze them for heavy metal concentrations and total hydrocarbon content for assessment.
- iii) And to use different elements quantification factors for assessment in order to proffer clean up measure for its ecosystem.

## 2. Materials and Methods

### 2.1. Study Location

Stubbs Creek Forest Reserve is located in the southern part of Akwa Ibom State between longitudes 7° 59' E to 8° 16' E and latitudes 4° 32' N to 4° 38' N. Soils of Akwa Ibom State are formed from varied parent materials, namely coastal plain sands, beach ridge sands or marine deposits, fresh water alluvium, sandstone

and shale materials (Udoh, 1994). Precisely, the study area falls into beach ridge which forms greater part of the study area and mangrove mudflat (Figure 1).

It is worthy to note that there are numerous anthropogenic activities in SCFR such as; crop farming, lumbering, palm wine tapping, oil exploration and exploitation and others (Umana, 2021). Accordingly, this Reserve adjoins almost the entire mining lease of Mobil Producing Nigeria Unlimited. Between 1970 and 1997, a total of three hundred hectares at the western part of SCFR was acquired by Mobil Producing Nigeria Unlimited for the expansion of Qua Iboe Terminal (QIT). In 1991, part of SCFR was also acquired for the proposed Qua Refinery by Shell Petroleum Company, which was evident during the author's fieldwork (Figure 2). Equally, the eastern part of SCFR is occupied by Universal Energy Resources Limited. In essence, oil and gas companies alone have taken more than one hundred and seventy-nine thousand hectares of SCFR between 1970 and 2005 (Ndoho, 2009), which could bring adverse effects to its ecosystems, hence this study to fill the research gap by carrying out soil analysis on the entire five land use types in SCFR which Ndoho (2009) only carried out soil analysis within the oil marginal field.

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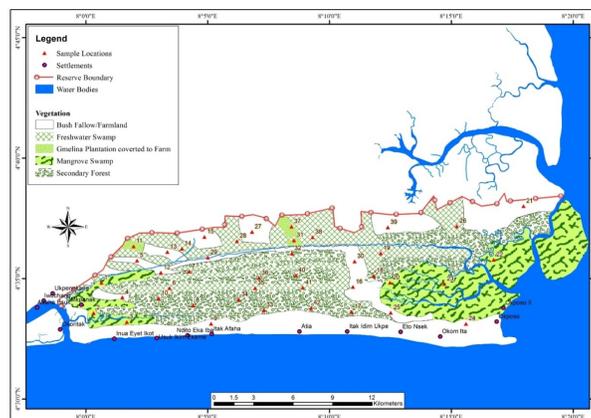


Figure 1: Map of Stubbs Creek Forest Reserve showing soil sampling locations  
Source: Researcher's Fieldwork (2021).



Figure 2: Shell Petroleum Development Company's abandoned oil well-head spotted within a degraded environment in SCFR. Source: Researcher's Fieldwork.

## 2.2. Methods of Data Collection

The study identified five major land use types within SCFR as deduced from the Landsat TM imageries, land use map of this area and ground trothing. These five land use types were bush fallow/farmland (BF/F) secondary forest (SF) freshwater swamp (FWS) mangrove swamp forest (MSF) and Gmelina plantation (GP). Typical tree species found in BF/F included: *Alstoniaboonei*, *Elaeisqueensis*, *Musangacecropoides*, *Anthonathamacrophylla* among others. This was the most affected land use type in SCFR in terms of tree heights, girths and so on. SF had *Xylopiarubescens*, *Xylopiaaethiopica*, *Xylopiavillosa*, *Symphoniaglobulifera*, *Staudtiastipitata* among others. FWS had *Spondiasmombin*, *Uapacastaudtii*, *Uapacaguineensis*, *Raphiahookeri* among others. MSF had *Rhizophoraharrisoni*, *Rhizophora mangle*,

*Rhizophoraracemosa* and *Nypafruticans* abundantly while GP had *Gmelinaarborea*, *Allanblakia floribunda*, *Alstoniacongensis* among others.

With the aid of global positioning system (GPS) and land use map, SCFR was classified into the five land use types and a stratified random sampling technique was used to obtain soil samples at two depths (0-15cm) and (15-30cm). Soil samples were collected at 14 locations in BF/F; 11 locations in SF; 8 locations in FWS; 6 locations in MSF and 3 locations in GP making a total of 42 locations. All together 84 soil samples were collected from the two depths with the aid of a soil auger into bags and labeled accordingly with marker on masking tape. The numbers of soil samples collected were based on the area of coverage of each land use type in SCFR.

