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Heavy Metal Concentration and Risk Assesment of Oil Spill Contaminated Soil from Ogoni in Rivers State, Nigeria

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Abstract:- This study investigated the level of Cu, Zn, Fe, Pb, V, Ni and Cd in sediment samples of an oil-spill-impacted site in Ogoni land, Okenta Alode, Eleme local government area, Rivers state, Nigeria. Soil sediments were collected from six different stations, with two from each station at surface (0 – 15 cm) and in-depth (15 – 30 cm) levels. One of the stations involves a bioremediated site, which was used as the control for the study, while the other station involves oil-spill-impacted sites. Bioremediated soil, obtained at about 200 meter away from the contaminated site was also collected making a total of twelve (12) samples, with the coordinates of the locations recorded with GPS device. Sample preparation and analysis were carried out using American Society of Testing Material (ASTM) D5708 (classic wet chemistry method) using the appropriate NIST standards. The filtrate which was containing the heavy metals in solution was then analyzed using the Shimadzu-1 model of Flame Atomic Absorption Spectrophotometer (APHA3111). The hierarchy of the concentrations of metals in the sediments appeared in the trend thus; Fe > Cu > Zn > Cd > Ni > V > Pb and metals concentration in the selected stations descended in the order of P1/S/O1 > P3/D/O2 > P2/S/O1 > P3/D/O2 > P4/S/O1 > P5/D/O1 > P5/S/O1 > P1/D/O1 > P4/D/O1 > P2/D/O1 > P1/D/CO1 > P1/S/CO1. The concentration of metals in the sediments were within the permissible limits and similarly have their ADI, THQ and HI lower than their respective reference dose (RfD) and less than 1, while the LCR of Cd were within the permissible range for carcinogens. Iron and Cd resulted to very high ecological risk and pollution. Also, Fe and Cd are implicated in resulting to high ecological risk and pollution. It is thus recommended that the rate of anthropogenic activities that tend to elevate heavy metals contamination and intoxication in this study location be reduced to curb the risk of heavy metals bioaccumulation and possible health effects in humans.

Keywords: *Heavy Metals, Sediment, Remediated, Contaminated, Human, Ecological, Health Risk, Permissible Limit.*

I. INTRODUCTION

Heavy metals are metallic elements with a relative density at least five times that of water [1]. These elements have several toxic effects in humans, and their toxicity is inter-related with their heaviness [1]. Recently, there has been an increase in ecological and global health concern regarding environmental contamination by heavy metals [2]. Although these metals occur naturally and are found throughout the earth's crust at low quantities, human exposure generally results from anthropogenic activities such as smelting, mining, and agricultural and industrial activities [3. Once released into the environment, heavy metals may be taken into the body by inhalation and ingestion. Rapid accumulation in body tissues greater than the detoxification pathways in the body can handle causes a gradual build-up of these metals [4, 5]. Oil spills are a source of heavy metal contamination of aquatic and terrestrial environments, especially in oil-producing regions [6]. Crude oil is a complex mixture of hydrocarbon and non-hydrocarbon compounds (including heavy metals) found in subsurface deposits worldwide.

Oil spillage results in the release of oil into the natural environment and is associated with activities such as extraction, refining, transportation, and storage of crude oil. Spillage also results from accidents, lack of maintenance of engineering equipment, and deliberate acts (including oil bunkering and sabotage). In addition, oil spills can also occur as a result of natural disasters such as earthquakes and hurricanes [6]. Because crude oil contains heavy metals, contamination of the environment with heavy metals is associated with oil spillage. The Niger Delta region where the study area is situated experiences a high number of oil spill incidents because it is the seat of crude oil activities in

Nigeria. The Niger Delta, a fan-shaped area with a landmass of approximately 70,000 km is located in the southern part of Nigeria and consists of 2 rivers, the Benue River and the Niger River that ultimately drain into the Atlantic Ocean. Its ecology is characterized by a very large floodplain created by the deposition and accumulation of sediments washed down from the Benue and Niger rivers [7]). The Niger Delta region forms about 7.5% of the total land mass of Nigeria, and it is inhabited by over 25 million people in 186 Local Government Areas in nine southern states of Nigeria [8]. History shows that oil was first discovered in commercial quantities in the Niger Delta in 1956. Since then, the region has continually suffered the negative environmental impacts of oil development [8]. These negative impacts are due mainly to oil spills in this region. Previous reports indicate that about 50% of oil spills in the Niger Delta result from pipeline corrosion and tanker accidents; other significant causes include operational error, mechanical failure, sabotage and terrorism [6, 8]. Nigeria is Africa's main producer of oil, and it has the second-largest oil reserve in Africa [9].

Conservative estimates have shown that Nigeria's oil reserve is about 35 billion barrels; this means that oil activities in the Niger Delta may continue for at least 40 years [10]. Each year, several post-impact assessment studies are carried out to assess the impact of hazards caused by oil activities and spills on the physical and social environments. Several of these studies have reported the negative socioeconomic impacts of oil spills, such as a decrease in agricultural productivity due to farmland degradation, pollution of traditional fishing grounds and destruction of aquatic life, as well as negative effects on soils, forests and water bodies [6, 11]. However, few of these studies have focused on the health hazards (both immediate and long-term) of oil contamination of the environment and the implications for the inhabitants of the affected communities [12]. Crude oil contamination has multiple adverse health effects, most of which are due to heavy metal toxicity. The purpose of this study was to evaluate the quantity of oil spilled into the Niger Delta region from 1976 through 2014 and the resulting exposure of occupants to heavy metals. a United Nations Environment Programme report, an Amnesty International report, a Nigerian Department of Petroleum Resources report, seminar and conference papers, and other published materials were also used [6, 13]. The quantity of oil spilled in the Niger Delta region from 1976 through 2014, the annual number of oil spill incidents, and the trend of oil spill incidents were recorded. All the obtained data were analyzed descriptively.

