Empirical Characterization of Heavy Metals in Crude Oil Spill Sites in Emohua, Rivers State, Nigeria

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ABSTRACT

The study assessed the concentration of heavy metals in three oil spill sites in Emohua local government area in Rivers State, Nigeria. Soil samples were collected at depth 0-30cm for surface soil samples and up to 10m for sub-surface soil samples depending on the depth of borehole. Groundwater samples were collected from drilled boreholes while the surface water samples were collected from fishponds or water bodies (rivers) close to the oil spill sites. The samples taken from the oil spill sites were analysed to determine the level of concentration of 10 Department of Petroleum Resource (DPR) specified heavy metals (Cd, Zn, Cu, Pb, Cr, Ba, Ni, Hg, As, and Co). BUCK Scientific Atomic Absorption Spectrophotometer (AAS) was used in detecting the concentration of the heavy metals. For the surface soil, Pb concentration in site A and B were significantly higher than what was obtained at site C, with a mean concentration of 219.70, 130.01 and 3.41mg/kg respectively for the three sites. The mean lead (Pb) concentration obtained in the surface soil was within DPR and United State Environmental Protection Agency (USEPA) acceptable limits. Barium also has significant concentration in both the surface soil and sub-surface soil. Kruskal Wallis test indicated significant difference in the Pb, Cd, Zn, Cu, Cr and Ba concentration in surface/topsoil among the three sites and also indicated significant difference in the concentrations of Pb, Cd, Cr, Ni, Ba and As in sub-surface soil among the sites. Little heavy metal concentration was found in both the groundwater and surface water. The study showed that even if some heavy metals were detected at the oil spill sites, they do not pose any serious health risk, as all the heavy metals in the four environmental media at the three sampling sites were below the national limit stipulated by the Department of Petroleum Resource (DPR), Nigeria.

Keywords: Concentration, Heavy Metals, Niger Delta Soil, pollution.

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I. INTRODUCTION

The Niger Delta region of Nigeria is known for its oil exploration and production activities [1]. Despite its rich abundant ecosystem and biodiversity, oil pollution and contamination remain a major problem in the region resulting to significant human health risk [2], [3]. [4] reported an unprecedented level of environmental contamination and pollution in the region. Several researchers have reported the impact of oil and gas pollution such as elevated toxic concentrations of heavy metals in various environmental media [5]-[7]. These contaminants have found their way into the food chain by bio-accumulating in plant and animal tissues which are then ingested by humans.

Heavy metals are introduced into the environment through natural geological phenomena such as ore formation, weathering of rocks, and leaching or various anthropogenic activities such as mining, burning of fossil fuel, oil spillage, etc. Oil spill is the main activity that potentially increases the

release of heavy metals to the environment in the Niger Delta.

Oil spills usually occur in the region due to the uncontrolled release of crude oil into the environment because of operational mishaps, equipment failures, pipeline ruptures due to integrity issues as well as due to the issue of oil theft, illegal refineries, and activities of vandals who intentionally damage pipelines and other facilities. Oil spills either as crude oil or refined products releases contaminants into the environment including heavy metals [8].

[9] stated that apart from the well-known heavy metals such as vanadium and nickel, crude oil contains a variety of heavy metals in different concentrations. [9] further stated that in addition heavy metals such as barium are usually added during the production process while some heavy metals migrate into crude oil via corrosion products of pipelines and process tanks/vessels. Heavy metals/metalloids are elements with relatively high density compared to water. [10] stated that heavy metals have densities greater than 5 g/cm³ while light metals have densities less than 5 g/cm³.

The main threats from heavy metals arise due to the toxicity of metals like lead, cadmium, mercury, and arsenic amongst others [11] and also due to the fact that heavy metals cannot be broken down easily to a non-toxic form, as such remains a potential threat for many years [12]. Toxicities from heavy metals exposure include a decrease in immunological defenses, intrauterine growth retardation, impaired psychosocial behavior and disabilities associated with malnutrition are just a few of the many health concerns [13], [14]. This paper assesses the concentration of some selected heavy metals in three oil spill sites in Emohua local government area in Rivers state Nigeria prescribed for understanding petroleum contaminated sites by the Department of Petroleum Resources (DPR).