In the laboratory, the soil samples were air dried at room temperature; gently crushed with mortar and sieved with 2 mm sieve. The sieved samples were properly stored and sub-sampled for the determination of the various elements. Bulk digestion was carried out by HF-HNO<sub>3</sub>-HCL-HClO<sub>4</sub>. The bio-availability of metals was carried out by a mixture of NaOH and acetic acid at a pH equal to 5 (Karbassi et al., 2015b). Metal contents were measured by atomic absorption spectroscopy (AAS) Buck Scientific (Buck 2010 AAS).

For total hydrocarbon content (THC) analysis, it was determined by shaking of 2g of the representation of soil samples with 10 ml of toluene, and the soil extracted and measured at 240 nm using spectrophotometer (Model Spectronic 20D) after which hydrocarbon content was calculated.

To quantify the degree of elemental accumulation in soil, Contamination factor (CF); Pollution load index (PLI) and Index of geo-accumulation (Igeo) were used. Contamination factor of Cd, Cr, Fe, Cu and Zn were determined by finding the ratio of the mean concentration of these metals in the soil to their tolerable levels (USEPA, 1999). The Pollution load index (PLI) was determined to assess the degree of pollution in the study area. It was computed as the concentration factor of each heavy metal with respect to the tolerable level (Agarwal, 2009).

Using the formular:  $5\sqrt{CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_5}$  while Geo-accumulation index (Igeo) of Cd, Cr, Fe, Cu and Zn were computed using the formular:  $I_{geo} = \log_2 (C/1.5B)$ .

Where C = the measured concentration of the metal in the soil

B = geochemical background concentration of the elements (Average Shale –World geochemical background concentration)

1.5 = the background matrix correlation due to lithological variations.

Moreover, a research hypothesis was stated thus:

H<sub>0</sub>: There are no significant variations in soil properties among the sampled land use types in SCFR.

H<sub>1</sub>: There are significant variations in soil properties among the sampled land use types in SCFR.

A two-way analysis of variance (ANOVA) was used to determine the variations in soil properties among the land use types in the study area. It is a technique used to obtain independent estimates of variance based on variability between and within samples (Udofia, 2011). In this research, variables that formed the groups include: Heavy metal concentrations (Fe, Cu, Zn, Cr, Cd) of soils among the five land use types in SCFR.

The model is stated as follows:

$$\sum^k \sum^h (xy - \bar{x})^2 + \sum \sum (xy - \bar{x})^2 + \sum \sum (xy - \bar{x})^2$$

$$i = i \quad i - 1 \quad i = ii - 1$$

$$TSS = BSS + WSS$$

Where k = number of samples or groups

n = number of observations in the sample

xy = value for all observations i.e the grand or overall mean

x<sub>1</sub> = Mean for the 1<sup>st</sup> sample

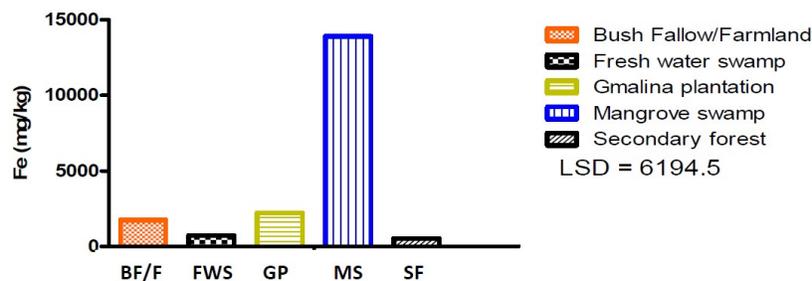
$\Sigma\Sigma$  = The two summation signs indicating the sum of all items in the matrix i.e all k columns.

### 3. Results

#### (a) Heavy Metals

##### (i) Iron (Fe)

The mean available Fe in bush fallow/farmland was 1742.0 mgkg<sup>-1</sup>, freshwater swamp was 729.0 mgkg<sup>-1</sup> (low), Gmelina plantation was 2222.0 mgkg<sup>-1</sup>, and mangrove swamp was 13893.0 mgkg<sup>-1</sup>, while secondary forest was 532.0 mgkg<sup>-1</sup> within 0-15 and 15-30 cm soil depth. Available Fe was significantly higher ( $p < 0.05$ ) in mangrove swamp soil than that of bush fallow/farmland, Gmelina plantation, secondary forest and freshwater swamp soils (Table 1, Figure 3). The trend was as follows: mangrove swamp > Gmelina plantation > bush fallow/farmland > freshwater swamp > secondary forest. Available Fe in bush fallow/farmland, Gmelina plantation and mangrove swamp soils were above the permissible limit of 1000 mg/kg for agricultural soils (USEPA, 1999). There was no significant difference in content of available Fe between 0-15 and 15-30 cm soil depths.



