ISSN No:-2456-2165

The Concentration, Spatial Distribution and the Potential Threats of High Cadmium Contamination Levels in Soils in the Niger Delta

Ifeyinwa L Nwankwo
*Groundscan Services Nigeria Limited,
Lydia Abam Lane, Trans-Amadi, Port Harcourt,
Nigeria

Tamunoene K S Abam
Institute of Geosciences and Environmental
Management, Rivers State Univesity, Port Harcourt,
Nigeria

Abstract:- The concentration level and distribution of Cadmium (Cd) were determined from hydrocarbon remediated soil and sediment samples in some parts of the Niger Delta. The results from the descriptive analysis, geo-accummulation index (Igeo) and comparison with guideline values were interpretated as having high potential threat to the environment and human health; the concentration level of Cadmium in the remediated soil and remained higher than the target value of 0.8mg/kg given by the Department of Petroleum Resources (DPR) in the Environmental Guidelines and Standards for Petroleum Industry in Nigeria (EGASPIN) and the World Health Organization (WHO) guideline of 0.003mg/kg. the mean Cadmium concentration values were as high as 50.5mg/kg and 7.29mg/kg in soil and sediment, respectively. Of the topsoil evaluated, 25% of the sample data have most of its Cd concentration values about 2 to 13 times greater than the 0.8mg/kg target value and more than 100% greater than WHO guideline value of 0.003mg/kg. Comparable high concentration values were observed in the median and upper quartile having 50% and 75% of the data, respectively. The acidity of most of the remediated sites evaluated showed low pH values (<5.6) below Food and Agricultural Organization of the United Nation's guideline for pH in soil which is known to encourage Cd accumulation and availability in soil and sediment. The study showed the widespread distribution of anomalous concentration levels of Cadmium in soil and sediment studied which deviates from the average geogenic concentration level of Cadmium in the environment. The result of this work serves as an important call for environmental and public health attention which should include comprehensive hazard assessment due to the observed high cadmium concentration levels and widespread distribution in the area under investigation which were already certified as remediated. And recommend further studies on modelling the transport, retention and accumulation of Cd in the soil, sediment and water in the Niger Delta.

***Keywords*:-** *Contamination, Soil, Cadmium, Spatial distribution, Concentration.*

I. INTRODUCTION

The Niger Delta Region of Nigeria has recorded several oil spill incidences with extensive negative environmental impacts (World Bank, 1995; UNEP, 2011; Enegide & Chukwuemeka, 2018; Okon & Ogba, 2018). The most documented impacts include the effect on biotic and abiotic components of the ecosystem; contamination of soil, groundwater, surface water, sediments, decline in air quality, and subsequent effects on aquatic life, human health, including socio-economic consequences.

There are numerous literatures on hydrocarbon and heavy metal contamination of soil and sediment in the Niger Delta, and associating the increasing contamination of soil and sediment to hydrocarbon exploration, production and related activities. Some of these literature include studies by (Madukosiri & Dressman, 2010; Wegwu, et al., 2011; Ogbeibu, 2011.; UNEP, 2011; Meindinyo & Agbalagba, 2012; Ogboi, 2012; Fatoba, et al., 2015; Aigberua, et al., 2016; Aigberua, et al., 2017). While studies exist on remediation of these contaminated sites, although much attention has not been given to the remediation of soil impacted by heavy metals unlike its co-contaminant petroleum hydrocarbons (TPH), the significant impacts, toxicity and sources of heavy metals such as Cadmium, Lead, Zinc and Chromium in soils in concentrations higher than their guideline values have been defined by several researchers, international Institutes, think tanks and organizations with the mandate of environmental and public health protection.

Cadmium is a bluish-white, soft and ductile metal which is rarely found in its pure form, and occurs mainly as Greenockite (CdS) and Otavite ($CdC0_3$), and principally sourced from processing of the sulfide ores of Lead, Zinc and Copper, where it is recovered as a by-product (USEPA, 1997). According to (Morrow, 2010),it is a rare metal in the earth crust with an average concentration between 0.1 and 0.5 parts per million (ppm). And the World Health Organization (WHO) stated an average concentration value of 0.2mg/kg for cadmium in the earth crust (WHO, 1992).

The Agency for Toxic Substances and Disease Registry (ATSDR) stated that the mining and processing of Zinc, lead, and copper ores contributes to the release of Cd and increase concentration value in the environment (ATSDR, 1999b; Morrow, 2010).

The use of cadmium in industries increased in 1930 to 1980 where it was used as an anti-corrosion agent for steel and iron, as stabilizer for PVC, coating agent and an alloy (Morrow, 2010). The major applications of Cd are in production of nickel-cadmium (NiCd) batteries, cadmium pigments, and cadmium coatings. Although there has been extreme decline in the use of Cd as stabilizers in plastics, alloys, and other applications to less than 1% of total consumption in 2009. Recently, about 22% of total cadmium production comes from recycled Nickel-Cadmium (NiCd) batteries because of increase in recycling of nickel-cadmium noticeably in developed countries such as North America, Europe, and Japan since the past twenty years ((Morrow, 2010).

And in 2006, Cadmium was banned by the European Union's Restriction on Hazardous Substances (RoHS) directive and restricted for the manufacture of electrical and electronic equipment (European Commission, 2006)**.**

Recently, the use of cadmium is generally decreasing due to its recognized toxicity, environmental and health regulations and the use of sustainable environmentally friendly alternatives. The aforementioned are is due to scientific research and discovery about Cadmium as an environmental hazard and a non-essential metal with high degree of toxicity and no known established biological function in higher organisms (Sinicropi, et al., 2010; Hogan, 2010; Goyer & Clarkson, 2001). A review about cadmium in soil and groundwater explained that it is widely distributed in the environment as a non-essential trace metal with elevated concentrations in associated rock types and its mobility is influenced by factors including clay minerals, and organic matter, pH, the redox state, and ionic strength of the solution (Kubier, et al., 2019). While the WHO stated that low soil pH (increased acidity) from acid rain and other processes increases soil cadmium concentration (WHO, 1992), the ATSDR stated that human exposures to environmental cadmium are primarily the result of fossil fuel combustion, phosphate fertilizers, natural sources, iron and steel production, cement production and related activities, nonferrous metals production, and municipal solid waste incineration. Cadmium was reported to be toxic to humans in acute oral doses of 20 to 130 mg/kg body weight, and a dose of Cd as low as 0.04 mg/kg can produce gastrointestinal distress in humans (ATSDR, 1999b). Long-term exposure to cadmium may induce breast cancer, early hypertension, cardiovascular disease, renal abnormalities, lung and prostate cancer. A study in Nigeria showed that Cd toxicity from occupational and lifestyle exposure is a possible cause of male infertility (Akinloye, et al., 2006). While reports on Cadmium contamination from different parts of the world have been made, including its toxicity to human organs, medical treatment, awareness, and measures to prevent further exposure (Rafati Rahimzadeh, et al., 2017). In plants and food, another experiment in Peru revealed that the concentration of Cadmium in potato tuber, leaves and agricultural soil exceeded the maximum allowable limit of 0.1 mg kg^{-1} set by the Codex Alimentarius and above the permissible limit set by the FAO and WHO, due to the use of Cadmium containing agrochemicals and resulting in contaminated soil and reduced crop health quality (Oliva, et al., 2019).

The World Health Organization (WHO) recommended limit for Cd in agricultural soil is 0.003mg/kg and the organization stated categorically that national, regional, and global actions are needed to decrease the global environmental cadmium releases and reduce occupational and environmental exposure because of its toxicity to the human kidney, respiratory organs, and skeletal system. Although present in low concentration in the environment but human activities have increased the level of cadmium present in the environment (World Health Organization, 2019). This could be the recent occurrence in the Niger Delta where many oil and gas companies operate and the widespread existence illegal artisanal refining of crude using rudimentary techniques with unsupervised measures to mitigate further environmental damage. Not left out include corrosion of metal materials leading to metal contamination and spillage of crude oil and gas from corroded pipelines (UNEP, 2011). According to (UNEP, 2011), heavy metals could be present in the soil as natural constituents and can interfere with remediation process, increasing contamination risk. Crude oil contamination of soil results to heavy metal toxicity in living organisms as soil serve as significant sink and source of heavy metals in the environment. Therefore, soil and sediment serve as sinks and sources of heavy metals in the environment (Mahurpawar, 2015; Asimiea & Lawal, 2017; Aigberua, et al., 2017; Aigberua & Inengite, 2019).

In Iran, the assessment of the risks of heavy metals in Ahvaz oil field, Iran revealed that Cd was found among nine (9) heavy metals (As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) to be several times higher than the baseline values. Cd was found to originate from anthropogenic sources such as petroleum leakage and the pollution caused by drilling mud from oil wells with high enrichment in surface soil. And the hazard to human health showed that the carcinogenic to non-carcinogenic diseases were found to be higher in children than in adults (Ghorbani, et al., 2020).

The impact of oil spill on the prevailing metal-soil association in crude oil contaminated soil showed that the elevated toxicity potential of heavy metal could be as a result of crude oil spillage. The research showed that the heavy metals exhibited significant association with the easily mobile and bioavailable fractions of the crude oil contaminated soil. And the control site showed that the concentration levels of metals like Iron and Chromium remained high but poorly mobile and non-bioavailable (Aigberua & Okere, 2019).

