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Assessing the extent of heavy metal contamination in crude oil-impacted soils in the Niger Delta, Nigeria using geochemical indicators

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ABSTRACT: The study presents heavy metal (HM) [copper-Cu, chromium-Cr, nickel-Ni, vanadium-V, lead-Pb, zinc-Zn and iron-Fe] contamination in genuine crude oil-impacted soils and pristine (control) soils. HM concentrations were measured using inductively coupled plasma (ICP). Using soil Contamination factor, Enrichment factor, Pollution load index and Geo-accumulation index, the extent of heavy metal contamination in soils were determined and compared. Results of contaminated factor (CF) of Cu, Cr, Ni, and V were very high in the impacted soils whereas CF of Pb indicated considerable level of contamination. Pollution load index was greater than 1 which implies severe pollution in all the impacted soils while; the control soils indicated a pollution load index of less than 1 showing no pollution. Enrichment factor values of the impacted soils were between 0 and 1, which reveals background enrichment showing the presence of the metals above the threshold values. This may be attributed to anthropogenic sources especially oil spill contamination. The results of geo-accumulation index of Zn, Pb, and V showed considerable accumulation whereas, Fe, Cu, Cr and Ni indicated unpolluted to moderately pollution. Results of V, Ni, Pb, and Cr may be attributed to anthropogenic origin, which are in agreement with the calculated values of the enrichment factor. Results suggest the need for environmental risk assessment and/or remediation of the numerous oil spill sites for soil health and wellbeing of humans.

Keywords: Crude oil-contaminated soil, geo-accumulation index, metal contamination, pollution load index, soil pollution.

INTRODUCTION

Soil contamination by heavy metals has been a significant concern to human health because of their potential transference via food chain (Lou et al., 2012). Heavy metal contamination in soil is both anthropogenic and natural. The anthropogenic sources include industrial activities, metal mining and processing, traffic emissions, and municipal wastes (Cai et al., 2015; Hu et al., 2013). Though metals exist in soils naturally, values exceeding the standard concentration levels are considered environmental contaminants. Metal contamination in agricultural soils may affect the soil structure, interfere with plant growth, and consequently cause damage to human health via food chain. The trend of accumulation of heavy metals in soil is slow, and its effects can be noticed after tens of years (Abbasnia et al., 2018; Song et al., 2017).

Sediments and soil, including materials originating from the terrestrial and land inputs, as well as atmospheric deposition and autogenetic matter from the marine seafloor, preserve a continuous record of regional and global environmental changes, which can be used in reconstructing environmental evolution (Dai et al., 2007; Wang et al., 2003). To some extent, sediment and soil are the mirror of any sedimentary environmental changes, because contaminants glue to soil particles.

Environmental changes are not only driven by natural forces, but also by anthropogenic effects (Kalis et al.,

2003). Especially in recent years, the anthropogenic impacts on the environment have been leading to eutrophication in coastal zone and offshore and the interaction of the natural force and human activities have exerted great effects on the whole environmental system (Cobelo–Garcia and Prego 2003; Wei et al., 2008).

Geochemical indicators including Geo–accumulation index, Pollution load index, Enrichment factor, etc have been previously employed to assess soil contamination and establish if metals concentrations represent background levels (Loska et al., 1997; Ruiz 2001). Some have been used to compare, evaluate, monitor, and managing the effects in soils (Abbasnia et al., 2018; Yousefi et al., 2018).

The aim of this paper was to determine the presence and the extent of heavy metals contamination in soils collected from crude oil-contaminated soil and pristine soil (control) samples in the Niger Delta region. The specific objectives of this study are to: (1) assess the concentrations of heavy metals in soils; (2) identify the possible sources of heavy metals contamination in soils; and (3) classify the level of heavy metal pollution using Geo-accumulation index (Igeo), Pollution load index (PLI), Enrichment factor (EFc) and contamination factor (CF) to provide preliminary data on the environmental conditions; and classify risks associated with heavy metal pollution in soils.