Vegetation Types:- Figure 3: Iron content in the study area. Source: Data analysis (2021).

##### (ii) Copper (Cu)

The mean available Cu in bush fallow/farmland was 2.0 mgkg<sup>-1</sup>, freshwater swamp was 4.5 mgkg<sup>-1</sup>, Gmelina plantation was 14.1 mgkg<sup>-1</sup>, and mangrove swamp was 4.1 mgkg<sup>-1</sup> while secondary forest was 1.6 mgkg<sup>-1</sup> within 0-15 and 15-30 cm soil depths (Table 1). Available Cu was significantly higher ( $p < 0.05$ ) in Gmelina plantation than others but within the permissible limit of 20.0mg/kg for agricultural soils (Agarwal, 2009). There was no significant difference in content of available Cu between 0-15 and 15-30 cm soil depths.

##### (iii) Zinc (Zn)

The mean available Zn in bush fallow/farmland was 29.4 mgkg<sup>-1</sup>, freshwater swamp was 27.6 mgkg<sup>-1</sup>, Gmelina plantation was 18.8 mgkg<sup>-1</sup>, and mangrove swamp was 23.8 mgkg<sup>-1</sup> while secondary forest was 15.9 mgkg<sup>-1</sup> within 0-15 and 15-30 cm soil depths (Table 1). Available Zn was significantly higher ( $p < 0.05$ ) in bush fallow/farmland than others. The trend was as follows: bush fallow/farmland > freshwater swamp > mangrove swamp > Gmelina plantation > secondary forest. Available Zn in the study area was within the permissible limit of 50 mg/kg for agricultural soils (Agarwal, 2009). There was no significant difference in content of available Zn between 0-15 and 15-30 cm soil depths.

##### (iv) Chromium (Cr)

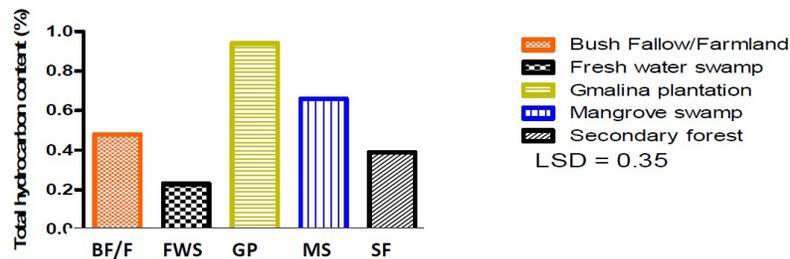
The mean available Cr in bush fallow/farmland was 1.5 mgkg<sup>-1</sup>, freshwater swamp was 1.2 mgkg<sup>-1</sup>, Gmelina plantation was 0.4 mgkg<sup>-1</sup>, mangrove swamp was 1.4 mgkg<sup>-1</sup> while secondary forest was 0.9 mgkg<sup>-1</sup> within 0-15 and 15-30 cm soil depths (Table 1). Available Cr in the study area fell within the permissible limit of 100 mg/kg for agricultural soils (USEPA, 1999) but there is need to curtail anthropogenic activities to guide against environmental pollution. There was no significant difference in content of available Cr between 0-15 and 15-30 cm soil depths and among the land use types under consideration.

##### (v) Cadmium (Cd)

The mean available Cd in bush fallow/farmland was 0.04 mgkg<sup>-1</sup>, freshwater swamp was 0.04 mgkg<sup>-1</sup>, Gmelina plantation was 0.10 mgkg<sup>-1</sup>, mangrove swamp was 0.10 mgkg<sup>-1</sup> while secondary forest was 0.03 mgkg<sup>-1</sup> within 0-15 and 15-30 cm soil depths (Table 1). Available Cd in the study area was within the permissible limit of 3.0 mg/kg for agricultural soils (Agarwal, 2009). There was no significant difference in content of available Cd between 0-15 and 15-30 cm soil depths and among the land use types under consideration.

