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Evaluation of Heavy Metal Contamination of Soil from Petroleum Crude Oil at an Illegal Refinery Site: A Case Study of Oshika Community in the Niger Delta Region of Nigeria

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ABSTRACT

The study was carried out at Oshika community of Rivers State in the Niger Delta region of Nigeria where petroleum crude oil illegal refining activity was terminated. Soil samples were collected at two different points at depths of 15 cm, 45 cm and 90 cm with a control for analysis of heavy metal pollutants (Pb, Cd, Cr, As, Zn, Cu, Ni, Co). The results from the analysis show that all the heavy metals investigated were present with their mean concentration values for top soil as 56.48±0.01 mg/kg, 53.49±0.00 mg/kg. 53.49±0.00 mg/kg, 84.75±0.01 mg/kg, 39.44±9.01 mg/kg, 35.46±0.00 mg/kg, 66.61±0.03 mg/kg and 40.66±0.00 mg/kg respectively which are all higher than the control values. Contamination factor, pollution index and geo-accumulation index were applied as index models for the evaluation of the extent and intensity of heavy metal contamination and pollution of the illegal refining at the site. All the index models used showed that the soil at the site was heavily contaminated and polluted by Cd and As, while also the result of the soil from the analysis indicated uncontaminated and unpolluted by Pb, Co, Ni, Cu, Cr and Zn. The toxicity of these heavy metals and the adverse impact on the health of the community cannot be over emphasized and the paper therefore advocated for discouraging illegal refining and implementation of integration policy into the modular refinery system.

1. INTRODUCTION

The Niger Delta region of Nigeria is experiencing a lot of environmental degradation arising from the petroleum industry and more especially the activities of illegal refineries as stated by Ikezam *et al.* (2021) has now reached an alarming proportion and becoming a cause for concern. These illegal refineries are usually located in the thick forest and swampy areas of the village far away from the prying eyes of ordinary

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members of the community and non-natives. Its refining equipment is made up of simple metal boiling tanks with no safety measures in place to protect its workers and the environment. Their method of production involves the theft of crude oil from vandalized network of pipelines at specific points crisscrossing the entire swampy and land terrain laid by the International Oil Companies (IOC) like Shell Petroleum Development Oil Company (SPDC), Mobil Exploration, Agip Oil within the oil producing communities. The crude oil is boiled at high temperature and petroleum products like petrol, diesel and kerosene are collected while the tars and other residues are discharged onto the soil, adjoining water creeks and rivers (Nwanyanwu et al, 2015). Most often than not, there are oil spillages, blow outs with the entire area being burnt as the products are highly inflammable. This causes environmental pollution of soil, water and air as it impacts negatively on the health and livelihood of the communities, nature, plants regeneration, loss of natural wild life habitats, disruption of crops, farming in general, water cycle and in most cases lead to loss of life (Obenade and Amangabara, 2014).

It has been shown by various researches that petroleum crude oil occurs naturally and contains both hydrocarbons and non-hydrocarbon compounds (including heavy metals), which is highly toxic to the environment at high concentrations (Akpomrere and Uguru, 2020).

The illegal petroleum refining activities generally increase the cumulative concentration of heavy metals in soil, although these heavy metals may be in low concentrations comparatively to other metals, are toxic in that quantity and could bio-accumulate in the tissues of plants and animals (Wong et al, 2002; Seaward, 2004) and negatively impacts on the environment and health of community members. Therefore analyzing the quantity of heavy metal in a particular environment can be used as a measure of pollution and contamination in the soil (Huaug *et al*., 2002, Sor, *et al*., 2020).

Edori and Kpee, (2017), posited that generally anthropogenic activities contribute immensely to the production and release of heavy metals into the environment as contaminants or pollutants and therefore necessitates the need to analyze and study the level and consequences of these heavy metal chemicals in soil. Ediene *et al.* (2016) and Bhattacharya *et al.* (2003) all agree that metals are naturally found within the earth crust which eventually changes its form to chemical/organic complexes by external activities, that could be toxic and altering the quality of the soil and ground water. Osam *et al*., (2011) also stated that some large quantities could also be found within an environment as a result of natural geographical ore formation, rock degradation or erosion. Sharma *et al.* (2014) stated that the soil acts as a natural sink that take in these chemical/organic complexes and compounds which are contaminants and pollutants that eventually alters the general properties and characteristics of the soil. The pollution and contamination of soil is now a source of concern as a result of proliferation of illegal refineries in the Niger Delta region with its attendant food insecurity implications. Hence, this paper aimed at assessing and evaluating the heavy metal contaminant in the soil from crude oil resulting from illegal petroleum refining operations in Oshika community, a suburb in the Niger Delta of Nigeria.

2. MATERIALS AND METHODS

2.1. Study Area

The site of non-active illegal refinery being selected for evaluation is located in Oshika community in Ahoada West Local Government Area of Rivers State, Nigeria. The Oshika community has coordinates, latitude 5.04 North (5.073665) and longitude 6.51(6.562638) East. of the State. The site and host community are situated in between SPDC pipeline (Right of Way) and the Agip Oil Company pipeline (Right of Way) that make up the Ebocha- Brass Pipeline (14" Okordia-Rumuekpe Trunk, Osika). Unfortunately, this unique situation makes the place attractive for illegal petroleum refiners as they tap from both lines with the surrounding stream into which waste products are emptied and also makes them prone to oil spills. The illegal refinery was destroyed in February 2022.