MATERIALS AND METHODS

Description and physiography of the study area

The study location is in Yenagaoa Local Government Area of Bayelsa State (Figure 1). The fields studied (Kalaba: N05 08' 33.6'' E006 26' 33.0''; Ikarama 1: N0509' 16.1'' E006 27' 11.6''; Ikarama 2: N05 08' 47.4'' E006 27' 32.5'') are in Okordia Zarama Clan. The topography is flat to gentle and sparsely vegetated with about eighty five percent (85%) of the people being farmers. It is within the environment of freshwater swamp geomorphic units of the Niger Delta Sedimentary basin. Taylor creek which drains into River Nun and empties into the Atlantic Ocean is the only creek which linked the two study sites. The study area is under the Niger Sedimentary basin. According to Allen (1965) and Ekweozor and Daukorue (1994), deposition of the Niger Delta Sedimentary basin started in the quaternary. The Niger Delta Sedimentary basin is cretaceous to recent, is a marginal sag basin with rollovers anticline, point bars, channels fields among others. It consists of three stratigraphic lithological units notably Akata, Agbada and Benin formations. With reference from the base, the Akata formation consists of marine shales with some sand beds ranging from 550 to 6,000 m (Ekweozor and Daukorue, 1994). It is Paleocene in age and consists of marine microorganisms. Above the Akata formation is the Agbada formation which is a paralic sequence of marine and the continent intertwine (transitional). It is Eocene in age and consists of paralic sequence of sand, clay and shale beds with thickness (ranging from 300 to 4,500 m) thinning both seawards and towards the delta margin. Overlying the Agbada formation is the Benin formation which comprises ninety percent (90%) sand and sandstone with minimal intercalations of clay (Offodile, 1992; Akujieze, 2004). The Benin formation is the thickest in the central area of the Delta. The Benin formation is aquiferous in which all the boreholes are drilled in this formation (Udom et al., 1998). Also, all the engineering structures are also built on the Benin formation. The intercalations of the clay and sand layers gave rise to multi- aquifer system in this layer with shallow unconfined aquifer occurring at depths varying from 20 to 40 m across the area (Etu-Efeotor and Odigi, 1983).

Sample collection and analysis

Soil samples (n=17) were collected from an oil spill site at different depths (3, 6, 9 m) at Ikarama, in the Niger Delta, Nigeria. The rationale behind soil sampling at different depths was to assess the extent of HM contamination down the soil. Three (n=3) pristine samples were collected as controls. Samples were kept in air-tight polythene bags to maintain field-moist status and labelled. Soils were stored in icebox and transported to Acme Laboratory Vancouver, Canada for HM analysis.

Prior to chemical analysis, soil samples were air-dried in the laboratory, sieved through a 1 mm nylon mesh sieve before grinding and homogenisation using mortar and pestle. 1 g soil of each sample was weighed in a high-pressure vessel and 20 mL of freshly prepared aqua regia was added. The solution (sample) was placed in a fume cupboard and kept overnight, to allow different reactions to subside. The pressure vessels containing the sample mixture was placed in a microwave digestion system (MDS) at 160^{o}C and holding time of 20 minutes each, and pressure of 800 W. The pressure vessels and its contents were allowed to cool and the digested samples were filtered.

The extracts (filtrates) were made up to mark with deionised water to obtain 20% aqua regia solution and these were further diluted. Replicates (n=3) were digested along with procedural blanks. Inductively coupled plasma (ICP, AQ300, Vancouver, Canada) was used to measure HM concentrations in digests and extract.