II. MATERIALS AND METHODS

A. Study Area

The three study sites are in Emohua Local Government Area (EMOLGA) of Rivers State Nigeria. Site A is located on longitude 6.695E and latitude 5.005N, Site B is located on longitude 6.69E and 5.028N, and Site C is located on longitude 6.773E and latitude 5.084N. EMOLGA has a land area cover of 837.21km² and a population of approximately 201,901 as of 2006 population census count. The study area lies within the tropical rainforest of the Niger Delta and is characterized by eight months and four months of the wet and dry seasons, respectively. The mean annual temperature of the area is 27 (±3) degrees Celsius with high humidity and the annual average rainfall is about 3000 mm with average evapotranspiration of about 1000 mm/year, leaving an effective rainfall of 2000 mm/year [15]. The major occupation of the people is farming with a few others engaging in trading and public service [16]. EMOLGA hosts a few oil processing facilities and an array of crude oil pipelines. Several oil spill incidents have been reported generally in this area due to pipeline vandalism.

Fig. 1. Map of the Study Area, EMOLGA.

B. Sample Collection

On each of the study sites (A, B and C); about 20 top/surface soil and sediment samples, 5 sub-surface soil samples, 3 surface water samples and 5 groundwater samples were randomly collected into air-tight containers. Surface soil

and sediment samples were collected at two horizons (0–15 cm and 15 cm to 30 cm) using a graduated hand auger. The samples completed from the two horizons were composited for analysis. About 0.5 kg of surface soil and sediment were collected and transferred into a wide mouth amber bottle. A total of 3 surface water samples each were collected from Sites A, B and C including community local fishponds and rivers. For groundwater and sub-surface sample, 5 wells were drilled at each site, and 5 sub-surface soil samples and 5 groundwater samples were collected at various depths in the well.

C. Determination of Heavy metals

Acid digestion of the soil/sediment samples was conducted prior to analysis. The concentration of each metal in the samples was obtained after digestion using Atomic Absorption Spectrophotometer (ASTM) methods. These were carried out using BUCK Scientific Atomic Absorption Spectrophotometer (AAS). Prior to the analysis, calibration was done with each metal standard of known concentrations. The concentration of each metal was ascertained from the data generated by the AAS and expressed in mg/kg for soil samples and mg/l for water samples.

D. Data Analysis

The results obtained from the laboratory analysis were subjected to both descriptive and inferential statistical analysis to determine the mean, standard deviation. Microsoft XLSTAT 2016 and SPSS were used in performing all statistical analyses.

III. RESULTS AND DISCUSSIONS

A. Heavy Metals Concentrations

The result of the heavy metal concentration for the four environmental media at the three sampling sites is shown in Fig. 2–5. For the heavy metals in the surface soil at the sampling sites (Fig. 2), Lead (Pb) had the highest concentration out of the ten selected heavy metals investigated in two out of the three sites. The concentration of Pb ranged from 0.0009 to 820.53mg/kg and 21.03 to 383.18 mg/kg in site A and B respectively. The mean concentration of Pb at Sites A, B and C were 219.70, 130.01 and 3.41, respectively. Barium had the second-highest concentration with mean concentrations of 18.85, 87.67, and 33mg/kg respectively. Chromium had mean concentrations of 29.19, 29.18, and 4.62 mg/kg for sites A, B and C respectively. A considerable amount of zinc was found in the surface soil at the three sites, with zinc having mean concentrations of 8.01, 8.72, and 11.26 mg/kg, respectively. Cadmium, copper, mercury, arsenic, and cobalt had negligible concentrations at the three sampling sites.