Ahmad, et al. (2015) studied the relationships between hydrocarbon spillage and heavy metal explained that oil contamination is a significant contributor of heavy metals to the environment. According to the study, Cadmium is one of the important heavy metals in oil spill contaminated environment which is evident in the result of the studies as the most frequently detected heavy metals were in order of Pb>Ni>V>Zn>Cd. The study recommended a post-spill and baseline studies of heavy metals to be conducted including continuous monitoring of the heavy metals for the interest of human health (Ahmad, et al., 2015). In another study which evaluated the chemical speciation, bioavailability and risk of some selected metals in soils around refined petroleum depot, the result showed that Lead, Zinc and Cadmium had extremely severe enrichment (Adebiyi & Ayeni, 2021). According to Aigberua & Inengite (2019), speciation and mobility of some heavy metal (including Cd) pollutants showed that there is significant affiliation of metals to the readily mobile fractions of crude oil contaminated soil of the Niger Delta, and the significant metal concentration could be as a result of the introduction of crude oil into the soil. The research also showed that Cd was potentially more available than Pb as it was found to be present in the easily mobile fractions of water soluble, exchangeable and carbonate bound fractions (Aigberua & Inengite, 2019). While Okoro et al. (2020) investigated the effects of heavy metals on lithofacies in drilled hydrocarbon wells, drilling crew and people in the environment. The result revealed that the concentration of Cadmium (together with Arsenic, Mercury and Nickel) was above the maximum allowable limit given by the United States Environmental Protection Agency (USEPA, 2002), and cadmium had the second highest Cancer risk in the order of As>Cd>Ni>Cr>Pb.

Some scientific research about hydrocarbon contamination and remediation of soil and sediments in the Niger Delta showed that heavy metals such as Cadmium remained in concentration above the guideline values and exceeded the concentration limits in soil and sediments sampled (Ololade, 2014). According to Madu, et al. (2011), the analysis of crude oil samples obtained from Escravos, Abiteye and Malu platforms in Warri, Delta State showed that Cadmium level was 0.084mg/kg in Malu and Abiteye crude samples while Cadmium was not detected in Escravos crude sample. While soil and water samples collected around Imirigin oil field Bayelsa State Nigeria and analyzed for radioactive and heavy metal concentrations showed that the mean value of Cd exceeded the recommended upper limit of Cadmium concentration in soil (0.08mg/kg given by the DPR EGASPIN), and the high concentration was attributed to oil spillage in the environment (Meindinyo & Agbalagba, 2012).

Aigberua, et al. (2020), studied the geochemical spreading and evaluation of environmental risk of some heavy metals including Cadmium in Taylor Creek sediments, in terms of ecological risk index, the result ranked other metals to have low contamination levels while Cadmium concentration as moderate contamination, depicting the impact of anthropogenic activities in the area.

The United State Environmental Protection Agency (USEPA) reported cadmium, lead, arsenic, chromium, nickel, and zinc as one of the heavy metals found in hydrocarbon contaminated soil. The report also included treatment methods for several metal contaminants in soil, with guide to remediation processes and selection of suitable methods for treatment of soil contaminated with metals using four in situ techniques currently in practice or under development which include electrokinetic remediation, phytoremediation, soil flushing, and solidification/stabilization. The outcome of the experiment revealed that electrokinetic remediation application in Europe was able to treat Cd and other heavy metals contaminated soil (USEPA, 1997).

With the increasing human and environmental health concerns associated with the cumulative concentration of heavy metals in soil, sediments, and water due to anthropogenic input, including metal accumulation associated with industrial activities such as oil and gas and associated sectors, international agencies are creating awareness on the toxicity implications through research and publications. The FAO, UNEP, USEPA, WHO have publications which create awareness about emerging heavy metal contaminants with negative environmental and public health impacts as a result of human development activities where Cadmium and its compounds have been classified as a group 1 human carcinogen (International Agency for Research on Cancer, 1993). The research work of the ATSDR gave detailed report with elaborate information about Cadmium and toxicity to human health. And it defined the properties of the metal, sources, exposure pathway, standard regulations, biological fate, pathologic and health effects, diseases emanating from Cd exposure, clinical evaluation, diagnostic tests and treatment and management (ATSDR, 1990b).

In this study, the sites evaluated for Cadmium concentration levels have been remediated using bioremediation technique, although the remediation targeted the petroleum hydrocarbon components which seemed as the most important contaminants. It is known that most remediation actions implemented are holistic rather than site -specific.

The UNEP recommended that while planning for remedial action, it is important during site characterization that the distribution, mobility and fate of heavy metal contaminants in soil and water media, particle size distribution (PSD) and soil profile information are known (UNEP, 2011). According to UNEP, these tests are used to determine the partitioning of this contaminant from solid to liquid phase and adsorption test for contaminant in surface and groundwater which will unravel the transport behavior of the contaminant and transfer to potential receptors, the distribution of contaminants, PSD and soil profile information determines the spread of contamination plumes.

II. THE STUDY AREA AND GEOLOGY

The study area described in figure 1 lies within latitudes 5.000 to 7.5000 and longitudes 4.500 to 6.000 and include oil and gas infrastructure host communities in Rivers, Bayelsa, Imo, Abia and Delta States.

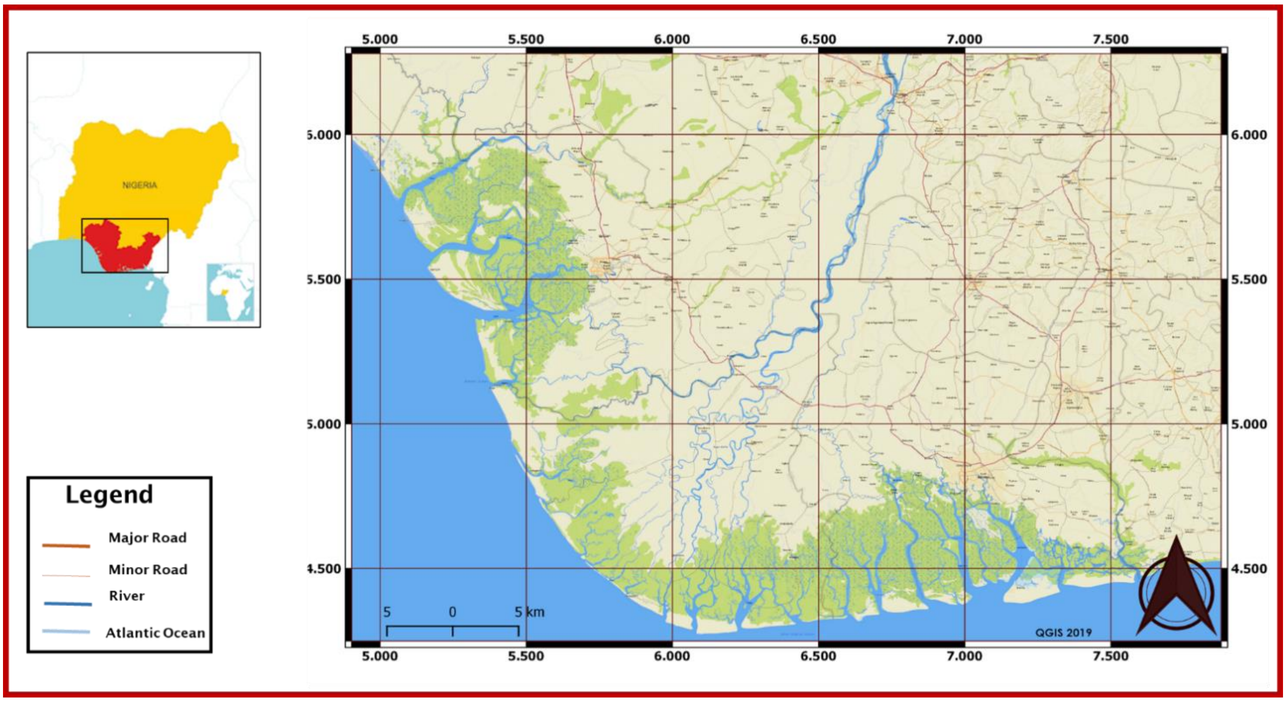

Fig. 1: Map of the Study Area

The geology of the study area comprises the deltaic deposits of marine, mixed and continental origin in the Niger Delta Sedimentary Basin. The geomorphology of the area described in table 1 include dry deltaic plain with rare freshwater swamps, extensive freshwater swamps flood plains and meander belt, saltwater mangrove swamps, estuaries, creeks and lagoon, abandoned and active coastal islands and beaches (Etu-Efeotor and Akpokodje, 1990).

The terrain of the area is extensively flat and few meters above mean sea level, with soil types ranging from sand to clay but predominantly clayey and silty loamy of fluvial origin at the topsoil. The soil in the Delta is rich in organic matter, constantly replenished due to favorable conditions in the Delta, and excellent for agriculture. Ecological zones in the area comprise of mangrove forest and coastal vegetation, freshwater swamp, and lowland rainforest with rivers, lakes, creeks, swamps, marshy lands and dry land of low relief (less than 500m).

Table 1: Geologic Units of the Niger Delta (Etu-Efeotor and Akpokodje, 1990).

GEOLOGIC UNIT	LITHOLOGY	AGE
Alluvium (General)	Gravel, sand, clay, silt	Quaternary
Freshwater Back Swamp, Meander Belt	Sand, clay, some silt, gravel	
Mangrove and Saltwater/Back Swamps	Medium – fine sands	
Active/Abandoned Beach Ridges	Sand, clay, and some silt	
Sombreiro-Warri Deltaic Ridges	Sand	
Benin Formation (Coastal Plain Sands)	Coarse to medium sand with subordinate silt and clay lenses	Eocene
Agbada Formation	Mixture of sand, clay and silt	Eocene
Akata Formation	Clay	Eocene

III. MATERIALS AND METHODS

A. *Data Source*

Method adopted in this research include extensive review of relevant works from literature about Cadmium contamination from oil and gas and related industrial activities and toxicity to environmental and public health. Data from DPR physicochemical analysis of topsoil (0-15m), bottom soil (15-30m) and sediment samples of past spill sites which have been remediated and their respective control data. The total data count obtained from DPR is 2508 physicochemical analysis of soil and sediment samples. The sample collection, handling and laboratory procedures were verified to ensure compliance with the DPR procedure.