**(b) Total Hydrocarbon Content**

The mean total hydrocarbon content in bush fallow/farmland was 0.48 %, freshwater swamp was 0.23%, Gmelina plantation was 0.94%, and mangrove swamp was 0.66% while secondary forest was 0.39% within 0-30 cm soil depths. Total hydrocarbon content was significantly higher (p <0.05) in Gmelina plantation than bush fallow/farmland, freshwater swamp and secondary forest and mangrove swamp soils. The trend was as follows: Gmelina plantation > mangrove swamp > bush fallow/farmland > secondary forest > freshwater swamp (Figure 4).



Vegetation Types: - Figure 4: Total hydrocarbon content Source: Data analysis (2021)

**Table 1: Essential and non-essential micronutrient contents of soils of the study area**

Land use types	Fe (mgkg <sup>-1</sup> )			Cu (mgkg <sup>-1</sup> )			Zn (mgkg <sup>-1</sup> )		
	Depth (cm)								
	0-15	15-30	Mean	0-15	15-30	Mean	0-15	15-30	Mean
Bush fallow/farmland	1837.0	1647.0	1742.0*	2.7	1.2	2.0*	30.9	27.9	29.4
Freshwater swamp	874.0	584.0	729.0*	3.2	5.9	4.5*	27.5	27.7	27.6
Gmelina plantation	1651.0	2793.0	2222.0*	13.1	15.0	14.1	20.6	17.0	18.8*
Mangrove swamp	15541.0	12246.0	13893.0	4.5	4.2	4.3*	24.7	22.9	23.8
Secondary forest	333.0	730.0	532.0*	1.2	2.0	1.6*	15.0	16.8	15.9*
Mean	4047.0	3600.0		4.9	5.7		23.7	22.4	
LSD (0.05)									
Land use types	6194.5			3.4			9.8		
Depth	3917.8			2.2			6.2		
Land use types x Depth	8760.4			4.8			13.8		

Land use types	Cr (mgkg <sup>-1</sup> )			Cd (mgkg <sup>-1</sup> )			Total Hydrocarbon Content (%)
	Depth (cm)						
	0-15	15-30	Mean	0-15	15-30	Mean	0-30
Bush fallow/farmland	2.0	0.9	1.5	0.08	0.006	0.04	0.48*
Freshwater swamp	0.6	1.9	1.2	0.006	0.08	0.04	0.23*
Gmelina	0.3	0.5	0.4	0.20	0.00	0.10	0.94
Mangrove swamp	1.3	1.4	1.4	0.08	0.13	0.10	0.66
Secondary forest	0.5	1.3	0.9	0.04	0.03	0.03	0.39*
Mean	0.9	1.2		0.08	0.05		
LSD (0.05)							
Land use types	1.2			0.07			0.35
Depth	0.7			0.04			
Land use types x Depth	1.7			0.10			

Source: Data Analysis (2021).

**(c) Elements quantification factors for pollution**

**(i) Contamination factor (CF)**

The result shows that the contamination factor of Cd, Zn and Cu in all the land use types under consideration were less than 1 (CF<1) indicating that they were at low contamination in the study area. But the Contamination factor of Fe and Cr were above 1 (CF>1) indicating that bush fallow/ farmland had the highest Cr contamination while mangrove swamp had the highest Fe contamination, signifying higher levels of pollution of these metals in the study area (Table 2).

**Table 2: Mean concentration and tolerable level of metals under consideration**

Land use Type	Fe	CF	Cu	CF	Zn	CF	Cr	CF	Cd	CF	PLI
Bush fallow/farmland	1742.0	17.29	2.0	0.1	29.4	0.59	1.5	6.0	0.04	0.01	0.074
Freshwater swamp	729.0	7.29	4.5	0.23	27.6	0.60	1.2	4.8	0.04	0.01	0.089
Gmelina plantation	2222.0	22.22	14.1	0.71	18.8	0.38	0.4	1.6	0.10	0.33	3.36
Mangrove swamp	13893.0	1389.3	4.3	0.22	23.8	0.48	1.4	5.6	0.10	0.33	36.37
Secondary forest	532.0	5.32	1.6	0.80	15.9	0.32	0.0	0.0	0.03	0.01	0.030
Tolerable level	100*		20**		50**		0.25**		3.0**		

Key: \*USEPA (1999), \*\*Agarwal (2009). Source: Researcher's fieldwork (2021).