II. MATERIALS AND METHODS

➢ *Sample Area:*

The study area is located in Ogoni land, Okenta Alode, Eleme Local Government Area in Rivers state of Nigeria. This area is vulnerable to crude oil pollution due to the network of pipelines, oil wells and reserves around this region. However, a section of this area has been bio remediated and that is where the control samples were collected.

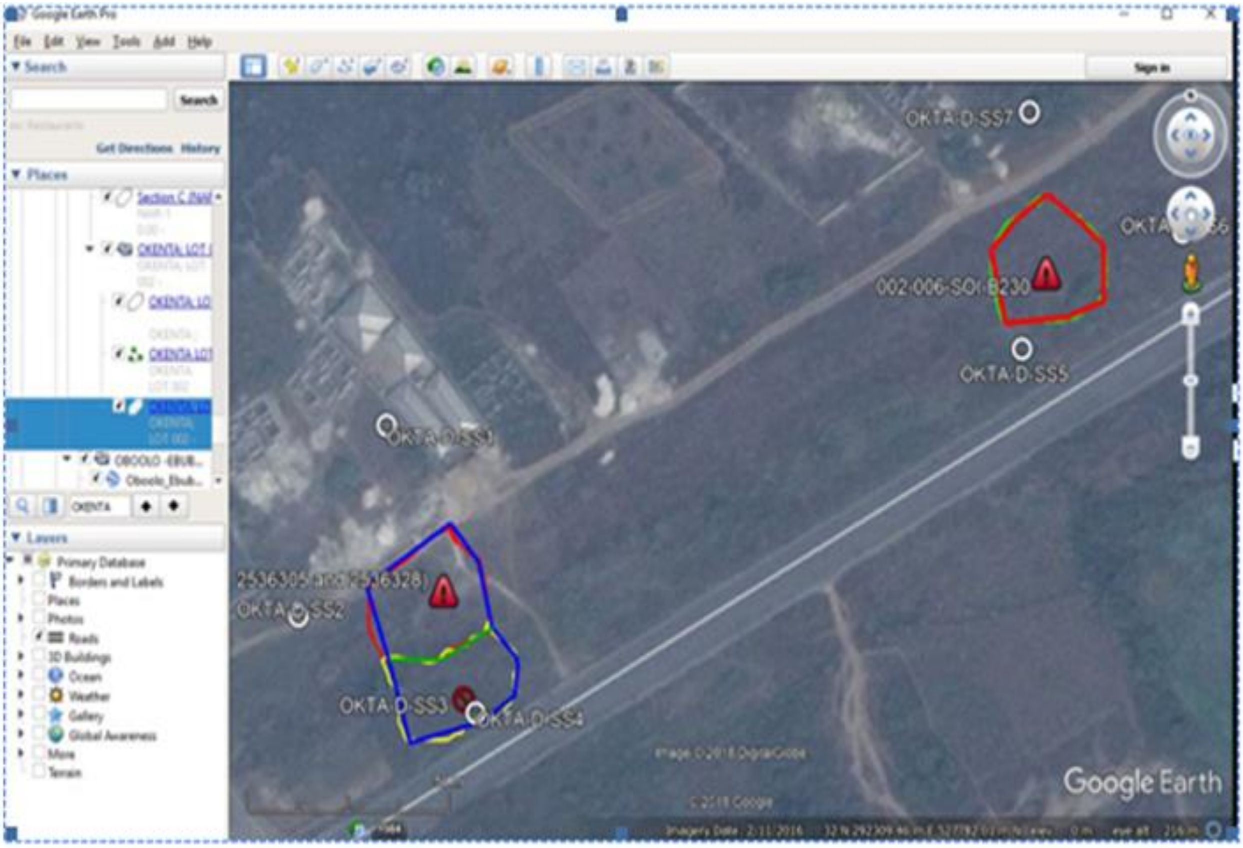

Fig 1 Google Map of Sites with Coordinates in UTM Grid

- *Sediment Sample Collection And Preparation:*

Soil samples of crude oil hydrocarbon contaminated soils were randomly collected from different points at the site of collection in Ogoniland, Okenta Alode, Eleme local government area, Rivers state, Nigeria. Samples were collected between 0 - 15cm (surface m level) and 15 - 30cm (in-depth level) with a soil auger and thereafter bulked to obtain the composite sample. Bio-remediated soil, obtained at about 200m away from the contaminated site was also collected and a total of twelve (12) samples were obtained. The GPS coordinates of the locations were recorded with a GPS device. The samples were collected in sterile non-reactive polythene bags and transported using ice packs to the laboratory for analyses. The sediments were stored at 6°C and extracted within 14 days of collection.

- *Sample Analysis:*

Beakers and flasks, Solar thermo elemental atomic absorption spectrophotometer (Flame AAS), Burner, Hollow cathode lamps, Graphical display and recorder, Pipette (micro liter with disposal tips), Pressure reducing valves, Glassware, Volumetric flask of suitable precision and accuracy. Air, Acetylene, Nitrogen dioxide gas, Metal free water, Stock metal solution, Potassium chloride solution, Aluminium nitrate solution, Hydrogen tetraoxosulphate (vi) acid (H_2SO_4), Trioxonitrate (v) acid (HNO_3), Perchloric acid ($HCLO_4$). A total volume of 100ml of H_2SO_4, HNO_3, and HCIO in the ratio of 40%: 40%: 20% was mixed together. A portion (1g) of the sample was weighed into a conical flask; 2ml of the mixed acid was taken to each of the samples in the conical flask. It was digested in a fume cupboard with a hot plate until white fumes appeared. After that, it cooled and was filtered into 100ml volumetric flask and made up to mark with distilled water.