B. *Laboratory Analysis and Quality Management*

Procedures of soil and sediment sample collection, transportation, storage, laboratory preparation and analysis followed the regulatory requirements as contained in the DPR EGASPIN (EGASPIN, 2002).

The laboratory analysis procedure reported that small volumes of the representative soil samples were collected from the oil spill impacted sites divided into grid sections at depths of 0-15cm and 15-30cm. The samples were collected

ISSN No:-2456-2165

in aluminum foil and transported to the laboratory in ice trunk not above 4ºC.

Observed quality control and assurance procedures ensured that the samples were representative of the sites, the collection equipment including grab sampling auger and bags were thoroughly cleaned before and after use, samples were appropriately labelled with date, time, and location (georeferenced) and registered in the laboratory.

The laboratory sample preparation and analysis ensured testing and documentation followed the DPR procedures using accurate and precise analytical methods.

Samples collected were analyzed for Cadmium and other heavy metals as well as hydrocarbons. The metal analysis was done using Atomic Absorption Spectroscopy (Varian Spectra AA 220FS) calibrated using certified heavy metal standard.

Cadmium containing samples were prepared using nitric acid digestion and the concentration of Cd in the samples were obtained using AAS calibrated using certified heavy metals standards.

Duplicate lab analysis was performed on each sample and the average concentration of the metals in Mg/Kg were determined and reported.

C. Spatial Distribution of Sample Data and Counts

The spatial distribution map of the remediated soil and sediment sample data and the data counts are shown in figure 2 and the pie chart in figure 3, respectively.

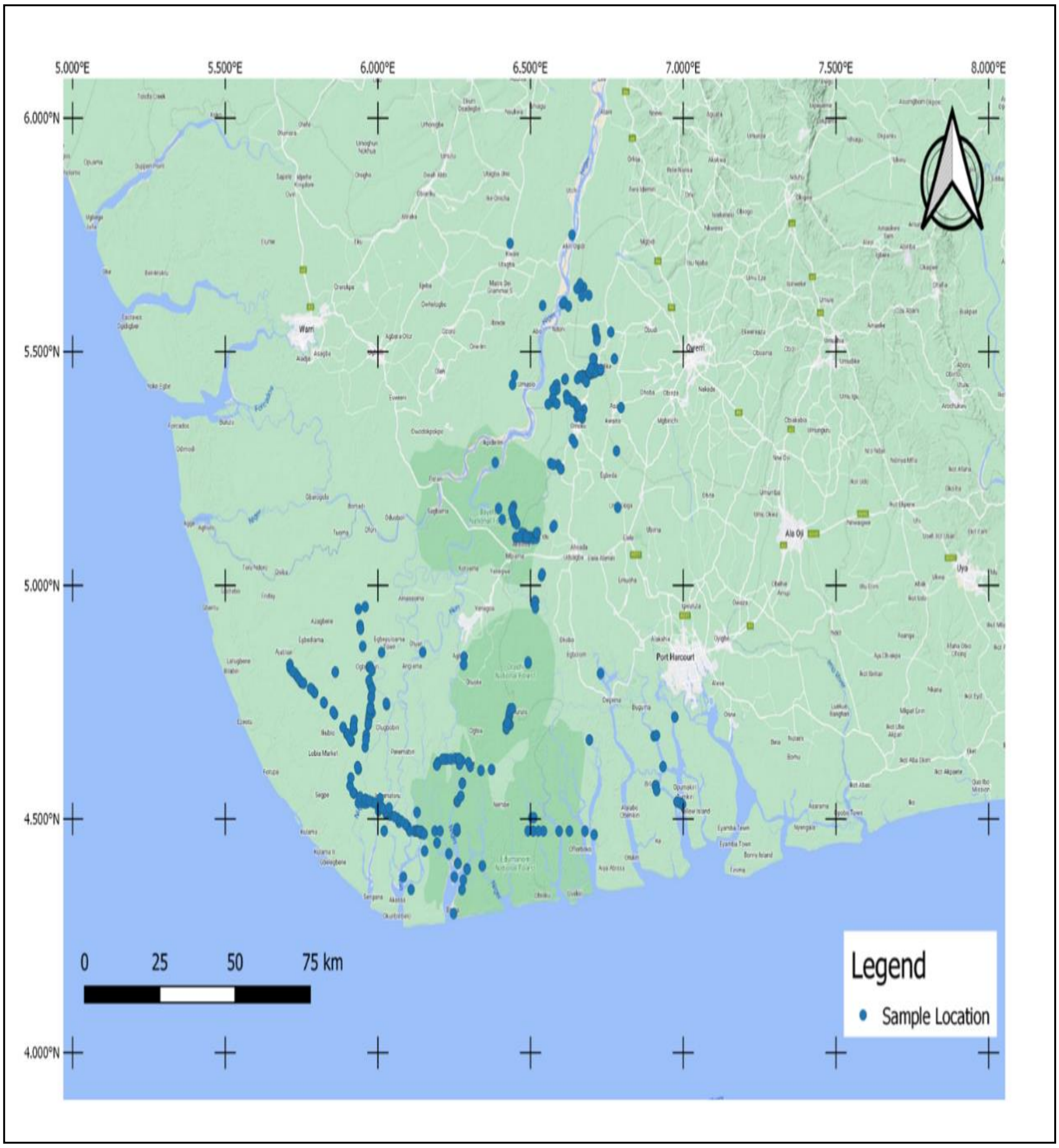

Fig. 2: Location of sample data points

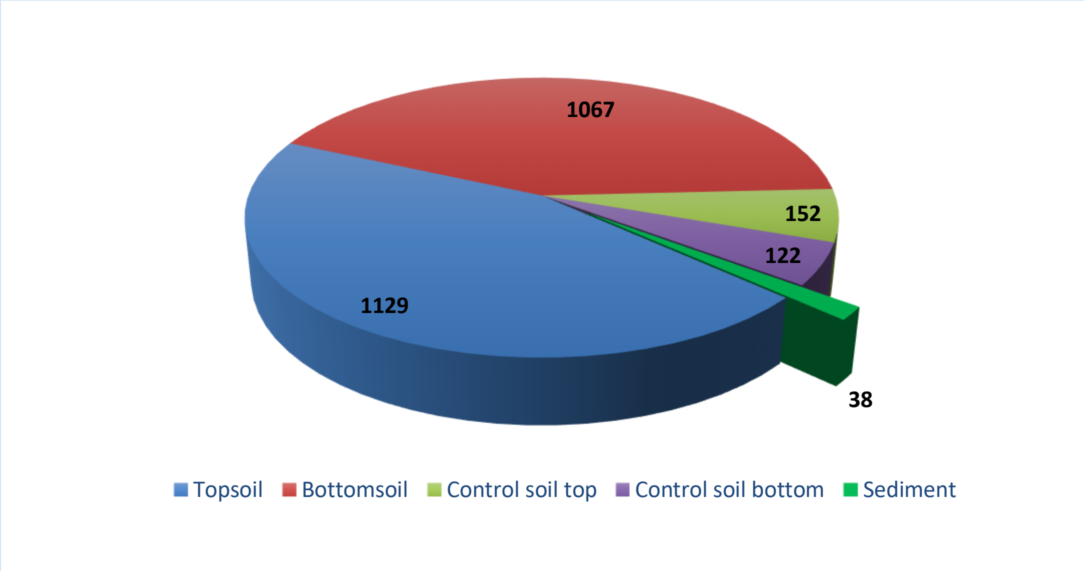

Fig. 3: Count of soil and sediment quality data used for analysis

D. Geostatistical Data Analysis

The data (containing Cd concentration level in mg/kg) was cleaned, sorted and quality checked in preparation for statistical analysis using Microsoft Excel 2019 and Minitab 17.

The descriptive statistical analysis enabled easy comparison of the soil and sediment sample cadmium concentration data with the reference values of the DPR and WHO. According to UNEP and WHO, these interpretations clearly present idea about the environmental quality by summarizing large data quantities in few figures and simplified to convey to non-experts with limited technical knowledge the significance of elevated concentration values in any environmental medium (Bartram, et al., 2006). The five number summary (minimum, first quartile, median, third quartile and maximum) used in this work were explanatory and useful, and evaluated the average concentration values, the dispersion of the Cd concentration values and gave visual summarization of the soil quality with respect to the Cd concentration values easing the comparison with the DPR and WHO standards. These descriptive statistics conducted were presented in tables and graphs as boxplots and linear graphs to explain the qualitative and quantitative spatial variability of Cd contamination values in soil and sediment with reference to the DPR EGASPIN target value and WHO guideline value.

The MS Excel IF formula was used for the ranking of the geo-accummulation index (Igeo) according to the values in table 2. And the assigned Igeo values was imputed into Surfer software to show the distribution of the soil cadmium contamination status of the area under investigation. This index, which is also known as the Müller index, and widely applied to evaluate metals accumulation in soil and sediment, describes the geogenic and anthropogenic status of pollution of the soil or sediment evaluated. And considers the measured cadmium concentration and the local background value of cadmium. And the MS Excel pivot table was used for evaluation of the percentage distribution of the Igeo values based on soil quality ranks.

The Igeo is represented as:

$$I_{geo} = Log_2 \left(\frac{C_m}{1.5*B_m}\right)$$

Where Cm is the measured concentration of the examined metal in the soil samples and Bm is the geochemical background value of the same metal (target value). 1.5 is a constant used for the possible variations of the background data due to the lithogenic effects.

Table 2: Values of Geo-accummulation Index based on Müller's Classification.