The metal concentration for the sub-surface soil at the three sites shown in Fig. 3 revealed that barium had the highest concentration out of the ten metals investigated at the three sampling sites. The barium concentration ranged from 26.8 to 90.6 mg/kg in site A, 11.7 to 25.1 mg/kg in site B and 35.6 to 61.00 mg/kg in site C. The mean concentration of barium at sites A, B and C were 45.46, 19.5 and 48.10 mg/kg. Copper, zinc, lead, and chromium had a metal concentration that was less than 10 mg/kg in all three sampling sites. Very negligible

concentrations of mercury, arsenic, and cobalt were recorded at the three sites.

Fig. 2. Heavy metals in surface soil of the study sites.

Fig. 3. Heavy metals in sub-surface soil of the study sites.

The metal concentration in the surface water at the three sites is shown in Fig. 4. The result showed that cobalt at site A had a concentration that was greater than 0.1 mg/l. The cobalt at site A ranged from 0.09 to 0.14 mg/l with a mean concentration of 0.113 mg/l. Nickel had a similar concentration in site B and C with a mean concentration of 0.096 mg/l. The other metals had concentrations that were less than 0.05 mg/l apart from zinc at site A which had a mean concentration of 0.056 mg/l. The metal concentration for groundwater at the three sites is shown in Fig. 5, which indicated that only zinc had a detectable concentration. The mean concentration of zinc was 1,028 mg/l and 0.332 mg/l at Sites A and B, respectively.

Fig. 4. Heavy metals in surface water of the study sites.

Fig. 5. Heavy metals in Groundwater of the study sites.

B. Kruskal Wallis Test of Significance for Heavy Metals between Sites

Kruskal Wallis non-parametric test of significance was used to investigate if there was a significant difference in the concentration of the heavy metals between the three sites. The result of the Kruskal Wallis test for heavy metal in the surface soil is shown in Table I. The result showed that there was a significant difference in the concentrations of Pb, Cd, Zn, Cu, Cr and Ba but no significant difference in the concentrations of Ni, As, Co and Hg among the three sites. Dunn multiple pairwise comparisons were used to establishing the difference lies and the result is shown in Fig. 2. The result showed that Pb and Cr concentrations at site A and B were significantly higher than site C. Barium concentration at site A was significantly lower than the concentration obtained at site B and C.

TABLE I: TEST OF SIGNIFICANCE OF HEAVY METALS IN SURFACE SOIL

Heavy Metals	K (Observed value)	K (Critical value)	DF	p-value (Two-tailed)
Pb	36.8008	5.9915	2	< 0.0001
Cd	30.1209	5.9915	2	< 0.0001
Zn	8.6457	5.9915	2	0.0133
Cu	37.3246	5.9915	2	< 0.0001
Cr	28.7866	5.9915	2	< 0.0001
Ni	0.8982	5.9915	2	0.6382
Ba	29.6514	5.9915	2	< 0.0001
As	0.1100	5.9920	2	0.8570
Co	0.2100	5.9920	2	0.7070
Hg	0.1700	5.9920	2	0.7570

For the sub-surface soil, the result of the Kruskal Wallis test is shown in Table II. The result showed that Pb, Cd, Cr, Ni, Ba and As had a significant difference in their concentration in the three sites. No significant difference was observed in the concentrations of Zn, Cu, Co, and Hg. The result from Dunn multiple comparison test showed that the lead concentration at site A was significantly different from the lead concentration at site C. Chromium concentration at site A and B were significantly higher than the concentration recorded at site C while barium concentration at site C was significantly higher than the concentration recorded at site B. Nickel concentration at site A was significantly higher than the concentration recorded at site C.

For the surface and ground water, Kruskal Wallis test of significance showed that there were significant differences in lead (Pb), chromium and cobalt concentrations among the

three sites for the surface water (Table III) while there was significant difference in only zinc concentration among the three sites for the ground water (Table IV).