Data analysis

Data evaluations employed in this study include estimation of the Enrichment factor (EFc), Contamination factor (CF), and Pollution load index (PLI) for assessing the degree of modification of these samples in the soil with respect to the analysed trace metals. Geo-accumulation index was also determined for comparison. Enrichment factor was applied

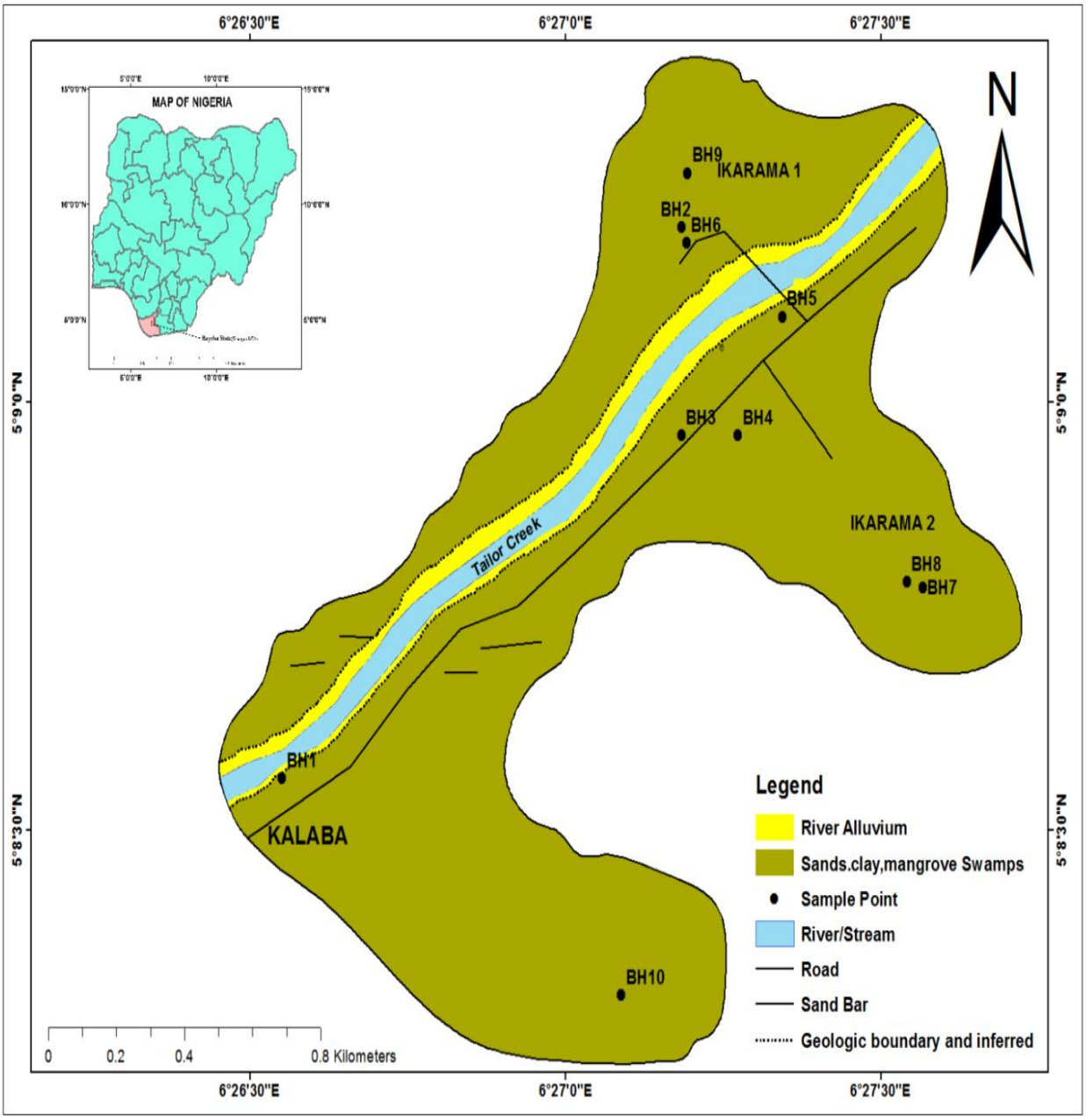

Figure 1. Location of the study area.