VALUE		SOIL QUALITY	REFERENCE
Igeo	*I*geo ≤ 0	Uncontaminated	(Müller, 1981)
	0 < *I*geo < 1	Uncontaminated to moderately contaminated	
	1 < *I*geo < 2	Moderately contaminated	
	2 < *I*geo < 3	Moderately to strongly contaminated	
	3 < *I*geo < 4	Strongly contaminated	
	4 < *I*geo < 5	Strongly to extremely contaminated	
	*I*geo > 5	Extremely contaminated	

ISSN No:-2456-2165

The spatial distribution map of cadmium concentration values and geo-accummulation indices were prepared using Surfer 15 and Google Earth Pro software. The data was gridded using the Kriging method and the contour and post maps of the Cd concentration values, Igeo and pH were generated.

IV. RESULTS AND DISCUSSION

The results of the geostatistical analysis showed that the Cd permissible concentration levels exceed the target value in soil and sediment samples, as shown in table 3 to 7 below which contained the descriptive statistical analysis of the soil and sediments.

The average mean values of the topsoil samples in table 3 exceed the Cd target value of 0.8mg/kg, the minimum values were above the WHO limit of 0.003mg/kg for agricultural soil. The lower quartile (Q1) having 25% of the data had most of its values about 2 to 13 times greater than the DPR 0.8mg/kg target value and more than 100% greater than WHO standard of 0.003mg/kg. Comparable high concentration values can be seen for the median and upper quartile where 50% and 75%, respectively, of the data existed. Similar trends of high cadmium concentration mean levels can be explained with the bottom soil and sediment data evaluated in table 4 and 5, respectively. And same for the control samples of the topsoil and bottom soil presented in table 6 and 7 below.

Table 3: Descriptive statistical analysis for topsoil Cd Concentration values

Variable Cd												
Month/Year	Mean	SE	StDev	Min	Q1	Median	Q3	Max	Range	IQR	Count	Percent
F11	14.467	0.585	4.377	7.24	11.165	13.67	16.34	31.83	24.59	5.175	56	4.9601
J11	3.699	0.395	2.432	0.13	2.293	3.33	4.322	14.18	14.05	2.03	38	3.3658
S11	2.737	0.221	1.21	0.405	1.9	3.145	3.505	4.42	4.015	1.605	30	2.6572
O11	8.742	0.421	1.576	6.29	7.66	8.55	9.663	12.04	5.75	2.003	14	1.24
Ja12	5.981	0.399	1.492	3.88	4.645	5.88	6.903	8.61	4.73	2.258	14	1.24
F12	7.937	0.583	3.031	1.54	4.97	8.17	10.55	12.82	11.28	5.58	27	2.3915
M12	10.017	0.563	2.76	4.34	8.195	10.16	11.807	16.02	11.68	3.612	24	2.1258
AP12	8.549	0.476	2.894	2.39	7.525	8.87	10.025	13.65	11.26	2.5	37	3.2772
MA12	5.942	0.441	2.753	0.85	4.36	5.8	7.76	12.56	11.71	3.4	39	3.4544
J12	9.355	0.344	1.538	4.83	8.438	9.655	10.405	11.07	6.24	1.967	20	1.7715
JU12	10.445	0.233	0.904	8.45	9.74	10.36	11.23	11.86	3.41	1.49	15	1.3286
Ja17	3.259	0.182	3.962	0.054	1.406	2.405	3.955	50.593	50.539	2.549	476	42.1612
JUE17	0.6009	0.0279	0.1045	0.467	0.501	0.5985	0.69	0.806	0.339	0.189	14	1.24
JUO17	0.9326	0.0414	0.575	0.028	0.53	0.854	1.342	2.306	2.278	0.812	193	17.0948
M18	0.8098	0.0529	0.2699	0.259	0.5593	0.8665	1.0322	1.218	0.959	0.473	26	2.3029
A18	0.9517	0.065	0.421	0.397	0.6568	0.9505	1.0562	2.212	1.815	0.3995	42	3.7201
MA18	1.035	0.23	1.84	0.218	0.416	0.743	1.188	15.102	14.884	0.772	64	5.6687

Table 4: Descriptive statistical analysis for bottom soil Cd Concentration values

Variable Cd Month/Year	Mean	SE Mean	StDev	Min	Q1	Med	Q3	Max	Range	IQR	Count	Percent
F11	3.63	0.478	2.865	0.79	1.92	2.545	4.168	16.34	15.55	2.248	36	3.3739
J11	3.343	0.409	2.419	0.003	2.09	2.555	3.28	10.36	10.358	1.19	35	3.2802
S11	6.229	0.303	1.515	4.17	4.97	5.88	7.475	9.33	5.16	2.505	25	2.343
O11	7.2	0.652	2.44	2.83	5.31	7.48	9.172	11.22	8.39	3.862	14	1.3121
Ja12	7.273	0.787	2.946	3.94	4.9	6.54	9.383	13.44	9.5	4.482	14	1.3121
F12	10.263	0.492	2.555	6.11	8.21	9.51	11.83	16.38	10.27	3.62	27	2.5305
M12	9.631	0.691	3.385	2.89	7.357	9.88	11.942	15.39	12.5	4.585	24	2.2493
AP12	6.312	0.509	3.098	0.98	4.06	6.44	8.32	14.18	13.2	4.26	37	3.4677
MA12	8.331	0.272	1.333	5.14	8.14	8.505	9.255	10.51	5.37	1.115	24	2.2493
J12	9.826	0.414	1.85	2.867	9.442	10.175	10.633	11.91	9.043	1.19	20	1.8744
Ja17	3.273	0.175	3.798	0.02	1.352	2.412	4.037	39.603	39.583	2.685	473	44.3299
JUE17	0.6544	0.0547	0.2048	0.139	0.5797	0.6795	0.7688	1.008	0.869	0.189	14	1.3121
JUO17	0.9413	0.0463	0.6434	0.04	0.526	0.738	1.218	2.561	2.521	0.692	193	18.0881
M18	0.8947	0.0767	0.3912	0.184	0.6282	0.903	1.0458	2.143	1.959	0.4175	26	2.4367
A18	0.9763	0.0625	0.405	0.0665	0.7757	0.9675	1.0875	2.433	2.3665	0.3117	42	3.9363
MA18	0.973	0.1	0.797	0.249	0.522	0.885	1.189	6.293	6.044	0.667	63	5.9044

ISSN No:-2456-2165

Table 5: Descriptive statistical analysis for sediment Cd Concentration values

Variable Cd Month/Year	Mean	SE	StDev	Min	Q1	Median	Q3	Max	Range	IQR	Count	Percent
J11	5.462	0.712	1.744	2.31	4.492	5.585	7.023	7.06	4.75	2.53	6	15.7895
Ja17	2.734	0.581	2.25	0.311	0.957	2.02	3.834	7.295	6.984	2.877	15	39.4737
A18	0.9437	0.0792	0.2376	0.493	0.756	1.028	1.106	1.253	0.76	0.35	9	23.6842
MA18	1.482	0.552	1.56	0.603	0.674		1.666	5.214	4.611	0.992	8	21.0526

Table 6: Descriptive statistical analysis of Cd Concentration for topsoil control values

Variable Cd Month/Year	Mean	SE Mean	StDev	Min	Q1	Median	Q3	Max	Range	IQR	Count	Percent
F11	13.166	0.956	4.586	7.08	10.34	12.2	15.42	27.81	20.73	5.08	23	15.1316
J11	3.847	0.845	3.379	0.99	2.023	2.541	4.755	15.11	14.12	2.732	16	10.5263
S11	3.026	0.495	2.04	0.34	1.565	2.68	4.195	8.31	7.97	2.63	17	11.1842
O11	7.89	1.01	2.26	4.42	5.9	7.93	9.87	10.27	5.85	3.96	5	3.2895
Ja12	3.683	0.252	0.436	3.23	3.23	3.72	4.1	4.1	0.87	0.87	3	1.9737
F12	5.82	1.37	4.1	2.44	3.11	4.21	7.9	15.24	12.8	4.79	9	5.9211
M12	8.53	1.34	4.25	3.84	5.08	7.4	11.9	17.21	13.37	6.81	10	6.5789
AP12	7.7	0.78	2.341	2.79	6.55	7.89	9.28	10.65	7.86	2.73	9	5.9211
MA12	6.708	0.663	2.967	0.77	5.045	5.995	9.285	13.76	12.99	4.24	20	13.1579
J12	10.33	1.18	3.34	4.92	9.49	10.28	10.52	17.21	12.29	1.03	8	5.2632
JU12	9.282	0.219	0.693	8.11	8.785	9.5	9.838	9.93	1.82	1.053	10	6.5789
Ja17	1.746	0.521	1.042	0.829	0.896	1.503	2.838	3.148	2.319	1.942	4	2.6316
A18	0.737	0.144	0.25	0.46	0.46	0.804	0.946	0.946	0.486	0.486	3	1.9737
MA18	1.156	0.245	0.949	0.347	0.653	1.016	1.216	4.369	4.022	0.563	15	9.8684

Table 7: Descriptive statistical analysis of Cd Concentration for bottom soil control values

Variable Cd Month/Year	Mean	SE	StDev	Min	Q1	Med	Q3	Max	Range	IQR	Count	Percent
J11	3.466	0.67	2.679	0.72	2.035	2.725	3.778	12.42	11.7	1.743	16	13.1148
S11	2.931	0.412	1.486	0.726	1.72	2.6	4.205	5.495	4.769	2.485	13	10.6557
O11	7.04	1.42	2.83	3.97	4.39	6.88	9.86	10.44	6.47	5.46	4	3.2787
Ja12	3.803	0.24	0.416	3.33	3.33	3.97	4.11	4.11	0.78	0.78	3	2.459
F12	5.02	1.15	3.45	1.87	2.54	3.97	7.04	12.27	10.4	4.5	9	7.377
M12	9.08	1.17	3.71	4.93	5.74	8.34	12.06	15.29	10.36	6.32	10	8.1967
AP12	6.19	1.18	3.13	1.7	3.35	5.9	8.79	10.42	8.72	5.44	7	5.7377
MA12	6.167	0.542	2.424	1.16	4.965	5.9	7.737	12.83	11.67	2.773	20	16.3934
J12	9.622	0.985	2.786	5.93	7.828	9.195	10.85	15.29	9.36	3.022	8	6.5574
JU12	9.052	0.396	1.251	7.2	8.143	9.155	10.012	11.08	3.88	1.87	10	8.1967
Ja17	2.25	1.24	2.47	0.78	0.84	1.14	4.78	5.95	5.17	3.94	4	3.2787
A18	0.838	0.157	0.272	0.596	0.596	0.786	1.132	1.132	0.536	0.536	3	2.459
MA18	2.23	1.27	4.92	0.34	0.57	1	1.5	19.95	19.61	0.93	15	12.2951

Figures 4 to 11 boxplots and line graphs showed that the topsoil cadmium concentration values were above the DPR target value of 0.8mg/kg (The red dash reference line). The median value, lower and upper quartiles which contained the greatest percentage of the Cd concentration data were above 0.8mg/kg. From the boxplot, it is evident that the lowest concentration values remained slightly and above the target value of the DPR, while most of the outliers were above the whiskers of the maximum values of the boxplots.