This technique operates on Beer-Lambert's law which states that Absorbance is directly proportional to concentration. Hence, absorption spectrometry is used to evaluate the concentrations of analyte in a sample; it requires standards with known analyte concentrations. The light source is a lamp with a cathode of the same element being determined since each element has a characteristic wavelength that is readily absorbed. An AAS consists of an atomizer burner to convert the element in the solution to free atoms in an acetylene flame, a monochromatic to disperse and isolate emitted and a photomultiplier to detect and amplify the light transitory through the monochromatic into its component wavelength. The photomultiplier then receives only the isolated resonance wavelength and absorption of its light by the sample. After the proper lamp for the test element has been inserted, the intensity of the light is measured by passing through the unrestricted flame. Then the sample is introduced into the flame and the concentration of the elements in the sample is determined by the increase in light intensity.

- *Human Health Risk Assessment (HHRA):*

It is used to estimate the after-effect on the health of humans when contact is made with substances that are carcinogenic and non-carcinogenic. This usually involves four stages: hazard identification, exposure assessment, toxicity (dose-response) assessment, and risk characterization [14]. Exposure assessment seeks to demonstrate the intensity, frequency, and duration of human exposure to an environmental contaminant. This was done by estimating the average daily intake (*ADI*) of heavy metals identified through ingestion, inhalation, and dermal contact by the general population from the location. Adults and the younger population were categorized based on behavioral and physiological differences [15].

Dose-response assessment evaluates the toxic effects occurring due to the amounts of chemicals one is exposed to. The cancer slope factor (*CSF*, a carcinogen potency factor) and the reference dose (*RfD*, a non-carcinogenic threshold) are two valuable toxicity parameters used. *RfD* values are derived from animal studies using the "No observable effect level" principle. For humans, *RfD* values are multiplied 10-fold to account for uncertainties [16]. Risk characterization vaticinates the possible cancerous and non-cancerous health risk of the children and adults in a location by homogenizing the data accumulated to reach at calculated assessment of cancer risk and hazard indices [17]. The possible means of contact with heavy metals in exposed soils are estimated using suggestions by some publicised American reports. *ADI* (mg/kg-day) for the different pathways were calculated using the following exposure Equations (6) – (8) as prescribed by USEPA, [16]

- *Statistical Analysis:*

The data was analyzed using statistical package for social science version 16.0 (SPSS Inc., Chicago, IL, USA). The mean and the standard deviation error were obtained to compare the variation between groups of same samples.

III. RESULT

- *Description of Soil Sediments Sample Label Obtained from Okenta Alode in Eleme, Rivers state, Nigeria*

The definition of the sample labels which contains the stations are shown in Table 1

Table 1 Soil Sediments Sample Label

SAMPLES	DESCRIPTION
P1/D/CO1	Control sample 1 collected at in-depth level from a remediated site
P1/S/CO1	Control sample 2 collected at surface level from a remediated site.
P1/D/O1	Sample 3 collected from station one at in-depth level
P1/S/O1	Sample 4 collected from station one at surface level

P2/D/O1	Sample 5 collected from station two at in-depth level
P2/S/O1	Sample 6 collected from station two at surface level
P3/D/O2	Sample 7 collected from station three at in-depth level
P3/S/O2	Sample 8 collected from station three at surface level
P4/D/O1	Sample 9 collected from station four at in-depth level
P4/S/O1	Sample 10 collected from station four at surface level
P5/D/O1	Sample 11 collected from station five at in-depth level
P5/S/O1	Sample 12 collected from station five at surface level

- *Concentrations of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria:*

The mean concentration of the analyzed sediments is shown in Table 2. The mean concentration of Cu in the analyzed in-depth and surface sediment samples obtained from the stations ranged from 2.25 ± 0.01 – 5.58 ± 0.01 mg/kg. The highest concentration of Cd in the analyzed sediment samples was recorded in sediment sample obtained from P1/D/O1 station, meanwhile, the lowest concentration of Cd was recorded in sediment sample obtained from P1/S/CO1 station. The average concentration of Zn in the analyzed sediment samples ranged from 1.06 ± 0.01 – 4.40 ± 0.01 mg/kg with the highest concentration of Zn seen in sediment samples obtained fromP2/D/O1and the lowest was recorded in sediment sample fromP1/D/CO1 station. The sediment samples analyzed for the mean level of Fe ranged between 2328.2 ± 0.01 – 3013.3 ± 0.01 mg/kg. The highest concentration was seen in sediment sample collected from P1/S/O1 whereas the lowest concentration was seen in sediment sample obtained from P1/D/CO1 station.

There was no Pb detected from the various sediment samples in the present study.

The mean concentration of V in the analyzed in-depth and surface sediment samples obtained from the stations ranged from BDL – 0.021 mg/kg. The highest concentration of V in the analyzed sediment samples was recorded in sediment sample obtained from P2/D/O1 station. The average concentration of Ni in the analyzed sediment samples ranged from 0.028 ± 0.004 – 0.080 ± 0.01 mg/kg with the highest concentration of Ni seen in sediment samples obtained fromP1/S/O1 and the lowest was recorded in sediment sample obtain fromP1/S/CO1 station. The mean concentration of Cd in the analyzed sediment samples ranged from 0.02 ± 0.01 – 3.06 ± 0.01 mg/kg with the highest concentration of Cd seen in sediment samples obtained fromP1/D/O1 and the lowest was recorded in sediment sample obtain fromP1/D/CO1 station.