**(ii) Pollution load index (PLI)**

The value of PLI in bush fallow/farmland, freshwater swamp and secondary forest were less than 1 (PLI<1) indicating low pollution or the pollution may not be attributed to anthropogenic activities but to natural weathering processes (Table 2). PLI values of Gmelina plantation and mangrove swamp soils were above 1 (PLI>1) indicating that the soils were polluted due to anthropogenic activities.

**(iii) Index of geo-accumulation (Igeo)**

The result of comparing the current measured mean concentration of the metals with the background or pre-industrial level reveals that the values were less than zero (Igeo<0) indicating uncontaminated state of the study area (Table 3). This implies that the content of the metals measured were mostly due to natural processes or crustal materials and very little of anthropogenic activities.

**Table 3: Geo-accumulation index of soils of the study area**

Land use Type	Fe	Igeo	Cu	Igeo	Zn	Igeo	Cr	Igeo	Cd	Igeo
Bush fallow/farmland	1742.0	-1.00	2.0	-1.00	29.4	-0.16	1.5	-1.48	0.04	-0.52
Freshwater swamp	729.0	-1.48	4.5	-0.63	27.6	-0.18	1.2	-1.58	0.04	-0.52
Gmelina plantation	2222.0	-1.00	14.1	-0.16	18.8	-0.36	0.4	-1.00	0.10	-0.14
Mangrove swamp	13893.0	-0.18	4.3	-0.70	23.8	-0.25	1.4	-1.48	0.10	-0.14
Secondary forest	532.0	-1.58	1.6	-1.18	15.9	-0.44	0.0	0.00	0.03	-0.63
Average shale	46,000.00		45.0		95.0		90.0		0.3	

Source: Researcher's fieldwork (2021).

In testing the hypothesis, the p-value of  $\leq 0.05$  alongside the value of LSD were used as basis for determining whether there were significant variations or otherwise. In this regard, the ANOVA result revealed that soil properties being heavy metals and total hydrocarbon content obtained F – statistic with P-value < 0.05 implying that the heavy metal concentrations and total hydrocarbon content of the soils varied significantly among the land use types. The alternative hypothesis was accepted while the null hypothesis was rejected established on the aforementioned parameters, indicating that there were significant differences in soil properties in the SCFR among the various land use types.

**4. Discussion**

As indicated in the result, the high content of available Fe in the mangrove swamp soil, Gmelina plantation and bush fallow/farmland compared to others could be attributed to anthropogenic activities resulting in high dissolved content of Fe in coastal water current from the land which in the presence of dissolved sulphides rapidly precipitated as iron pyrite. Also Fe(III) has an influence on sulphur cycling in sediments because it is involved in the oxidation of reduced free sulfide, sulphato-reduction being the main process of organic

matter decomposition in mangrove swamp soil (Holmer *et al.*, 1994). The high content of Cu in the Gmelina plantation soil compared to others could be attributed to anthropogenic activities resulting in the reduction in soil pH and increasing the acidity of the soil. This is because reducing the acidity, increases the solubility of Cu (Holmer *et al.*, 1994). There is need for caution because excess human intake of Cu may result in a number of health problems such as capillary damage (Argun *et al.*, 2007). The low content of Zn in Gmelina plantation and secondary forest compared to others could be attributed to anthropogenic activities resulting in high clay translocation from surface horizons to deep horizons leaving a high sand fraction in the surface soil. This is because increase in coarse (sand) fraction of the soil decreases Zn content (Homer *et al.*, 1994). Zn is considered to be relatively non-toxic, especially if taken orally. However, excess amount can cause system dysfunctions that result in impairment of growth and production (Duruibe *et al.*, 2007).

For Cr, available Cr in the study area fell within the permissible limit of 100 mg/kg for agricultural soils (USEPA, 1999) but there is need for curtailing of anthropogenic activities to guide against environmental pollution by Cr because Cr (IV) is a strong oxidizing agent and is highly toxic. Cr is reported to cause shifts in the composition of soil microbial populations (Shun-hong *et al.*, 2009) while available Cd content in the study was within the permissible limit of 3.0 mg/kg for agricultural soils (Agarwal, 2009). There was no significant difference in the content of available Cd between 0-15 and 15-30cm soil depths and among the land use types under consideration, but there is need for caution because Cd is a well-known heavy metal toxicant with a specific gravity of 8.65 times greater than water. The target organs for Cd toxicity have been identified as liver, placenta, kidneys, lungs, brains and bones (Sobha *et al.*, 2007). The Itai-itai disease in Japan brought environmental dangers of Cd to the world's attention. In terms of THC, its high content in Gmelina plantation soil compared to others could be attributed to crude oil exploration and exploitation in the study area. In terms of CF, Cr value, was >1 in BF/F while Fe value was >1 in MSF indicating pollution state. For Pollution load index, GP and MSF values were >1 indicating high levels of pollution while Igeo values for the five metals were < 0 (Igeo<0) which could be natural with little human factor. Besides, the stated and tested hypothesis with ANOVA revealed that there were significant variations in soil properties among the land use types. Therefore, phytoremediation method is recommended for its sustainability.