TABLE II: TEST OF SIGNIFICANCE OF HEAVY METALS IN SUB-SURFACE SOIL

Heavy Metals	K (Observed value)	K (Critical value)	DF	p-value (Two-tailed)
Pb	9.0600	5.9915	2	0.0108
Cd	7.6207	5.9915	2	0.0221
Zn	4.5600	5.9915	2	0.1023
Cu	6.0667	5.9915	2	0.0500
Cr	7.9685	5.9915	2	0.0186
Ni	10.5188	5.9915	2	0.0052
Ba	9.9979	5.9915	2	0.0067
As	14.0000	5.9915	2	0.0009
Co	0.1400	5.9920	2	0.7270
Hg	0.2500	5.9920	2	0.6970

TABLE III: TEST OF SIGNIFICANCE OF HEAVY METALS IN SURFACE WATER

Heavy metals	K (observed value)	K (critical value)	Df	P-value (two-tailed)
Pb	8.0000	5.9915	2	0.0183
Cd	0.0800	5.9915	2	0.9840
Zn	6.0000	5.9915	2	0.0500
Cu	0.0800	5.9915	2	0.9840
Cr	8.0000	5.9915	2	0.0183
Ni	2.9388	5.9915	2	0.2301
Ba	0.0800	5.9915	2	0.9840
As	0.0800	5.9915	2	0.9840
Co	7.6235	5.9915	2	0.0021
Hg	0.0800	5.9915	2	0.9840

TABLE IV: TEST OF SIGNIFICANCE OF HEAVY METALS IN GROUNDWATER

Heavy Metals	K (Observed value)	K (Critical value)	DF	p-value (Two-tailed)
Pb	0.08	5.9915	2	0.984
Cd	0.08	5.9915	2	0.984
Zn	10.659	5.9915	2	0.0048
Cu	4.2857	5.9915	2	0.1173
Cr	0.08	5.9915	2	0.984
Ni	1.0769	5.9915	2	0.5836
Ba	0.08	5.9915	2	0.984
As	0.08	5.9915	2	0.984
Co	0.08	5.9915	2	0.984
Hg	0.08	5.9915	2	0.984

C. Discussion

The high lead concentration in the surface soil at the three sites especially at Site A can pose a significant problem if remediation processes are not carried out. Lead is among the 10 chemicals identified by the World Health Organization as a contaminant of major public health concern and requires action to protect the health of workers, children, and women of reproductive age [17]. The mean concentration of Pb obtained in the surface soil in the three sites in this study was lower than the maximum permissible limit stipulated by the Nigeria Department of Petroleum Resources (530 mg/kg) and USEPA (400 mg/kg) but the maximum Pb concentration in Site A was higher than the limits. Site A had the highest lead concentration than site B and C. Result from the Kruskal Wallis test indicated that the Pb concentrations at site A and B were not significantly different but the Pb concentration at site C was significantly different from site A and B. The relatively high concentration of lead in site A can cause serious health issues such as impaired children's brain development resulting in reduced intelligence quotient (IQ). [18] reported that some 70,000 children in Bangkok, Thailand risk losing four or more points of IQ because they were