to characterise the degree of soil pollution to establish enrichment ratios; and to evaluate the enrichment or depletion of trace metals contamination in the soils. Enrichment factors were calculated owing to the abundance of the species as provenance material in the earth crust (Huheey, 1983; Atgin et al., 2000). Because of the contribution from various natural and anthropogenic sources, the chemical composition of soils or sediments may be affected at each sampling point due to different source contributions at each sampling location (Atgin et al., 2000). The following equation was used to calculate the EFc:

$$EFc = \left({}^{C_M}/_{C_{Fe}}\right) sample / \left({}^{C_M}/_{C_{Fe}}\right) Earth's\ crust \qquad (1)$$

Where, $\left({}^{C_M}/_{C_{Fe}}\right) sample$ is the ratio of concentration of the trace element C_M to that of Fe C_{Fe} in the soil sample and $\left({}^{C_M}/_{C_{Fe}}\right) Earth's\ crust$ is the same reference ratio in the Earth's crust.

The trace elements selected for this study are Cu, Zn, Ni, V, Pb, Ti Ba, Mo, Mn, Ca and Cr. Fe was selected as the reference element, due to its abundance and it is one of

Table 1. Calculated soil pollution load index in the study area.

Soil sample code	Degree of contamination	Modified degree of contamination	Pollution load index
1.IKA/BH2/SS/TS	105.231	10.523	8.244
2.IKA/BH2/SS/3m	44.405	4.441	3.976
3.IKA/BH2/SS/9m	128.659	12.866	10.722
4.IKA/BH6/SS/TS	71.423	7.142	5.219
5.IKA/BH6/SS/3m	40.217	4.022	4.123
6.IKA/BH7/SS/TS	70.633	7.063	6.17
7.IKA/BH7/SS/6m	62.166	6.217	5.644
8.IKA/BH7/SS/9m	68.498	6.85	6.077
9.IKA/BH8/SS/TS	97.667	9.767	6.823
10.IKA/BH8/SS/6m	97.117	9.712	8.095
11.IKA/BH8/SS/9m	75.145	7.515	5.857
13.IKA/BH9/SS/6m	68.85	6.885	6.194
14.IKA/BH9/SS/9m	124.74	12.474	10.424
15.IKA/BH10/SS/TS	95.196	9.52	8.421
16.KAL/BH10/SS/6m	65.88	6.588	5.858
17.IKA/BH10/SS/6m	54.528	5.453	4.48
18.IKA/BH5/SS/Control	16.518	1.652	0
19.IKA/BH3/SS/Control	15.676	1.468	0
20.IKA/BH1/SS/Control	13.587	1.296	0

TS = top soil.

the reference elements commonly used (Nyangababo, 2005; Shanshan et al., 2007; Kamaruzzaman et al., 2008). The reference value of Fe is 983.30 μgg^{-1}. Elements which are naturally derived have an EFc value close to 1, while elements of anthropogenic origin have EFc values of several orders of magnitude. Six categories are recognized: < 1 background concentration, 1–2 depletion to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 very high enrichment and > 40 extremely high enrichments (Sutherland, 2000). The Geo-accumulation index (I_{geo}) which was postulated by Muller in 1969 is the degree of contamination of metal with reference to the metal Enrichment factor. The Geo-accumulation index indicates inter-elemental relationship with respect to the metal sources and pathways in the geo-environment. *Igeo was* calculated as using the equation:

$$I\text{geo} = \log 2\ [Cn/1.5Bn] \quad (2)$$

Where *Cn* is the measured concentration in the sediment for the metal *n*, *Bn* is the background value for the metal *n* (Turekian and Wedepohl, 1961), and the factor 1.5 is used because of possible variations of the background data due to lithological variations.

Muller determined the descriptive classes for increasing *I*geo values (Muller, 1969). Pollution Index (PI) for each of the sample point was evaluated by adopting the equation previously used by Tomlinson et al. (1980).

$$\text{Pollution Index (PI)} = (CF_1 * CF_2 * \ldots\ldots * CF_n)^{1/n} \quad (3)$$

Where, n is the number of metals (Eleven in the present study, i.e. Fe, Cu, Ba, Ni, V, Pb, Ti, Mo, Mn and Ca) and CF is the contamination factor. The contamination factor was calculated using:

Contamination factor (CF) = metal concentration in contaminated soil sample/background values of the metal.