## 5. Conclusion/ Recommendations

It was discovered that mangrove swamp forest had the highest content of available Fe compared to others which could be traced to anthropogenic activities resulting in high dissolved content of Fe in coastal water current from the land which in the presence of dissolved sulfides rapidly precipitated to iron pyrite. Accordingly, available Fe in mangrove swamp forest, bush fallow/ farmland and Gmelina plantation were above the permissible limit of 1000 mg/kg for agricultural soils which could be attributed to anthropogenic activities. Bush fallow/farmland had the highest value of Zn which could be traced to anthropogenic activities such as fertilizer input to soils but was within the permissible limit for agricultural soils. For Cr bush fallow/farmland had the highest value but was within the permissible limit for agricultural soils. For Cu, Gmelina plantation had the highest value compared to others while Gmelina plantation and mangrove swamp forest had the same value higher than others of Cd but fell within the permissible limits for agricultural soils. Equally, Gmelina plantation had the highest value of THC in the study area. Consequently, Contamination factor (CF) of the metals (Cd, Cr, Fe, Cu, and Zn) revealed that Cr and Fe were above 1 indicating that bush-fallow/farmland had the highest Cr contamination while mangrove swamp forest had the highest Fe contamination signifying pollution state of these metals in these land use types. For pollution load index (PLI), Gmelina plantation and mangrove swamp forest values were greater than 1 indicating pollution state of Gmelina plantation and mangrove swamp forest while Igeo result indicated that the values for the five metals were less than zero (Igeo< 0) meaning that the contents of the measured metals were mostly due to natural processes with little human factor. However, it is hereby recommended that anthropogenic activities such as crop farming, oil and gas exploration and exploitation should be restricted in this area while remedial measures such as phytoremediation method (planting of specialized plants) should be implemented to clean-up soil pollutants in SCFR.

**5.1. Availability of data and material:** All the needed data are available in this manuscript and have electronic supporting information (ESI).