Table 2 Concentrations of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria

Samples	**Cu (mg/kg)**	**Zn (mg/kg)**	**Fe (mg/kg)**	**Pb (mg/kg)**	**V (mg/kg)**	**Ni (mg/kg)**	**Cd (mg/kg)**
P1/D/CO1	2.38 ± 0.01	1.06 ± 0.01	2328.2 ± 0.01	<0.001	<0.001	0.038 ± 0.01	0.02 ± 0.01
P1/S/CO1	2.25 ± 0.01	1.26 ± 0.01	2239.3 ± 0.02	<0.001	<0.001	0.028 ± 0.004	0.06 ± 0.01
P1/D/O1	5.58 ± 0.01	2.32 ± 0.01	2736.8 ± 0.02	<0.001	<0.001	0.080 ± 0.01	3.06 ± 0.01
P1/S/O1	3.51 ± 0.01	3.42 ± 0.01	3013.3 ± 0.01	<0.001	<0.001	0.080 ± 0.01	3.00 ± 0.01
P2/D/O1	4.98 ± 0.02	4.40 ± 0.01	2681.4 ± 0.02	<0.001	0.021	0.068 ± 0.01	1.06 ± 0.01
P2/S/O1	4.39 ± 0.01	3.12 ± 0.02	2981.4 ± 0.01	<0.001	<0.001	0.058 ± 0.01	1.03 ± 0.01
P3/D/O2	3.05 ± 0.01	3.85 ± 0.01	2954.6 ± 0.01	<0.001	<0.001	0.078 ± 0.004	3.00 ± 0.01
P3/S/O2	3.40 ± 0.02	2.91 ± 0.01	2997.8 ± 0.02	<0.001	<0.001	0.066 ± 0.01	2.00 ± 0.01
P4/D/O1	3.17 ± 0.02	2.23 ± 0.01	2712.9 ± 0.02	<0.001	<0.001	0.055 ± 0.01	1.56 ± 0.01
P4/S/O1	3.15 ± 0.01	2.33 ± 0.02	2909.6 ± 0.01	<0.001	<0.001	0.050 ± 0.01	1.26 ± 0.01
P5/D/O1	2.55 ± 0.01	3.20 ± 0.01	2875.9 ± 0.02	<0.001	0.011	0.072 ± 0.01	0.09 ± 0.01
P5/S/O1	2.78 ± 0.02	2.76 ± 0.01	2800.1 ± 0.02	<0.001	<0.001	0.065 ± 0.004	0.08 ± 0.01
Permissible Limits							
FAO/WHO	100	300	15.0	100	-	50	3
Bn	45	94	5.46	21	4.05	35	0.3

Bn = Biochemical background in soil

- *Average Daily Dose (ADDing) and Average Daily Intake (ADIing) (mg/kg/day) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria:*

The average daily dose (ADDing) of metals in the sediment samples analyzed is shown in Table 3. The average daily dose (ADDing) of Cd in the sediment from the study area in the adult and children populations ranged from 3.2E-06 – 8.0E-06 and 3.0E-05 - 7.4E-05 mg/kg/day respectively. The highest ADDing value of Cd in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1 whereas the lowest ADDing level of Cd was recorded in the sediment extracted from PI/S/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIing) of Cd via ingestion for the adult and children populations were 15.7E-05 and 5.3E-04 mg/kg/day respectively.

The average daily dose (ADDing) of Zn in the sediment from the study area in the adult and children populations ranged from 1.5E-06 – 6.3E-06 and 1.4E-05 - 5.9E-05 mg/kg/day respectively. The highest ADDing value of Zn in the analyzed sediment samples was recorded in the sediment samples obtained from P2/D/O1 whereas the lowest ADDing level of Zn was recorded in the sediment extracted from PI/D/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIing) of Zn via ingestion for the adult and children populations were 4.7E-05 and 4.4E-04 mg/kg/day respectively.

The average daily dose (ADDing) of Fe in the sediment from the study area in the adult and children populations ranged from 3.2E-03 – 4.3E-03 and 3.0E-02 - 4.0E-02 mg/kg/day respectively. The highest ADDing value of Fe in the analyzed sediment samples was recorded in the sediment samples obtained from PI/S/O1, P2/S/O1 and P3/S/O2 stations for both the adult and children populations whereas the lowest ADDing level of Fe was recorded in the sediment samples extracted from PI/S/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIing) of Fe via ingestion for the adult and children populations were 4.8E-02 and 4.4E-01 mg/kg/day respectively.

In this current study, there was no Pb detected in the analyzed sediment samples, hence, no ADDing or ADIing calculated for it. The average daily dose (ADDing) of V in the sediment from the study area in the adult and children populations ranged from BDL – 3.0E-08 and BDL - 2.8E-07 mg/kg/day respectively. The highest ADDing value of V in the analyzed sediment samples was recorded in the sediment samples obtained from P2/D/O1 for both the adult and children populations. Furthermore, the average daily intake (ADIing) of V via ingestion for the adult and children populations were 4.6E-08 and 4.3E-07 mg/kg/day respectively. The average daily dose (ADDing) of Ni in the sediment from the study area in the adult and children populations ranged from 4.0E-08 – 1.1E-07 and 3.7E-07 - 1.1E-06 mg/kg/day respectively. The highest ADDing value of Ni in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1, PI/S/O1 and P3/D/O2 stations for both the adult and children populations whereas the lowest ADDing level of Ni was recorded in the sediment samples extracted from PI/S/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIing) of Ni via ingestion for the adult and children populations were 1.0E-06 and 9.9E-06 mg/kg/day respectively.

The average daily dose (ADDing) of Cd in the sediment from the study area in the adult and children populations ranged from 2.9E-08 – 4.4E-06 and 2.7E-07 - 4.1E-05 mg/kg/day respectively. The highest ADDing value of Cd in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1 station for both the adult and children populations.