The Cd concentration values of the topsoil, bottom soil and their respective controls and the sediment were above the DPR target value (the red dashed line in the graphs) and the WHO guideline. The accompanying line graphs representing the averages (mean) followed similar pattern with the generated boxplot mean connect lines (both were created for easy visualization and understanding). The graphs explained that the concentration levels of Cd in soil and sediment after remediation were above the DPR and WHO guideline values.

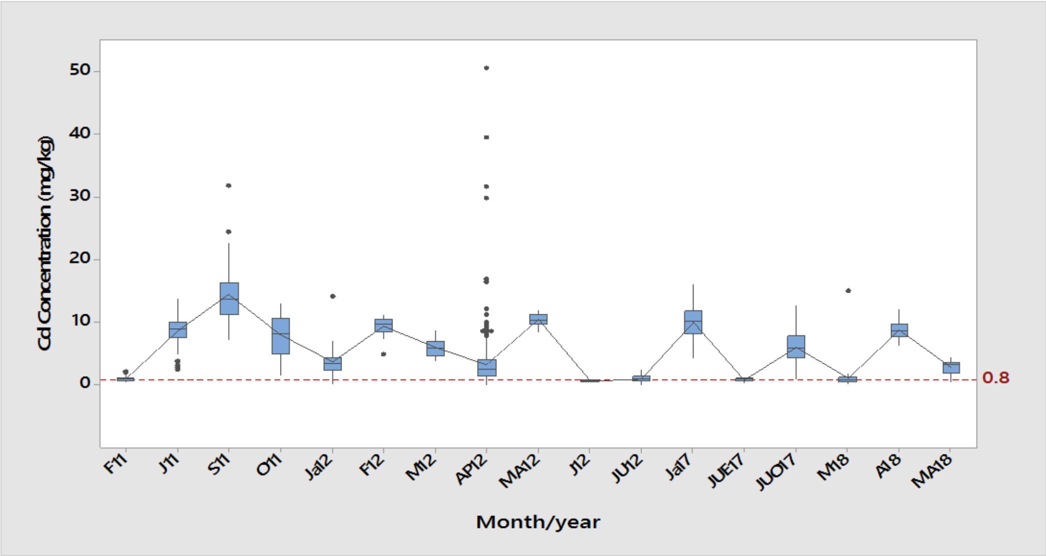

Fig. 4: Boxplot of Topsoil Cadmium Concentration Values

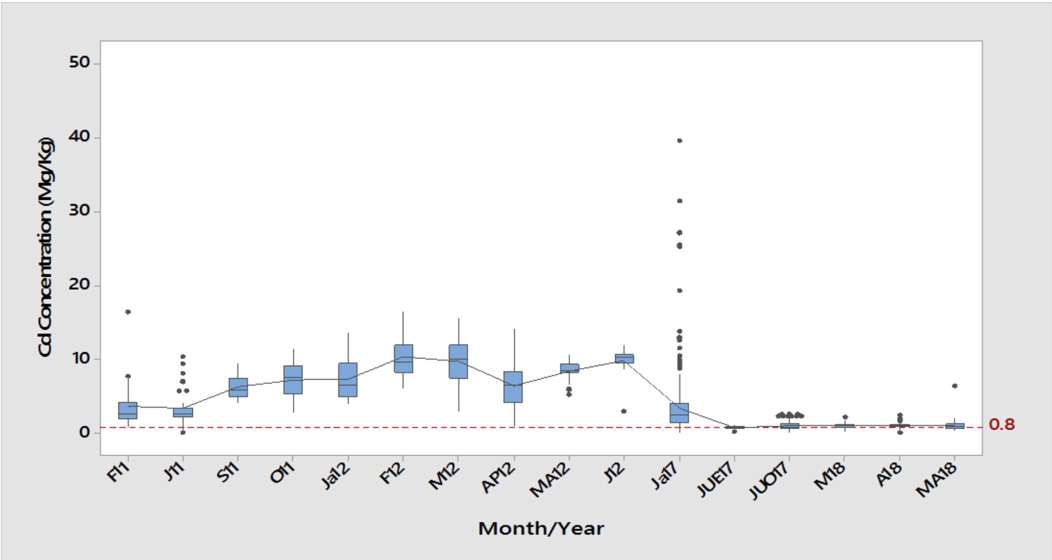

Fig. 5: Boxplot of Bottom Soil Cadmium Concentration Values

Fig. 6: Mean Cd Concentration of topsoil and bottom soil in mg/kg

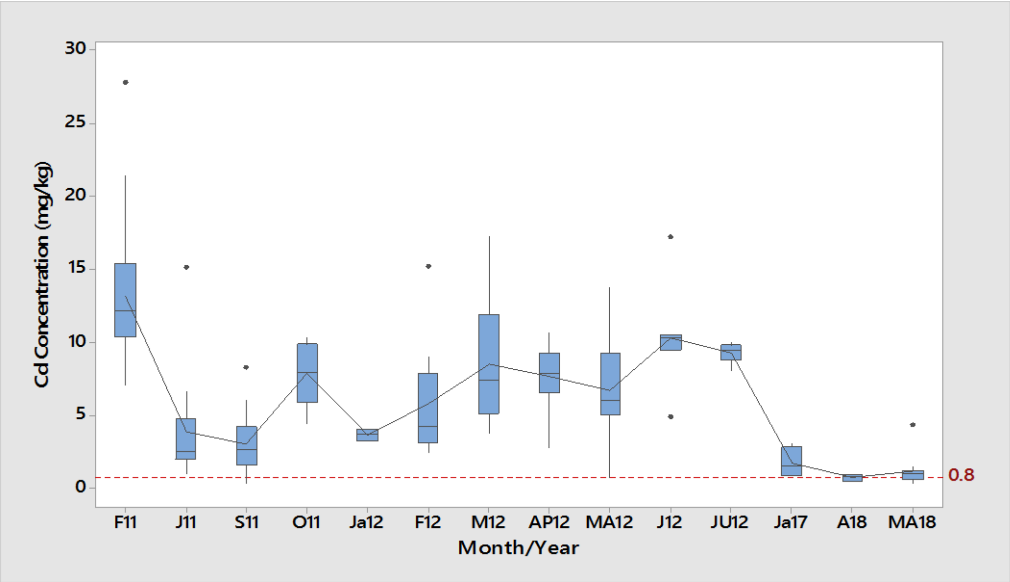

Fig. 7: Boxplot of Topsoil Control Cadmium Concentration Values

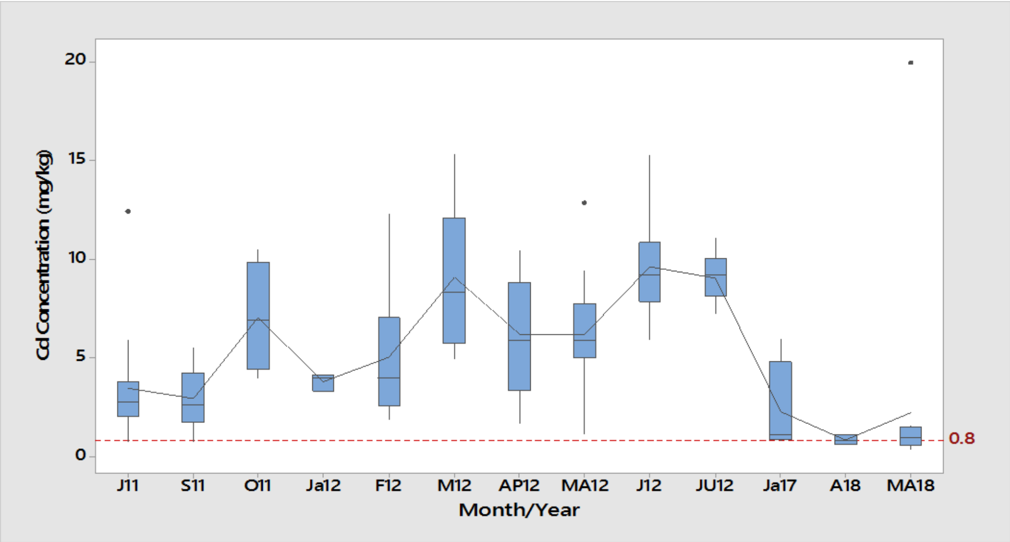

Fig. 8: Boxplot of Bottom Soil Control Cadmium Concentration Values

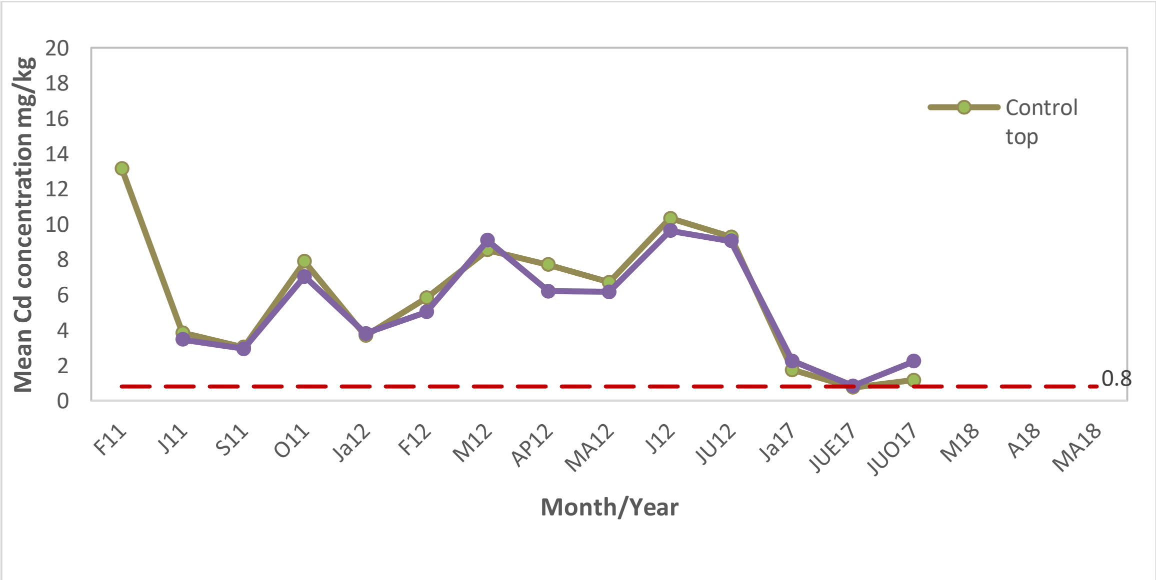

Fig. 9: Mean Cd Concentration of topsoil and bottom soil control in mg/kg

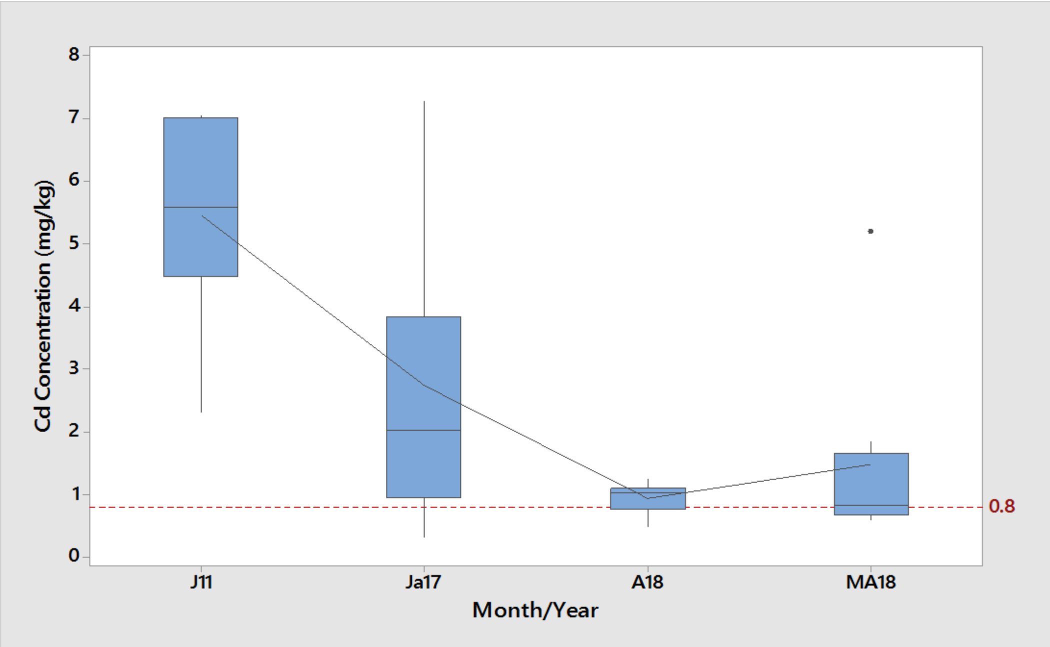

Fig. 10: Boxplot of Sediment Cadmium Concentration Values