**5.2. Funding:** This research was not funded by any Governmental or Non-governmental agency.

## References

- Agarwal, S. K. (2009). Environmental biotechnology. First Edition, APH Publishing Corporation, New Delhi, India, pp. 267-289.
- Argun M.E., Dursun S., Ozdemir C. and Karatas M. (2007). Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials*, 141: 77–85.
- Akpomuvie, O. B. (2011). Tragedy of commons: Analysis of oil spillage, gas flaring and sustainable development of the Niger Delta of Nigeria. *Journal of Sustainable Development*, 4:200-10.
- Asonye, C. C., Okolie, N. P., Okenwa, E. E. and Iwuanwu, U. G. (2007). Some physico-chemical characteristics and heavy metal profiles of Nigerian rivers, streams and waterways. *African Journal of Biotechnology*, 6(5):617-624.
- Babatunde, B. B., Sikoki, F. D., Onojake, M. C., Akpiri, R. U. and Akpuloma, D. (2013). Heavy metal profiles in various matrices of the Bonny/New Calabar River Estuary, Niger Delta, Nigeria. *Global Journal of Environmental Sciences*, 12, 1-11.
- Chen G.Q., Chen Y., Zeng G.M., Zhang J.C., Chen Y.N., Wang L. and Zhang W. J. (2004). Speciation of cadmium and changes in bacterial communities in red soil following application of cadmium-polluted compost. *Environmental Engineering Science*, 27(12): 1019- 1026.
- Chindah, A. C., Braide, A. S. and Sibeudu, O. C. (2004). Distribution of hydrocarbons and heavy metals in sediment and a crustacean (*Penaeus notialis*) from the Bonny River/New Calabar River Estuary, Niger Delta. *African Journal Environmental Assessment and Management*, 9:1-17.
- Davies, O. A., Allison, M. E. and Uyi, H. S. (2006). Bioaccumulation of heavy metals in water, sediment and periwinkle (*Tympanotonus fuscatus var radula*) from the Elechi creek, Niger Delta. *Afri. J. of Biotech.*, 5:968-973.
- Duruibe J.O., Ogwuegbu M.O.C. and Ekwurugwu J.N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5): 112-118.
- Garrido S., Campo G.M.D., Esteller M.V., Vaca R. and Lugo J. (2002). Heavy metals in soil treated with sewage sludge composting, their effect on yield and uptake of broad bean seeds (*Vicia faba L.*). *Water, Air, and Soil Pollution*, 166, 303–319.
- Gerhardt, K. Huang, X., Glick, B., Greenberg, B. (2009). Phytoremediation and rhizoremediation of organic soil contaminants, potentials and challenges. *Plant Sci.*, 176(1) 20-30.
- Hassani, A. H., Nouri, J. Mehregan, I., Moattar, F., Sadeghi Benis, M. R. (2015). Phytoremediation of soils contaminated with heavy metals resulting from acidic sludge of Eshtehard Industrial Town using native pasture plants. *J. Environ. Earth Sci.*, 5(2) 87-93.
- Hinojosa M.B., Carreira J.A., Ruiz R.G., and Dick R.P. (2004). Soil moisture pre-treatment effects on enzyme activities as indicators of heavy metal contaminated and reclaimed soils. *Soil Biology & Biochemistry*, 36: 1559–1568.
- Holmer, M., Kristensen, E., Banta G., Hansen, K., Jensen, M.H. and Bussawarite, N. (1994). Biogeochemical cycling of sulfur and iron in sediments of South-east Asian mangrove, Phuket Island, Thailand. *Bioelectrochemistry*, 26: 145-161.
- Jamabo, N. and Chinda, A. (2010). Aspects of the ecology of *Tympanotonus fuscatus var fuscatus* (Linnaeus, 1758) in the mangrove swamps of the upper Bonny River, Niger Delta, Nigeria. *Curr. Res. J. Biol. Sci.*, 2:42-47.
- Karaca A., Cetin, S.C., Turgay O.C., Kizilkaya R. (2010). Effects of Heavy Metals on Soil Enzyme Activities. In: I. Sherameti and A. Varma (Ed), *Soil Heavy Metals*, Soil Biology. Heidelberg, 19: 237-265
- Karbassi, A. R., Abduli, M. A., Mahin, Abdollahzadeh, E. (2007). Sustainability of energy production and use in Iran. *Energy Policy*, 35(10): 5171-5180.
- Karbassi, A. R., Pazoki, M. (2015a). Environmental quality assessment of rivers sediments. *Global J. Environ. Sci. Manage.*, 1(1) 109-116.
- Karbassi, A. R., Tajziehchi, S., Afshar, S. (2015b). An investigation on heavy metals in soils around oil field area. *Global J. Environ. Sci. Manage.*, 1(4):275-282.
- Lin, W., Xiao, T., Wu, Y., Ao, Z., Ning, Z. (2012) Hyper accumulation of zinc by *Corydalis davidii* in Zinc polluted soils. *Chemosphere*, 86(8): 837-842.
- Lokeshwari, E., Chandrappa, G. T. (2006) Heavy metal contents in water, water hyacinth and sediments of Lalbagh tank, Bangalore. *India, J. Environ. Sci. Eng.*, 48(3):183-188.
- Mehrdadi, N., Nabi Bidhendi, G. R., Nasrabadi, T., Hoveidi, H., Amjadi, M., Shojaei, M. A. (2009) Monitoring the arsenic concentration in groundwater resources, Case study: Ghezel Ozan water basin, Kurdistan, Iran. *Asian J. Chem.*, 21 (1): 446-450.