Table 3 Average Daily Dose (ADDing) and Average Daily Intake (ADIing) (mg/kg/day) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria

Samples	**Cu (mg/kg)**		**Zn (mg/kg)**		**Fe (mg/kg)**		**Pb (mg/kg)**		**V (mg/kg)**		**Ni (mg/kg)**		**Cd (mg/kg)**	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
PI/D/CO1	3.4E-06	3.2E-05	1.5E-06	1.4E-05	3.3E-03	3.1E-02					5.4E-08	5.1E-07	2.9E-08	2.7E-07
PI/S/CO1	3.2E-06	3.0E-05	1.8E-06	1.7E-05	3.2E-03	3.0E-02					4.0E-08	3.7E-07	8.6E-08	8.0E-07
PI/D/O1	8.0E-06	7.4E-05	3.3E-06	3.1E-05	3.9E-03	3.6E-02					1.1E-07	1.1E-06	4.4E-06	4.1E-05
PI/S/O1	5.0E-06	4.7E-05	4.9E-06	4.6E-05	4.3E-03	4.0E-02					1.1E-07	1.1E-06	4.3E-06	4.0E-05
P2/D/O1	7.1E-06	6.6E-05	6.3E-06	5.9E-05	3.8E-03	3.6E-02			3.0E-08	2.8E-07	9.7E-08	9.1E-07	1.5E-06	1.4E-05
P2/S/O1	6.3E-06	5.9E-05	4.5E-06	4.2E-05	4.3E-03	4.0E-02					8.3E-08	7.7E-07	1.5E-06	1.4E-05
P3/D/O2	4.4E-06	4.1E-05	5.5E-06	5.1E-05	4.2E-03	3.9E-02					1.1E-07	1.0E-06	4.3E-06	4.0E-05
P3/S/O2	4.9E-06	4.5E-05	4.2E-06	3.9E-05	4.3E-03	4.0E-02					9.4E-08	8.8E-07	2.9E-06	2.7E-05
P4/D/O1	4.5E-06	4.2E-05	3.2E-06	3.0E-05	3.9E-03	3.6E-02					7.9E-08	7.3E-07	2.2E-06	2.1E-05

P4/S/O1	4.5E-06	4.2E-05	3.3E-06	3.1E-05	4.2E-03	3.9E-02					7.1E-08	6.7E-07	1.8E-06	1.7E-05
P5/D/O1	3.6E-06	3.4E-05	4.6E-06	4.3E-05	4.1E-03	3.8E-02			1.6E-08	1.5E-07	1.0E-07	9.6E-07	8.6E-08	8.0E-07
P5/S/O1	4.0E-06	3.7E-05	3.9E-06	3.7E-05	4.0E-03	3.7E-02					9.3E-08	8.7E-07	5.7E-08	5.3E-07
Average Daily I. (mg/kg/day)														
ADIing	5.7E-05	5.3E-04	4.7E-05	4.4E-04	4.8E-02	4.4E-01			4.6E-08	4.3E-07	1.0E-06	9.9E-06	2.3E-05	2.2E-04
RfD	0.037		0.3		0.7		0.0035		0.007		0.008		0.05	

- *Average Daily Dose (ADDinh) and Average Daily Intake (ADIinh) (mg/kg/day) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria:*

The average daily dose (ADDinh) of sediment sample is represented in Table 4. The average daily dose (ADDinh) of Cd in the sediment from the study area in the adult and children populations ranged from 4.9E-10 – 1.2E-09 and 1.2E-09 - 2.9E-09 mg/kg/day respectively. The highest ADDinh value of Cd in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1 for both populations whereas the lowest ADDing level of Cd was recorded in the sediment extracted from PI/S/CO1 for adults and PI/D/CO1 and PI/S/CO1 for children population. Furthermore, the average daily intake (ADIinh) of Cd via inhalation for the adult and children populations were 8.8E-09 and 2.1E-08 mg/kg/day respectively.

The average daily dose (ADDinh) of Zn in the sediment from the study area in the adult and children populations ranged from 2.3E-10 – 9.7E-10 and 5.4E-10 - 2.3E-09 mg/kg/day respectively. The highest ADDinh value of Zn in the analyzed sediment samples was recorded in the sediment samples obtained from P2/D/O1 whereas the lowest ADDinh level of Zn was recorded in the sediment extracted from PI/D/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIinh) of Zn via inhalation for the adult and children populations were 7.2E-09 and 1.7E-08 mg/kg/day respectively.

The average daily dose (ADDinh) of Fe in the sediment from the study area in the adult and children populations ranged from 4.9E-07 – 6.6E-07 and 1.1E-06 - 1.5E-06 mg/kg/day respectively. The highest ADDinh value of Fe in the analyzed sediment samples was recorded in the sediment samples obtained from PI/S/O1, P2/S/O1 and P3/S/O2 stations for both the adult and children populations whereas the lowest ADDinh level of Fe was recorded in the sediment samples extracted from PI/S/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIinh) of Fe via inhalation for the adult and children populations were 7.3E-06 and 1.7E-05 mg/kg/day respectively. In this current study, there was no Pb detected in the analyzed sediment samples, hence, no ADDinh or ADIinh was calculated for it.

The average daily dose (ADDinh) of V in the sediment from the study area in the adult and children populations ranged from BDL – 4.6E-12 and BDL - 1.1E-11 mg/kg/day respectively. The highest ADDinh value of V in the analyzed sediment samples was recorded in the sediment samples obtained from P2/D/O1 for both the adult and children populations. Furthermore, the average daily intake (ADIinh) of V via inhalation for the adult and children populations were 7.0E-12 and 1.7E-11 mg/kg/day respectively. The average daily dose (ADDinh) of Ni in the sediment from the study area in the adult and children populations ranged from 6.2E-12 – 1.8E-11 and 1.4E-11 - 4.1E-11 mg/kg/day respectively. The highest ADDinh value of Ni in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1 and PI/S/O1 stations for both the adult and children populations whereas the lowest ADDinh level of Ni was recorded in the sediment samples extracted from PI/S/CO1 for both the adult and children populations. Furthermore, the average daily intake (ADIinh) of Ni via inhalation for the adult and children populations were 1.6E-10 and 3.8E-10 mg/kg/day respectively. The average daily dose (ADDinh) of Cd in the sediment from the study area in the adult and children populations ranged from 4.4E-12 – 6.7E-10 and 1.0E-11 - 1.6E-09 mg/kg/day respectively. The highest ADDinh value of Cd in the analyzed sediment samples was recorded in the sediment samples obtained from PI/D/O1 station for both the adult and children populations.