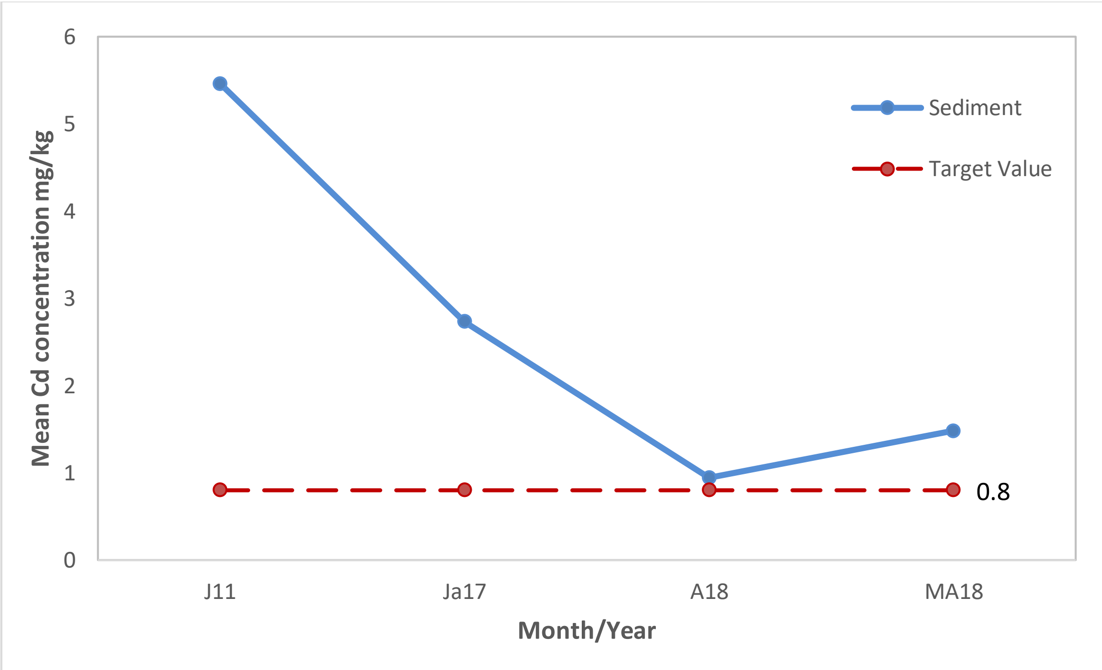

Fig. 11: Mean Cd Concentration of sediment in mg/kg

V. SPATIAL DISTRIBUTION MAP OF CADMIUM CONCENTRATION INDEX OF GEO-ACCUMMULATION (IGEO)

Figures 12 to 14 represent the georeferenced and calibrated thematic maps which described the Igeo ranks of the soil and sediment in different areas of the remediated sites. With observable displays of the extent of Cd contamination and its spatial and percentage distribution in the study area. The maps showed the extensiveness of the Cd contaminated areas (red-yellow theme) in the topsoil, bottom soil and sediments which on the average can be qualitatively interpreted as moderately to extremely contaminated. The results of the geostatistical analysis used in plotting the Igeo maps showed that the topsoil has mean Igeo and maximum values of 3.5 and 4.7, respectively, these values are within the range of moderately to strongly contaminated with uncontaminated having smaller area. Similarly, the bottom soil has mean and maximum Igeo values as high as 3 and 5, respectively, and the sediment Igeo values ranged from uncontaminated (half of the analyzed sample data) to strongly contaminated, with mean and maximum values as high as 2.1 and 2.6, respectively.