exposed to lead emission from motor vehicles. Also, other health issues related to exposure to lead include increased antisocial behavior and reduced educational attainment. Lead exposure has also been associated with hypertension, renal impairment, immunotoxicity, and toxicity to the reproductive organs. The neurological and behavioral effects of lead are believed to be irreversible [17]. Lead is a cumulative toxicant that has no level of exposure that is known to be without harmful effects [17]. The Pb concentration obtained in this study was higher than similar soils contaminated with crude oil or soil close to the oilfields. In study [19], it was reported that the Pb concentration of contaminated Niger Delta soil within an oilfield was 6.53 mg/kg in the dry season and 10.2 mg/kg in the wet season. [20] reported that contaminated soil close to Imirigin oil field in Bayelsa State, Nigeria had Pb concentration of 8.0 mg/kg. [21] reported that the Pb concentration in contaminated soil in Ab-Teymour oil field in Iran was 29 mg/kg. [22] reported that for agricultural soil, the concentration of Pb found in the soil was within the range of 27.22-73.66 mg/kg with a mean concentration of 53.97 mg/kg. The lead concentration obtained from this study revealed that the mean Pb concentration at site A exceeded the mean concentration of Pb obtained in agricultural soil in [22] study by a factor of 4. Site A and B had relatively similar concentrations of chromium in the surface soil with concentrations of 29.194 and 29.177 mg/kg, respectively while site C had the least chromium concentration of 4.016 mg/kg. [22] reported that chromium recorded in agricultural soil in their study was within the range of 0-0.21 mg/kg with mean concentration of 0.03 mg/kg. [23] in a similar study of oil-polluted site reported that the mean chromium concentration recorded was 4.2 mg/kg. [19] in their study reported Cr concentration to be 15.74 mg/kg during the wet season and 11.20 mg/kg during the dry season. The chromium recorded in this study was higher than what was recorded in [23] and [19]. The chromium recorded in this study was lower than the DPR permissible limit of 380 mg/kg and USEPA permissible limit of 230mg/kg. Hence Cr is not a major contaminant of concern. Site B had the highest concentration of barium in the surface soil than the other two sites. The presence of barium in the surface soil indicates that the soil has been contaminated with crude oil, as barium is an additive during the production of crude oil. The barium concentration recorded at Site B exceeded the barium concentrations recorded at Sites A and C by a factor of 5 and 2.6, respectively. [24] reported a mean barium concentration of 1634 mg/kg in the soil of Ahvaz oilfield which is higher barium concentration than what was obtained in the current study. [24] attributed the elevated barium concentration in the soil as a result of barite addition in drilling mud. The barium concentration did not exceed the DPR limit of 625 mg/kg, therefore there should be little concern from exposure to barium at the three sites and hence barium is not identified as a major contaminant of concern. The Nickel concentrations found in the surface soil of the three soil were relatively low. The Nickel concentrations found in sites A, B, and C were 11.044, 6.828, and 1.023 mg/kg, respectively. The low nickel concentrations in the three sites could be attributed to the fact that Nigeria's crude oil has little nickel content [25]. [19], [5] reported a similar concentration of Ni in contaminated soil close to oilfields in the Niger Delta region of Nigeria.

Comparing the Ni concentration in contaminated soil close to oilfields or oil facilities in the Niger Delta region to other countries' oilfields revealed a higher concentration of Ni in the soils outside Nigeria. [21] reported that the Ni concentration in Ab-Teymour oil field soil was 328 mg/kg. [24] reported a mean Nickel concentration of 46.19 mg/kg in the soil close to Ahvaz oilfield. The Ni concentration in the soil of the current study was lower than the DPR limit of 210 mg/kg and USEPA limit of 1600 mg/kg. This result indicates that there is no significant risk associated with exposure to soil contaminated with Nickel at the three sites and hence Nickel is not a major contaminant of concern. The zinc concentration in surface soil showed a relatively low concentration. The concentration of zinc in the soil at Sites A, B, and C were 8.015, 8.715 and 11.260 mg/kg, respectively. [21] reported that the Zn concentration in Ab-Teymour oil field soil was 329 mg/kg. [19] reported Zn concentration in dry soil to be 23.06 mg/kg and in wet soil to be 38.13 mg/kg. [24] reported zinc concentration in soil in Ahvaz oil field to be 145.5 mg/kg. The zinc concentration obtained in this study was lower than DPR limit of 720 mg/kg and USEPA limit of 23,600 mg/kg. This result indicates that no significant risk is associated with exposure to soil contaminant with zinc at the three sites and hence zinc is not a major contaminant of concern for these sites. The other metals investigated at the three sites had very little concentrations and posed no associated health risk to residents exposed to the contaminated soil in the three sites. For the sub-surface soil, surface water and ground water, the metal concentrations were all relatively low and within acceptable limit by DPR and USEPA standards.

IV. CONCLUSION

The following conclusions were drawn from the study:

1. Significant concentration of Lead was found especially at Site A with elevated maximum concentration that is greater than the regulatory limit prescribed by DPR.
2. The concentration of most of the heavy metals studied was within the acceptable DPR limit and therefore pose no significant risk at the studied sites.

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