Table 4 Average Daily Dose (ADDinh) and Average Daily Intake (ADIinh) (mg/kg/day) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria

Samples	**Cu (mg/kg)**		**Zn (mg/kg)**		**Fe (mg/kg)**		**Pb (mg/kg)**		**V (mg/kg)**		**Ni (mg/kg)**		**Cd (mg/kg)**	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
PI/D/CO1	5.2E-10	1.2E-09	2.3E-10	5.4E-10	5.1E-07	1.2E-06					8.4E-12	1.9E-11	4.4E-12	1.0E-11
PI/S/CO1	4.9E-10	1.2E-09	2.8E-10	6.5E-10	4.9E-07	1.1E-06					6.2E-12	1.4E-11	1.3E-11	3.1E-11
PI/D/O1	1.2E-09	2.9E-09	5.1E-10	1.2E-09	6.0E-07	1.4E-06					1.8E-11	4.1E-11	6.7E-10	1.6E-09
PI/S/O1	7.7E-10	1.8E-09	7.5E-10	1.8E-09	6.6E-07	1.5E-06					1.8E-11	4.1E-11	6.6E-10	1.5E-09
P2/D/O1	1.1E-09	2.6E-09	9.7E-10	2.3E-09	5.9E-07	1.4E-06			4.6E-12	1.1E-11	1.5E-11	3.5E-11	2.3E-10	5.4E-10
P2/S/O1	9.6E-10	2.3E-09	6.9E-10	1.6E-09	6.6E-07	1.5E-06					1.3E-11	3.0E-11	2.3E-10	5.3E-10
P3/D/O2	6.7E-10	1.6E-09	8.5E-10	2.0E-09	6.5E-07	1.5E-06					1.7E-11	4.0E-11	6.6E-10	1.5E-09
P3/S/O2	7.5E-10	1.7E-09	6.4E-10	1.5E-09	6.6E-07	1.5E-06					1.5E-11	3.4E-11	4.4E-10	1.0E-09
P4/D/O1	7.0E-10	1.6E-09	4.9E-10	1.1E-09	6.0E-07	1.4E-06					1.2E-11	2.8E-11	3.4E-10	8.0E-10
P4/S/O1	6.9E-10	1.6E-09	5.1E-10	1.2E-09	6.4E-07	1.5E-06					1.1E-11	2.6E-11	2.8E-10	6.5E-10
P5/D/O1	5.6E-10	1.3E-09	7.0E-10	1.6E-09	6.3E-07	1.5E-06			2.4E-12	5.6E-12	1.6E-11	3.7E-11	1.3E-11	3.1E-11
P5/S/O1	6.1E-10	1.4E-09	6.1E-10	1.4E-09	6.2E-07	1.4E-06					1.4E-11	3.3E-11	1.8E-11	2.1E-11
Average Daily Intake ingestion (mg/kg/day)														
ADIing	8.8E-09	2.1E-08	7.2E-09	1.7E-08	7.3E-06	1.7E-05			7.0E-12	1.7E-11	1.6E-10	3.8E-10	3.6E-09	8.2E-09
RfD	0.037		0.3		0.7		0.0035		0.007		0.008		0.05	

- *Hazard Quotient (HQ) and Hazard Index (HI) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria:*

The Hazard Quotient (HQ) which comprises of the Hazard Quotient ingestion (HQing), Hazard Quotient inhalation (HQinh) and Hazard Quotient dermal (HQder) were used to estimate the level of non-carcinogenic risk in the present study. Hazard Quotient (HQ) and Hazard Index (HI) of heavy metals. The Hazard Quotient (HQ) of the sediments is represented in Table 5. The Hazard quotient (HQing, HQinh and HQder) of Cu in the sediment samples collected from the study area in the adult and children populations ranged from 2.4E-07 – 1.6E-03 and 5.7E-07 - 1.4E-02 respectively. The highest HQ value of Cu in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway whereas the lowest HQ value of Cu was recorded in the hazard quotient via inhalation (HQinh) pathway for the adult and children populations. Furthermore, the hazard index (HI) of Cu for the adult and children populations were 1.6E-03 and 1.4E-02 respectively.

The Hazard quotient (HQing, HQinh and HQder) of Zn in the sediment from the study area in the adult and children populations ranged from 2.4E-08 – 1.6E-04 and 5.6E-08 - 1.5E-03 respectively. The highest HQ value of Zn in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway whereas the lowest HQ value of Zn was recorded in the hazard quotient via inhalation (HQinh) pathway for the adult and children populations. Furthermore, the hazard index (HI) of Zn for the adult and children populations were 1.6E-04 and 1.5E-03 respectively.

The Hazard quotient (HQing, HQinh and HQder) of Fe in the sediment samples obtained from the study area in the adult and children populations ranged from 1.0E-05 – 6.8E-02 and 2.4E-05 - 6.3E-01 respectively. The highest HQ value of Fe in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway whereas the lowest HQ value of Fe was recorded in the hazard quotient via inhalation (HQinh) pathway for the adult and children populations. Furthermore, the hazard index (HI) of Fe for the adult and children populations were 6.8E-02 and 6.3E-01 respectively.

In this current study, there was no Pb detected in the analyzed sediment samples, hence, no Hazard quotient calculated for it.