ISSN No:-2456-2165

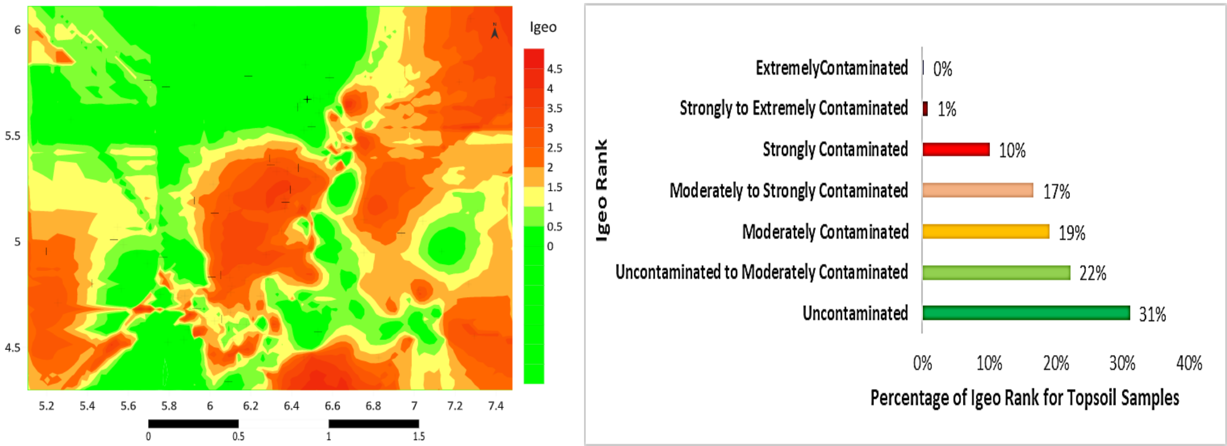

Fig. 12: Spatial and percentage distribution of Cd Igeo values in the topsoil

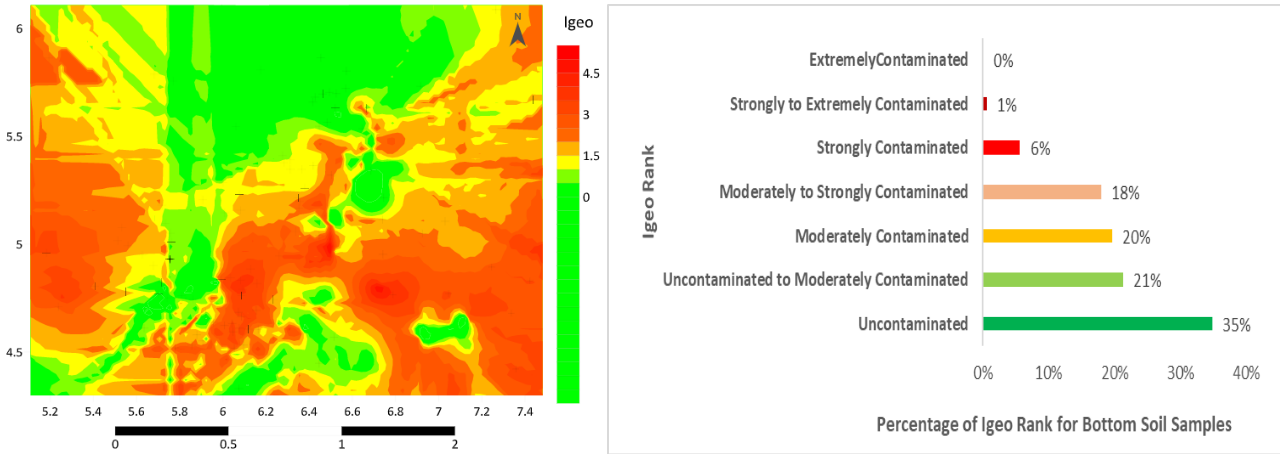

Fig. 13: Spatial and percentage distribution of Cd Igeo values in the bottom soil

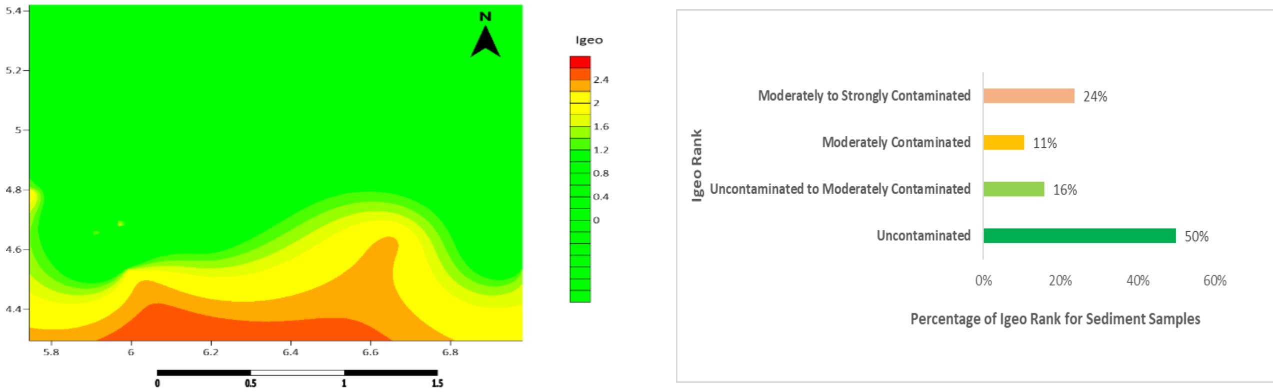

Fig. 14: Spatial and percentage distribution of Cd Igeo value in sediment

VI. CONCLUSION AND RECOMMENDATION

Oil and gas development are the major economic activities taking up extensive area of land, water and swamp in the Niger Delta. Although subsistence farming is mostly practiced by host communities, yet, the impacts of oil spillage continue to reduce the quality and size of arable land. With records of several oil spillages in the Niger Delta including remediation programme, it was noted that some of the remediation carried out were not effective in cleaning up the heavy metal components of the spill. These metals were mentioned in the guideline for environmental management and pollution abatement policy of the DPR and guidelines of other international regulatory bodies as toxic environmental and health hazards.

Cd which is the metal evaluated in this study showed the existence of critically high concentration levels with respect to the DPR and WHO guideline of 0.8mg/kg and 0.003mg/kg, respectively, in soil and sediment. The retention and accumulation of Cd in the soil could create an easy contaminant pathway from the soil through crops and water to higher organisms when consumed. According to the WHO (1992), Cadmium increased uptake can occur via contaminated crop and tobacco but the uptake of Cadmium from the soil by plants is greater at low soil pH, creating an increased soil and crop cadmium concentration levels and

ISSN No:-2456-2165

increase in dietary cadmium exposure. This is the case with the Niger Delta soil with predominantly low pH values recorded. The low pH values have been attributed to some factors which include the impact of hydrocarbon in soil according to Ogboi et al., (2011).

According to Davis & Coker (1980) and Page et al. (1981), soil pH and cadmium concentration are most important soil factors influencing plant cadmium Accumulation. While the Department of Petroleum Resources (DPR) in Nigeria has set the pH limit of soil and sediment at 6.5 - 8.5, several studies have reported low soil pH concentration level (acidic) in the Niger Delta soil. One example is Iwegbue et al. (2006 and 2007) who reported that low soil and sediments pH values are characteristics of woody areas and wetlands such as the Niger Delta.

In this study, evaluating the distribution of the topsoil pH concentration using the FAO ranking for soil (< 5.6 low value (LV), 5.6 - 7.6 medium value (MV), and > 7.6 high value (HV) (FAO, 1988)), showed that the average pH values were within the acidic range in most of the sampled locations (Figure 15).

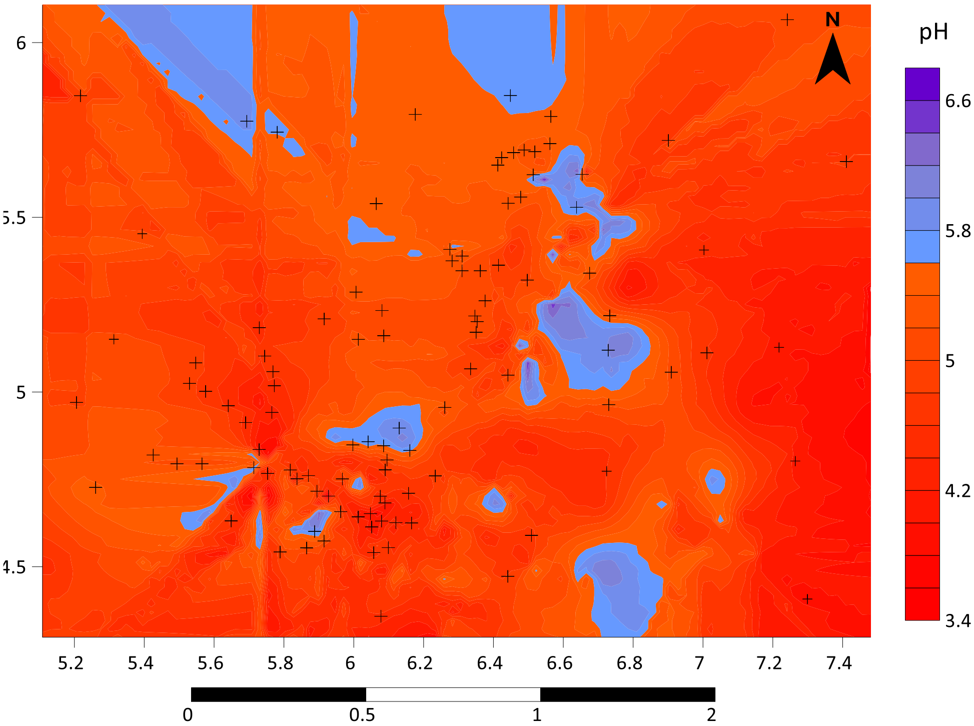

Fig. 15: Distribution and Concentration level of Topsoil Ph

Similar to the case of the Niger Delta and as evaluated in this studies, other studies have shown that the sources of Cd are geogenic in origin and made readily available in the environment through anthropogenic processes including oil spill contamination of the environment and other processes which enhance acidity.

The result also explained the lack of compliance to the DPR EGASPIN guideline for environmental management and pollution abatement for petroleum hydrocarbon and associated metal permissible concentration levels in soil, sediments, and water. Including the lack of application of the risk-based corrective action (RBCA) for the planning of remediation programme for contaminated land. And the lack of follow-up on the mandatory post-remediation monitoring requirement for Crude oil and product contamination from oil spillage in soil and sediment. This is because, according to the EGASPIN, the closure and post closure monitoring information for the metal content in receptors should ensure that the total metal contents shall not exceed that of the native soil conditions by 10% which is alarmingly contrary to the result of this study.

The findings in this work are concern to public and environmental health because of the widespread distribution, high concentration levels, retention and accumulation of Cd in the soil and the presence of favorable environmental factors which has the potential of creating an easy contaminant pathway from the soil through crops and water to higher organisms when consumed. It is recommended that the implementation of comprehensive risk assessment and identification of hazardous metals and remediation programme should be carried out and the assessment should include soil, sediment and water. This should encompass the review of past contaminated site programme and reports to draw out lessons learned, design new programme which should also follow the guidelines and recommendations in EGASPIN and international guidelines on contaminated site risk assessment and planning for remediation of heavy metals. This assessment exercise should include site specific characterization based on geology, soil, and other environmental factors in consideration. Importantly, the modeling of the transport and interaction of metal contaminants based on pore size distribution should be carried out. Including the understanding of the spatial distribution of soil texture as documented in publications of

ISSN No:-2456-2165

Osei & Okusami (1994); Law-Ogbomo & Nwachokor (2010) and UNEP (2011).