PI value less than 1 is acceptable; PLI equal to 1 indicates pollutant in baseline, whereas PI greater than 1 indicates pollution (Chakravarty and Patgiri, 2009).

RESULTS AND DISCUSSION

Table 1 showed pollution load index (PLI) of soil concentration in the sampled locations in the study area. Pollution load index is a measure which is used to characterize pollution trend qualitatively. Pollution load index less than 1 implies acceptable, whereas a pollution load index greater than 1 implies pollution (Chakravarty and Patgiri, 2009). In the current study, all the impacted sites indicated pollution load greater than 1; showing pollution in all the boreholes of the impacted sites. The un-impacted sites samples of BH3, BH1 and BH5 (control sites); values were less than 1; which means that the environment was not contaminated by crude oil. Mean PLI and mCd were also determined from Table 1. Based on Banerjee and Gupta (2012) classification, the mean of PLI (6.25) indicates that the studied sites are extremely polluted. Furthermore, the mean of mCd (7.47) also

Table 2. Calculated Soil Contamination Factor in study area.

Soil Sample Code	Depth (m)	Contamination factor							
		Cu	Pb	Cr	Ni	Ca	V	Ti	Mo
1.IKA/BH2/SS/TS	3m	13	4.5	5.166	7.5	12	8.2	3.615	0
2.IKA/BH2/SS/3m	6m	6	3.00	3.00	3.50	5	4.4	2.385	0
3.IKA/BH2/SS/9m	9m	18	6.5	7.00	10.00	16	10.8	4.769	0
4.IKA/BH6/SS/TS	3m	24	3.5	3.166	4.50	5	4.6	2.077	0
5.IKA/BH6/SS/3m	6m	6	4.00	2.833	3.50	3	4.8	1.462	0
6.IKA/BH7/SS/TS	3m	9	5.00	4.166	4.50	10	6.6	3.231	0
7.IKA/BH7/SS/6m	6m	9	4.5	6.66	5.00	5	6.8	4.385	0
8.IKA/BH7/SS/9m	9m	10	4.5	4.5	5.00	5	7.2	4.538	0
9.IKA/BH8/SS/TS	3m	13	4.5	5.833	8.50	13	8.6	0.462	0
10.IKA/BH8/SS/6m	6m	13	4.5	5.166	8.50	12	7.6	4.385	0
11.IKA/BH8/SS/9m	9m	10	6.00	4.66	5.00	2	9.6	2.077	0
13.IKA/BH9/SS/6m	6m	10	5.00	4.83	0.66	5	7.4	4.462	0
14.IKA/BH9/SS/9m	9m	17	7.00	6.66	5.50	16	10.00	4.462	0
15.IKA/BH10/SS/TS	3m	14	6.5	6.66	10.00	11	11.4	4.462	0
16.KAL/BH10/SS/6m	6m	3	2.5	1.5	7.50	0	2.40	1.077	0
17.IKA/BH10/SS/6m	9m	9	4.00	4.33	7.50	2	8.6	2	0
18.IKA/BH5/SS/C	3m	9	1.5	0.666	4.5	9	1.2	3.308	0
19.IKA/BH3/SS/C	6m	9	1.5	1.666	1.50	9	1.6	3.462	0
20.IKA/BH1/SS/C	9m	3	3.00	1.333	1.50	3	0.8	1.538	0

TS = top soil, C = control.

showed high degree of contamination according to Abrahim and Parker (2008).