The Hazard quotient (HQing, HQinh and HQder) of V in the sediment samples from the study area in the adult and children populations ranged from 3.6E-09 – 6.5E-06 and 2.3E-09 - 6.1E-05 respectively. The highest HQ value of V in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway whereas the lowest HQ value of V was recorded in the hazard quotient via inhalation (HQinh) pathway for the adult and children populations. The Hazard quotient (HQing, HQinh and HQder) of Ni in the sediment samples from the study area in the adult and children populations ranged from 2.0E-08 – 1.3E-04 and 4.7E-08 - 1.2E-03 respectively. The highest HQ value of Ni in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway whereas the lowest HQ value of Ni was recorded in the hazard quotient via inhalation (HQinh) pathway for the adult and children populations. Furthermore, the hazard index (HI) of Ni for the adult and children populations were 1.3E-04 and 1.2E-03 respectively.

The Hazard quotient (HQing, HQinh and HQder) of Cd in the sediment samples collected from the study area in the adult and children populations ranged from 7.1E-08 – 4.6E-04 and 1.7E-07 - 4.3E-03 respectively. The highest HQ value of Cr in the analyzed sediment samples was recorded in the hazard quotient via ingestion (HQing) pathway.

Table 5 Hazard Quotient (HQ) and Hazard Index (HI) of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria

Samples	**Cu (mg/kg)**		**Zn (mg/kg)**		**Fe (mg/kg)**		**Pb (mg/kg)**		**V (mg/kg)**		**Ni (mg/kg)**		**Cd (mg/kg)**	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Child
HQing	1.6E-03	1.4E-02	1.6E-04	1.5E-03	6.8E-02	6.3E-01			6.5E-06	6.1E-05	1.3E-04	1.2E-03	4.6E-04	4.3E-03
HQinh	2.4E-07	5.7E-07	2.4E-08	5.6E-08	1.0E-05	2.4E-05			3.6E-09	2.3E-09	2.0E-08	4.7E-08	7.1E-08	1.7E-07
HQder	3.9E-06	2.5E-05	3.9E-07	2.5E-06	1.7E-04	1.1E-03			1.6E-08	1.0E-07	3.3E-07	2.1E-06	1.1E-06	7.4E-06
HI	1.6E-03	1.4E-02	1.6E-04	1.5E-03	6.8E-02	6.3E-01			6.5E-06	6.1E-05	1.3E-04	1.2E-03	4.6E-04	4.3E-03
Reference	1		1		1		1		1		1		1	

IV. DISCUSSION

➢ *Concentrations of Heavy Metals in Sediment Obtained from Okenta Alode in Eleme, Rivers state, Nigeria:*

This study investigated the concentration of heavy metals in sediment samples from six stations vulnerable to crude oil pollution due to the network of pipelines, oil wells and reserves around this region and bio-remediated section where the control samples were collected in Okenta Alode in Eleme, Rivers state, Nigeria. The metals analyzed were Copper (Cu), Zinc (Zn), Iron (Fe), Lead (Pb), Vanadium (V), Nickel (Ni) and Cadmium (Cd) in sediments (in-depth and surface level). The average concentrations of the heavy metals descended in the order of Fe > Cu > Zn > Cd > Ni > V > Pb. Similarly, the concentration of the metal in the six stations showed descending trend ofP1/S/O1 > P3/D/O2 > P2/S/O1 > P3/D/O2 > P4/S/O1 > P5/D/O1 > P5/S/O1 > P1/D/O1 > P4/D/O1 > P2/D/O1 > P1/D/CO1 > P1/S/CO1. The concentrations of metals in the sediment samples obtained from these crude oil polluted areas and the remediated control stations were compared to the FAO/WHO standard maximum allowable limit (MAL) for metals [18] and the geochemical background concentration of heavy metals (Bn) [19].

The level of copper (Cu) in the sediment samples of the study area was below the stipulated maximum allowable safe standard of 100 and 45 mg/kg as recommended by FAO/WHO [20] and geochemical background [19] of sediment indicating that the sediment may not be contaminated as a result of high level of copper accumulated in the soil. However, the Copper concentrations in the stations polluted with crude appear to be higher than the sediments collected from the remediated stations (control).

The Cu concentrations in this study suggest that there may not be contamination of the examined sediment samples as a result of a high level of Cu, however, it is pertinent to note that the stations polluted with crude oil may continue having elevated levels of Cu if not properly controlled as it has shown in the higher concentrations recorded in the polluted stations as against the controlled stations (remediated stations) which may represent a risk to the exposed population over time.

The average concentration of Zn in the analyzed sediment samples ranged from 1.06 ± 0.01 – 4.40 ± 0.01 mg/kg. The iron(Fe) content in the sediment samples collected from the different stations in Okenta Alode, Rivers State exceeded the FAO/WHO maximum permissible limit of 15.0 mg/kg [18] (Ciroma et al., 2014). This suggests that there may be contamination in the sediments collected from the sampled stations in Okenta Alode, Eleme of Rivers State as a consequence of iron buildup and accumulation in the sediment, which may result in the contamination of the sediments in the study area. Dolealováet al[19] reported Fe (4.45–20.64 mg/kg) concentrations which contradicts the Fe concentration in the current study. This high concentration of Fe observed in the present study may be due to the activities of excessive spillage of crude oil by companies and illegal bunkering carried out within the study area. This crude oil spill into the environment and gradually accumulate in the sediments leading to the high level of metals in the sediment. Iron is required for chlorophyll production and activates a variety of respiratory enzymes in plants. Plants suffer from severe chlorosis when they are deficient in Fe. High amounts of Fe dust exposure may result in respiratory illnesses such as chronic bronchitis and breathing problems.

There was no Pb detected in all the sediment samples obtained from all the sampled stations.