- Mora A.P., Calvo J.J.O., Cabrera F. and Madejon E. (2005). Changes in enzyme activities and microbial biomass after “in situ” remediation of a heavy metal-contaminated soil. *Applied Soil Ecology*, 28: 125–137.
- Morillo, J., Usero, J., Gracia, J. (2002). Partitioning of metals in sediments from the Odielriver, Spain. *Environ. Int.*, 28(4) 263-271.
- Muller, G. (1979). Schwermetalle in den sedimenten des rheinsveranderungenseitumschau, 79(24) 778 – 783.
- Nasehi, F., Hassani, A. H., Kabassi, A. R., Monavari, S. M., Khorasani, N. (2008) Evaluation metallic pollution of riverine water and sediments: A case study of Aras river. *Environ. Monit. Assess.*, 185(1): 197-203.
- Ndoho, J. T. (2009). *Exploitation of biodiversity in Stubbs Creeks Forest Reserve, Akwa Ibom State, Nigeria*. Ph. D Thesis University of Calabar, Calabar, Nigeria.
- Nouri, J., Mahvi, A. H., Jahed, G. R., Babaei, A. A. (2008). Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. *Environ. Geol.*, 55(6) 1337-1343.
- Obire, O., Tamuno, D. C. and Wemedo, S. A. (2003). Physicochemical quality of Elechi creek in Port Harcourt, Nigeria. *J. Appl. Sci. Environ. Mgt.*, 7:43-49.
- Omoigberale, M. O. and Ogbeibu, A. E. (2005). Assessing the environmental impacts of oil exploration and production on the Osse River, Southern Nigeria: I. Heavy metals. *Afri. J. of Environ. Poll. and Health.*, 4(1):27-32.
- Persans, M., Salt, D. (2013). Possible molecular mechanisms involved in nickel, zinc and selenium hyperaccumulation in plants. *Biotechnol. Genet. Eng. Rev.*, 17(1) 389-413.
- Rascio, N. and Izzo F.N. (2011). Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting? *Plant Science*, 180:169–181.
- Shun-hong H., Bing P., Zhi-hui Y. Li-yuan C., and Li-cheng, Z. (2009). Chromium accumulation, microorganism population and enzyme activities in soils around chromium-containing slag heap of steel alloy factory. *Transactions of Nonferrous Metals Society of China*, 19, 241-248.
- Siegel, F. R. (2002) Environmental geochemistry of potentially toxic metals. Springer-Verlag Berlin Heidelberg, e-Book: 978-3-662-04739-2, Germany.
- Sobha K., Poornima A., Harini P., and Veeraiah K. (2007). A study on biochemical changes in the fresh water fish, catlacatla (hamilton) exposed to the heavy metal toxicant cadmium chloride. *Kathmandu University Journal of Science, Engineering and Technology*, 1(4): 1-11.
- Speira T.W., Kettlesb H.A., Percivalc H.J. and Parshotam A. (1999). Is soil acidification the cause of biochemical responses when soils are amended with heavy metal salts? *Soil Biology and Biochemistry*, 31, 1953-1961.
- Tajziehchi, S., Monavari, S. M., Karbassi, A. R., Shariat, S. M., Khorasani, N. (2013) Quantification of social impacts of large hydropower dams: A case study of Alborz dam in Mazandaran Province, Northern Iran. *Int. J. Environ. Res.*, 7 (2): 377- 382.
- Udo, E. J. (1994) Soils and crops production of Akwa Ibom State. In Akwa Ibom State: The land of promise. A compendium edited by Sunday W. Petters, Edet R. Iwok and Okon E. Uya.
- Udofia, E. P. (2011) Applied statistics with multivariate methods. Enugu, Nigeria. Immaculate Publication Limited.
- Umana, U. S. (2021). *Anthropogenic activities on the ecosystem components of Stubbs Creek Forest Reserve, Akwa Ibom State, Nigeria*. PhD Thesis Submitted to Department of Geography and Natural Resources Management, University of Uyo, Nigeria.
- United States Environmental Protection Agency (USEPA) (1999). Risk assessment guidance for super fund value. Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment): Washington D. C. U.S.A
- Vaezi, A., Karbassi, A. R., Valavi, S., Ganjali, M. R. (2015). Ecological risk assessment of metals contamination in the sediment of the Bamdezh wetland, Iran. *Int. J. Environ. Sci. Tech.*, 12(3) 951-958.
- Wang Y. P., Shi J.Y., Wang H., Li, Q., Chen X.C. and Chen Y.X., (2007). The influence of soil heavy metals pollution on soil microbial biomass, enzyme activity, and community composition near a copper smelters. *Ecotoxicology and Environmental Safety*, 67:75–81.
- Yan, X., Jibiao, F., Weixi, Z., Erick, A. Yanhong, L., Liang, C. and Jinmin, F. (2016). Effect of heavy metals pollution on soil microbial diversity and bermudagrass genetic variation. *Frontiers in Plant Science*, 7:755
- Xiao-yong, L., Tong-bin, C., Xiu-Ian, Y., ZH.Li-mei, X., Can-jun, N., X.Xi-yuan, A., Bin, W. (2007). Heavy metals in plants growing on Ni/Cu mining areas in desert Northwest China and the adaptive pioneer species. *J. Nat. Res.*, 22 (3):486-495.