The contamination factor (CF) of copper ranges from 3 mg/kg BH10/6m to 24mg/kg in BH6/top soil. Borehole 6, 7, 8, 9 and the top soil and 6 m depth of borehole 2 are all interpreted as having very high contamination (Table 2). Boreholes 1, 3 and 5 which are also used as control boreholes recorded 3 to 9 mg/kg are all interpreted as having moderate to considerable contamination. The CF of lead spans from 3 mg/kg BH4/3m to 7.00 mg/kg BH9/9m. Boreholes 2, 6, 7, 8 and 10 showed considerable contaminations while borehole 9 (9 m) has a CF value of 7.00 mg/kg; showing very high contamination. Borehole 1, 3 and 5 which serve as a control indicated 1.5 to 3.00 mg/kg are interpreted to have moderate contamination. The CF of chromium ranges from 2.83 mg/kg BH6 (3 m) to 7.00 mg/kg in BH2 at depth of 9 m (Table 2). Borehole 6, 7 8 and 10 [except borehole 2 (9 m)] and borehole 8 recorded very high CF. Borehole 1, 3 and 5 recorded 0.66 to 1.3 mg/kg; indicating low contamination. The CF of nickel ranges from 0.66 mg/kg in BH9/6m to 10.00 mg/kg in BH2 (9 m) (Table 2). Borehole 2 (top soil and 9 m), borehole 8 (top soil, 6 m), and borehole 10 (top soil, 6 m and 9 m) indicated very high CF values. Boreholes 6, 7, 8 and 9 indicated moderate to considerable contamination. Borehole 5, 3, and 1 had concentration values ranging from 1.50 to 45 mg/kg; indicating low to moderate contamination (Table 2). The CF of calcium ranges from 0.00 to 16.0 mg/kg. BH2 (top soil, 9 m), BH7 (top soil), BH8 (top soil; 6 m) and BH9 (top soil; 9 m), indicated very high contamination. Also, at 3 m depth of BH2, top soil and 3 m of BH6, 6 and 9 m of boreholes 7 and 9 and 6 m of borehole 8 and 9 indicated low to moderate contamination. Similarly, boreholes 1, 3 and 5 also indicated moderate contamination.

The concentration of the CF of vanadium ranges from 4.4 mg/kg in BH2 (3 m) to 11.4 mg/kg in BH10 (top soil). BH2: top soil, 9 m; BH7: top soil, 6 m;

Table 3. Calculated Soil Enrichment Factor in study area.

Soil sample code	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Ca	V	Ti	Mo
1. IKA/SSBH2/I/3m	1	2.381	1.037	1.065	0.147	0.423	0.614	0.983	0.672	0.296	0
2.IKA/SSBH2/I/6m	1	0.952	0.835	0.884	0.177	0.442	0.516	0.736	0.648	0.351	0
3. IKA/SSBH2/I/9m	1	1.476	1.046	1.065	0.154	0.414	0.592	0.947	0.639	0.282	0
4. IKA/SSBH10/I/3m	1	1.535	0.961	3.145	0.183	0.415	0.59	0.655	0.603	0.272	0
5. IKA/SSBH6/I/TS	1	1.447	1.163	1.163	0	0.549	0.679	0.582	0.931	0.283	0
6. IKA/SSBH6/I/6m	1	1.137	1.168	0.955	0.212	0.442	0.478	1.061	0.701	0.343	0
7. IKA/SSBH6/I/9m	1	0.664	1.015	0.945	0.189	0.49	0.525	0.525	0.714	0.46	0
8. IKA/SSBH7/I/3m	1	0.838	0.944	0.913	0.164	0.411	0.457	0.457	0.658	0.415	0
9. IKA/SSBH7/I/ 6m	1	1.227	0.96	0.892	0.123	0.4	0.583	0.892	0.59	0.032	0
10. IKA/SSBH7/I/9m	1	1.844	1.085	1.144	0.158	0.454	0.748	1.056	0.669	0.386	0
11.IKA/SSBH8/ I/TS	1	1.148	0.698	0.722	0.173	0.337	0.361	0.144	0.694	0.15	0
13.IKA/ SSBH8/I/6m	1	0.786	1.003	0.941	0.188	0.455	0.517	0.47	0.696	0.42	0
14.IKA/ SSBH8/I/9m	1	1.589	1.049	1.07	0.176	0.419	0.629	1.007	0.629	0.281	0
15 IKA/SSBH9/I/TS	1	0.516	0.802	0.864	0.16	0.411	0.463	0.679	0.703	0.275	0
16 KAL/SSBH1/ C	1	0.506	0.745	1.118	0.373	0.559	0.559	0	0.894	0.401	0
17 IKA/SSBH9/I/9m	1	0.357	0.776	0.872	0.155	0.42	0.485	0.194	0.834	0.194	0
18KAL/SSBH10/I/TS	1	0.958	1.228	1.036	0.23	0.461	0.518	1.036	0.737	0.381	0
19KAL/SSBH10/I/9m	1	0.876	1.289	0.994	0.199	0.46	0.552	0.994	0.729	0.382	0
20IKA/SSBH9/I/3m	1	1.716	0.745	0.838	0.335	0.373	0.419	0.838	0.559	0.43	0