The concentration of Vanadium (V) in the analyzed sediments samples obtained from the studied stations in Okenta Alodein Eleme of Rivers State fall within the 4.053 mg/kg concentration of the geochemical background [19]. This suggests that the sediment samples analyzed may not be contaminated as a consequence of vanadium buildup or accumulation in the soil. The present study disputed the study of Doležalová et al [19] who reported higher vanadium concentrations compared to level of vanadium in the present study.

The Nickel (Ni) concentrations in the analyzed sediment samples from the polluted and remediated stations were within the 50 mg/kg maximum allowable limit recommended by FAO/WHO (Ciroma et al., 2014) and 35 mg/kg geochemical background [19]. The Ni concentration found in this study suggests that there may not be contamination of the sediments due to Ni contamination. Cabrera et al [21] reported higher Ni concentration which range from (10.1 - 23.2 mg/kg) in the study, heavy metal contamination of soils impacted by the Guadiamar hazardous flood, which contradicted the Ni concentration of this study. This slight abundance of Ni in the study reported may be attributed to the flood which consistently carry huge amount of crude oil deposits and empty them in the study area, hence elevating the level of metals in the soil.

The level of Cadmium in the sediment samples in the current study were lower than the maximum allowed levels of 3.0 mg/kg established by FAO/WHO [18] and slightly higher than the 0.12 mg/kg geochemical background concentration of heavy metals (Bn) [19], this suggests that there may be Cd contamination in the analyzed sediment samples from this crude oil and remediated stations. The concentration of Cd obtained from the current study conforms with the study of Bahrami et al[20] which has Cd concentration in the range of (0.25 – 0.37 mg/kg) in the evaluation, source apportionment, and health risk assessment of heavy metal and polycyclic aromatic hydrocarbons in soil and vegetable of Ahvaz metropolis which recorded similar Cd concentrations when compared to the Cd concentrations in sediment samples from the present study. This high metal concentration can also be ascribed to oil spill and the activities of illegal oil bunkering of crude oil in the area. The study of Ogunkunle and [22] showed a disparity to the Cd concentration to the present study because they found a higher concentration of Cd (156.6 mg/kg) in the Pollution Loads and Ecological Risk Assessment of Soil Heavy Metals near a Mega Cement Factory in Southwest Nigeria. This high concentration may be ascribed to the creation of smoke, gas, and dust from cement, as well as excessive vehicular movements, which may contribute to the buildup of metals (Cd) in soil. Cadmium exposure has been linked to renal damage and high blood pressure [23].

- *Human Health Risk Assessment (HHRA):*

The Average Daily Intake (ADI) of metals through the accidental intake of sediments in adult and children populations via ingestion (oral), inhalation or dermal pathways obtained from the study stations in Okenta Alode in Eleme of Rivers State showed the trends of the analyzed metals in descending order as thus: Fe > Cu > Zn > Cd > Ni > V > Pb. The daily intake of metals by the adults and children through sediment intake (ingestion, inhalation and dermal routes) from the present study were compared with the recommended reference doses (RfD) of the individual metals [25] as to determine the estimated daily intake of the metals put into the body system of the exposed population.

The results of the ADI in exposed population from the present study were all lower than the recommended reference dose (RfD) of the metals as stipulated by USEPA [24]. This suggests that there may not be any potential health risk as a result the accumulation of these metals in the body system because they are within the metals required level in the body system hence, there may be no risk posed to the exposed population. It is imperative to note that appropriate care should be taken to reduce the spilling of crude oil which may be the major source of these heavy metals to avoid deleterious health effects over time.

It is also important to note from the present study that the average daily intake of the metals in children were higher than that of the adults, according to the result of the present study which may be due to the lesser weight of the children compared to the adult weight. There are more effects of metals toxicity to lesser weight compared to higher weight. The hazard quotient (HQ) which is the characterization of the individual metals was also used to further determine the non-carcinogenic health risk that the individual metals may cause to the exposed population. The HQ of the heavy metals via sediment intake (oral, inhalation, and dermal) obtained from this study in the exposed population were all less than 1. Hence, no adverse non-carcinogenic health risk is directed to the health of both adults and children by the studied metals.

The Hazard Index (HI) of oral exposure to sediment contamination in the study area by the exposed population, showed values less than 1, which showed that there may not be health risk posed to the exposed population of the study area. According to USEPA [24], HI < 1 means the exposed individual is unlikely to experience obvious adverse health effects. On the contrary, HI > 1 means that there may not be a non-carcinogenic effect directed to the exposed populace.

The HQ and HI of metals values recorded in the present study for both populations were less than 1. It can be concluded that the heavy metals in the sediments of the study area may not have the tendency to cause non-carcinogenic adverse health risks to the exposed populace when the sediment is ingested accidentally into the body system via any of the three ingestion pathways.

The carcinogenic risk of the analyzed metals with the tendency of causing cancer namely (Cd) in sediment samples were calculated through the ingestion, inhalation and dermal pathways. The CR values of Cd in both populations were within the 10^{-6} to 10^{-4} permissible predicted range for carcinogens as recommended by USEPA [25]. This is an indication that there may not be any significant carcinogenic risk caused by the carcinogenic intake of Cd via the accidental sediment intake over time. Thus, based on internationally accepted precautionary criterion, the carcinogenic risks of these metals in these sediment samples may not have the tendency to cause cancer in both populations since the CR of all the analyzed Cd in the sediment fell within the permissible predicted range for carcinogens as recommended by USEPA [25].

V. CONCLUSION

Conclusively, the metal concentrations were below the permissible limits, indicative of low or no contamination of the sediments with metals. The human health risk assessment showed no accumulation of metals in the body system since the average daily intakes (ADI) via the three pathways were below their RfD. The HQ, HI, LCR, and TLCR were lower than their permissible range indicating no non-carcinogenic and carcinogenic risk via metals intake through accidental sediment ingestion. The result of the present study suggests that these sediments may be contaminated with metals which have the tendency to pose human and ecological health risks.

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