REFERENCES

[1.] Adebiyi, F. M. & Ayeni, D. A., 2021. Chemical speciation, bioavailability and risk assessment of potentially toxic metals in soils around petroleum product marketing company as environmental degradation indicators.

[2.] Ahmad, D. M. et al., 2015. Oil Spill Related Heavy Metal: A Review. *Malaysian Journal of Analytical Sciences,* 48(1), pp. 1348-1360.

[3.] Aigberua, A. O., Ekubo, A. T., Inengite, A. K. & Izah, S. C., 2016. Seasonal variation of nutrient composition in an oil spill contaminated soil: a case of Rumuolukwu, Eneka, Port Harcourt, Nigeria. *Biotechnological Research,* 2(4), pp. 179-186.

[4.] Aigberua, A. O., Ekubo, A. T., Inengite, A. K. & Izah, S. C., 2017. Assessment of some selected heavy metals and their pollution indices in an oil spill contaminated soil in the Niger Delta: a case of Rumuolukwu community. *Biotechnological Research,* 3(1), pp. 11-19.

[5.] Aigberua, A. O. & Inengite, A. K., 2019. Chemical Speciation and Mobility of Heavy Metal (Pb, Cd, Zn, Mn) Pollutants in Crude Oil Contaminated Soils of Niger Delta, Nigeria. *Elixir International Journal; Applied Chemistry,* Volume 126, pp. 52543-52548.

[6.] Aigberua, A. O., Ogbuta, A. A. & Izah, S. C., 2020. Selected heavy metals in sediment of Taylor creek due to anthropogenic activities in the Niger Delta region of Nigeria: geochemical spreading and evaluation of environmental risk. *Biodiversity International Journal,* 4(2), pp. 67-80.

[7.] Aigberua, A. O. & Okere, U. V., 2019. The impact of oil spills on prevailing metal-soil associations. *International Journal of Scientific and Engineering Research* , 10(5), pp. 1339-1365.

[8.] Akinloye, O., Arowojolu, A. O., Shittu, O. B. & Anetor, J. I., 2006. Cadmium toxicity: a possible cause of male infertility in Nigeria. 6(1), pp. 17-30.

[9.] Asimiea, A. O. & Lawal, O., 2017. Investigation of relationship between sediment characteristics and heavy metals across seasons in the Lower Focardos River, Nigeria. *Journal of Applied Sciences and Environmental Management,* 21(1), pp. 208-215.

[10.] ATSDR, 1990b. *Case studies in environmental medicine: Cadmium toxicity,* Atlanta, GA: Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services.

[11.] ATSDR, 1999b. *Toxicological Profile for Cadmium,* USA: US Department of Human and Health Services..

[12.] Bartram, J., Ballance, R., Organization, W. H. & Programme, U. N. E., 2006. *Water quality monitoring : a practical guide to the design and implementation of freshwater quality studies and monitoring programs / edited by Jamie Bartram and Richard Ballance.* London: E & FN Spon.

[13.] EGASPIN, 2002. *Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). Revised Edition,* Lagos: s.n.

[14.] Enegide, C. & Chukwuemeka, C. K., 2018. Oil Spillage and Heavy Metals Toxicity Risk in the Niger Delta, Nigeria. *Journal of Health and Pollution,* 8(19), pp. 1-8.

[15.] European Commission, 2006. *Environment: EU ban on hazardous substances in electrical and electronic products takes effect.* Brussel, European Commission.

[16.] Fatoba, P. O., Ogunkunle, C. O. & Ihazai, C. O., 2015. Assessment of Metal Pollution of Soil and Diagnostic Species Associated with Oil Spills in the Niger Delta, Nigeria. 71(3), pp. 13-22.

[17.] Ghorbani, M. R. et al., 2020. 15(11).

[18.] Goyer, R. A. & Clarkson, T. W., 2001. Toxic effects of metals. In: C. D. C. a. D. T. Klaasen, ed. *The Basic Science of Poisons.* 6 ed. New York: McGraw-Hill, pp. 861-867.

[19.] Hogan, M. C., 2010. *Heavy Metals, Encyclopedia of Earth.* Ed ed. Washington D C: National Council for Science and the Environment. eds .

[20.] International Agency for Research on Cancer, 1993. Beryllium, cadmium, mercury, and exposure in the glass manufacturing industry. *IARC Monographs on the evaluation of the Carcinogenic Risk of Chemicals to Humans,* Volume 58.

[21.] Kubier, A., Wilkin, R. T. & Pichler, T., 2019. Cadmium in soils and groundwater: A review. *Appl Geochem,* 1(108), pp. 1-16.

[22.] Law-Ogbomo, K. & Nwachokor, M., 2010. Variability in selected soil physic-chemical properties of five soils formed on different parent materials in southeastern Nigeria. *Res. J. Agric. Biol. Sci.,* Volume 6, p. 14–19.

[23.] Madu, A. N., Njoku, P. C. & Iwuoha, G. A., 2011. Extent of Heavy Metals in Oil Samples in Escravous, Abiteye and Malu Platforms in Delta State Nigeria.. *Learning Publics Journal of Agriculture and Environmental Studies,* 2(2), pp. 41- 44.

[24.] Madukosiri, C. H. & Dressman, T. N., 2010. Some biochemical parameters in Gallus domesticus and heavy metal content of oil polluted areas of Yenagoa, Bayelsa State, Nigeria. *Journal of Life and Physical Sciences,* 3(2), pp. 124-128.

[25.] Mahurpawar, M., 2015. Effects of heavy metals on human health. *International Journal of Research - GRANTHAALAYAH,* 3(9), pp. 1-7.

[26.] Meindinyo, R. K. & Agbalagba, E. O., 2012. Radioactivity Concentration and Heavy Metal Assessment of Soil and Water in and around Imirigin Oil Field, Bayelsa State, Nigeria.. *Journal of Environmental Chemistry and Ecotoxicology,* 4(2), pp. 29-34.

[27.] Morrow, H., 2010. *"Cadmium and Cadmium Alloys".* 4 ed. s.l.:Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons.

[28.] Müller, G., 1981. Index of Geoaccumulation in Sediments of the Rhine River. *GeoJournal,* 2(3), p. 108–118.

[29.] Ogbeibu, A. E., 2011.. *Oil Spill Tracking and Characterization-Case Study of Oil Pollution in the*

Ethiope-Benin River, Niger Delta, Nigeria. Puebla, Mexico, International Association for Impact Assessment.

[30.] Ogboi, E., 2012. Heavy Metal Movement in Crude Oil Polluted Soil in Niger Delta Region. *Journal of Agriculture and Veterinary Sciences,* Volume 4, pp. 71-78.

[31.] Okon, I. E. & Ogba, C. O., 2018. The Impacts of Crude Oil Exploitation on Soil in Some Parts of Ogoni Region, Rivers State, Southern Nigeria.. *Open Access Library Journal,* Volume 5, pp. 1-20.

[32.] Okoro, E. E., Amarachi, G. O., Samuel, E. S. & Maxwell, O., 2020. Toxicology of Heavy Metals to Subsurface Lithofacies and Drillers during Drilling of Hydrocarbon Wells. *Scientific Reports,* 10(1), p. 6152.

[33.] Oliva, M. et al., 2019. Quantitative Determination of Cadmium (Cd) in Soil-Plant System in Potato Cropping (Solanum tuberosum var. Huayro). *Advances in Agriculture,* Volume 2019.

[34.] Ololade, I. A., 2014. An Assessment of Heavy-Metal Contamination in Soils within Auto-Mechanic Workshops Using Enrichment and Contamination Factors with Geoaccumulation Indexes. *Journal of Environmental Protection,* 5(11), pp. 970-982..

[35.] Osei, B. A. & Okusami, T. A., 1994. Classification of soils derived from amphibolite parent material in south-western Nigeria. *Ghana Journal of Agricultural Science,* Volume 24, p. 123–132.

[36.] Rafati Rahimzadeh, M., Rafati Rahimzadeh, M., Kazemi, S. & Moghadamnia, A. A., 2017. Cadmium toxicity and treatment: An update. *Caspian J Intern Med,* 8(3), pp. 135-145.

[37.] Sinicropi , M. S., Amantea, D. & Saturnino , C., 2010. Chemical and biological properties of toxic metals and use of chelating agents for the pharmacological treatment of metal poisoning.. *Arch. Toxicol.,* Volume 84, pp. 501-520.

[38.] UNEP, 2011. *Assessment of Contaminated Soil and Groundwater. Environmental Assessment of Ogoni Land,* s.l.: s.n.

[39.] USEPA, 1997. *Recent Developments for In Situ Treatment of Metal Contaminated Soils,* United States: United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC 20460, (United States).

[40.] USEPA, 2002. *Supplemental guidance for developing soil screening levels for superfund sites,* Trenton, New Jersey: Office of Emergency and Remedial Response, and peaceful coexistence Africa World Press.

[41.] Wegwu, M. O., Uwakwe, A. A. & Enyi, C. N., 2011. Post-Impact Assessment of Crude Oil Spilled Site Four Years after Recorded Incidence. *Annals of Biological Research,* 2(2), pp. 72-78.

[42.] WHO, 1992. *Environmental Health Criteria 134: Cadmium,* Geneva: WHO, ILO, UNEP.

[43.] World Bank, 1995. *Defining an Environmental Development Strategy for the Niger Delta,* West Central Africa: s.n.

[44.] World Health Organization, 2019. *Exposure to cadmium: a major public health concern.* [Online] Available at: https://www.who.int/publications/i/item/WHO-CED-PHE-EPE-19-4-3
[Accessed 20 October 2022].