TS = top soil, C = control.

borehole 8 top soil; BH9: 6 and 9 m and BH10: top soil and 6 m indicated very high CF value. BH2: 3 m; BH6: top soil, 3 m and BH10: 6 m are interpreted as having low contamination factor. The control boreholes: 1, 3 and 5 had values ranging from 1.5 to 3.4 mg/kg which were interpreted as having low to moderate contamination.

Overall, the CF (Table 2); pollution load index and the modified degree of contamination (Table 1) across the studied sites are all below maximum allowable heavy metal concentration (mg/kg) limits in soils (WHO, 1996). However, since crude oil spill (petroleum hydrocarbon) contributes to soil heavy metal pollution in soils, monitoring, and risk assessment and/or remediation of oil spill sites is recommended to enhance the soil health and the environment.

The calculated soil enrichment factors (EF) in Table 3 indicates that some selected metals such as Fe, Mn, Cu, Pb, Cr, Ni, Ca, V and Ti lies between 0 and 1; which implies background enrichment. Furthermore, the mean EF shows no enrichment of metals across the studied boreholes except Mn (1.155) and Cu (1.085) with minor enrichment (Sakan et al., 2009). The presence of these elements may due anthropogenic sources (potentially oil spill and related activities), as they were not enriched to the environment via natural processes. The higher concentration of the soil geochemical values of the impacted sites above the permissible limits as opposed to the control sites are strong indication that these elements were introduced to the environment via man-made sources. Furthermore, Pb, Cr, Ni and V are metals that are associated with hydrocarbon. Hence the calculated enrichment factor is consistent with the results of the geochemical surface water and borehole water as well as the 2D resistivity models pointing to pollution.

Geochemical data evaluation (Geo-accumulation Index of soil)

Table 4 shows the values of calculated geo-

Table 4. Calculated Geo-accumulation Index of soil.

Soil sample code	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Ca	V	Ti
IKA/SSBH2/C/TS/01	3.025	4.277	3.078	3.115	4.223	3.784	4.232	3.000	2.848	1.269
IKA/SSBH2/C/6M/02	2.178	2.108	1.918	2.000	3.943	2.344	3.654	1.737	2.451	0.669
IKA/SSBH2/C/9M/03	3.494	4.055	3.558	3.585	3.143	2.222	2.737	3.415	1.553	1.669
IKA/SSBH3/CS/04	2.347	2.965	2.290	1.021	0.100	1.078	0.543	1.737	0.321	0.469
IKA/SSBH6/C/TS/05	1.782	2.315	2.000	2.000	5.342	2.781	2.321	1.000	1.678	1.000
IKA/SSBH6/C/6M/06	2.651	2.837	2.874	2.585	4.323	1.474	1.585	2.737	2.138	1.107
IKA/SSBH6/C/9M/07	2.667	2.075	2.688	2.585	3.213	1.637	1.737	1.737	2.181	1.547
IKA/SSBH7/C/TS/08	2.868	2.613	2.784	2.737	4.654	1.585	1.737	1.737	2.263	1.597
IKA/SSBH7/6M/09	3.281	3.576	3.222	3.115	3.987	1.959	2.503	3.115	2.519	1.123
IKA/SSBH7/9M/10	2.922	3.805	3.040	3.115	3.543	1.784	2.503	3.000	2.341	1.547
IKA/SSBH8/TS/11	3.206	3.405	2.688	2.737	3.657	1.637	1.737	0.415	2.678	1.234
IKA/SSBH8/C/6M/13	2.825	2.478	2.830	2.737	3.324	1.688	1.874	1.737	2.303	1.573
IKA/SSBH8/C/9M/14	3.406	4.073	3.474	3.503	3.231	2.152	2.737	3.415	2.737	1.573
IKA/SSBH9/C/TS/15	3.434	2.478	3.115	3.222	3.134	2.152	2.322	2.874	2.926	1.573
KAL/SSBH1/CS/16	0.840	-0.144	0.415	0.980	0.585	0.000	0.000	0.000	0.678	-0.478
IKA/SSBH9/C/9M/17	2.782	1.294	2.415	1.000	3.654	1.531	3.543	1.210	2.342	0.415
KAL/SSBH10/C/TS/18	2.533	2.472	2.830	2.585	4.456	2.415	3.321	2.585	2.193	1.141
KAL/SSBH10/C/9M	2.593	2.402	2.959	2.585	3.865	1.474	3.123	2.585	2.093	1.206
IKA/SSBH9/C/6M/20	1.255	2.034	0.830	2.585	4.321	2.361	2.231	1.000	2.519	0.037

TS = top soil, CS = control site.

accumulation index of the study site. The calculated values were as follows: Fe (1.255 to 3.05), which implies unpolluted to moderately polluted; Mn (2.034 to 4.277), meaning as moderately unpolluted to moderately polluted; Zn (0.830 to 3.078), which means background concentration to moderately polluted; Cu (1.00 to 3.115), interpreted as unpolluted to moderately polluted; Pb (0.263 to 2.630), meaning background concentration to moderately unpolluted; Cr (1.000 to 2.222), interpreted as unpolluted to moderately unpolluted. Others are: Ni (1.222 to 2.503) meaning unpolluted to moderately unpolluted; V (0.415 to 2.926) and Ti (0.037 to 1.597). The high values of iron, manganese, zinc and copper, which showed moderate contamination compared to V, Ni, Pb, Cr, and titanium (Ti). This shows background concentration and cannot be attributed to crude oil spill. The results of V, Ni, Pb, and Cr confirmed that these elements were not introduced to the environment via natural processes which seems to agree with the calculated values of the enrichment factor which confirmed these metals as having anthropogenic origin. Also, the mean values of Fe, Mn, Zn, Cu, Pb, Cr, Ni, Ca, V, and Ti across the study sites were calculated to be 2.63 (moderate contamination, MC), 2.69 (MC), 2.58 (MC), 2.52 (MC), 3.51 (heavy pollution, HP), 1.89 (low contamination, LC), 2.34 (MC), 2.05 (MC), 2.14 (MC), and 1.07 (LC) respectively. This conclusion was drawn based on Bhuiyan et al. (2010) classification.

Conclusions

This paper reports on the usefulness of geochemical indicators including Contamination factor (CF), Pollution load index (PLI), Enrichment factor (EFc), and Geo-accumulation index (*Igeo*) for the evaluation of the intensity of heavy metal (HM) contamination in oil-impacted soils and pristine (control) soils in the Niger Delta region of Nigeria. Results showed that the HM concentrations at the oil-impacted soils were higher

than those at the control soils. Similarly, HM concentration values were also observed to be higher than the permissible limits. Furthermore, both the mean PLI (6.25) and mean modified degree of contamination (mCd= 7.47) were calculated. PLI value showed that the studied sites are extremely polluted while mCd indicated high degree of contamination. Interestingly, the mean EF values showed no enrichment of metals across the studied boreholes except for Mn (1.155) and Cu (1.085) with minor enrichment. Thus, the higher geochemical indicator values of HMs observed at the impacted sites can be attributed to some form of anthropogenic input from crude oil spills. The recorded concentrations of Pb, Cr, Ni and V (which are commonly known to be associated with petroleum hydrocarbons) also confirmed anthropogenic input. Therefore, there is need for the assessment of crude oil-contaminated land sites to minimise the risk to both the environment and human health.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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