2.2. Sample Collection

A hand auger was designed and constructed for this research of 4inches size with an extension handle of up to 6 feet which was used at site (Oshaki community) to drill two different positions[holes of up to 3 feet, (0.9144 m) randomly selected at 25 ft. (7.62 m) apart from which soil samples were collected after every 6 inches (0.152 m) depth and put on flex mat of 4 ft by 6 ft (1.22 m x 1.83 m) The various samples with hand gloves were then put into marked sample polythene bags for various depths. The hand auger is marked every six inches for ease of soil sample collection. The above process was repeated also for control soil sample which was taken from about 45km away from the illegal petroleum refinery site, where there was no known history of illegal petroleum refining or crude oil spillage following the same process.

2.3. Sample Preparation

The soil samples marked Top 0-15 cm ‘A’. Middle 45 cm ‘A’ and Bottom 90 cm ‘A’ for the first sample collection point while the second collection point was marked Top 0-15 cm ‘B’, Middle 45 cm ‘B’ and Bottom 90 cm ‘B’. Some quantities from each of the samples were collected and dried at 105 ^{o}C using Mamert digital oven for 6hrs after which a 300 μm mesh size sieve was used to sieve the soil samples. Sieved soil quantity of 20 g was measured into a 250 ml conical flask for digestion and chemical extraction. The digested sample solutions were prepared and finally analyzed according to American Public Health Association (APHA) 3111B test method (APHA, 1992) with the Atomic Absorption Spectrophotometer (AAS) for Nickel, Arsenic, Zinc, Copper, Cobalt, Chromium, Lead and Cadmium.

2.4. Statistical Analysis

Statistical analysis was carried out using Statistical Package for Social Statistics (SPSS) software for the data got from the field work for heavy metals in soil. The various means and standard deviations were separated with the aid of The Duncan’s New Multiple Range (DNMR) Test ($p \leq 0.05$).

2.5. Index Models for Pollution

2.5.1. Contamination factor

This model was introduced for the assessment and interpretation of degree of contamination for soil for heavy metals by Lacatusu (2000). The factor is the ratio of the concentration of heavy metal value found in the soil to the expected background target values being stipulated in that environment. It is calculated using Equation (1).

$$\text{Contaminated factor (Cf)} = Cm/Cb \qquad (1)$$

Where Cm = Concentration of the heavy metal, Cb is the background/base values as adapted by Edori and Kpee, (2017) using the Department of Petroleum Resources (DPR), (2002).

The significance of intervals of contamination/pollution index (C/P) for the assessment and interpretation of degree of contamination of soil for heavy metals is shown in Table 1.

Table 1: Significance of intervals of contamination/pollution index (C/P) (Chiroma et al., 2014 adopted from Lacatuse 2000)

C/P	Significance	Symbols
< 0.1	Very Slight Contamination	Vsl
0.1 – 0.25	Slight Contamination	sl
0.26 – 0.5	Moderate Contamination	ml
0.51 – 0.75	Severe Contamination	stl
0.76 – 1.0	Very Severe Contamination	vstl
1.1 – 2.0	Slight Pollution	sp
2.1 – 4.0	Moderate Pollution	mp
4.1 – 8.0	Severe Pollution	stp
8.1 – 16.0	Very Severe Pollution	vstp
>16	Excessive	ep

2.5.2. Pollution index

This model measures the extent of total contamination from the site the sample was obtained as indicated by Tomlinson *et al* (1980) and was used to calculate and find the pollution index for a specific site as in the following Equation (2).

$$\text{Pollution index (PI)} = (Cf1 \times Cf2 \times Cf3 \times Cf4 \times Cf5 \ldots\ldots\ldots Cfn)^{1/n} \qquad (2)$$

Where Cf is the contamination factor value of individual heavy metal at site being analyzed, n is the number of heavy metals being analyzed.

A useful tool for pollution assessment of heavy metals. The result calculated in this study from these two equations will be used for assessment and pollution range with its significance.

2.5.3. Geo-accumulation index (Igeo)

This was used to assess and calculate the level of contamination of soil or sediment by various metals in a specific environment and was proposed by Muller (1981) using the formula in Equation 3.

$$Igeo = \log_2 (Cn/1.5Bn) \quad (3)$$

Where, Cn is the metal element concentration in the soil, Bn is the geochemical background of the metal element or world average of the metal element in shale

The constant 1.5 covers the potential variations arising from baseline data (Zhiyuan et al, 2014)

The geo-accumulation Index is a measure to assess the heavy metal intensity pollution of soil and marine ecosystems and has seven (7) classifications as follows (Birch, 2022).

Class 0 = $Igeo \leq 0$ practically uncontaminated

Class 1 = $0 < Igeo < 1$ uncontaminated to moderately contaminated

Class 2 = $1 < Igeo < 2$ moderately contaminated

Class 3 = $2 < Igeo < 3$ moderately to heavily contaminated

Class 4 = $3 < Igeo < 4$ heavily contaminated

Class 5 = $4 < Igeo < 5$ heavily to extreme contaminated

Class 6 = $5 < Igeo < 6$ extremely contaminated

Values higher than class 6, which can be higher than the background value of the metal is put in open class. The background value used in this study is adopted from the world average values in shale (mg/kg) (Edori and Kpee, 2017)

3. RESULTS AND DISCUSSIONS

The values recorded for heavy metals concentrations in soil at site are shown in Table 2.

Table 2: Soil characteristics of the illegal refinery site

Heavy metals (mg/kg)	Heavy metals content									WHO* standard
	Point 1			Point 2			Control			
	15 cm	45 cm	90 cm	15 cm	45 cm	90 cm	15 cm	45 cm	90 cm	
Pb	56.24±0.01	35.40±0.02	38.71±0.04	56.71±0.00	43.18±0.00	22.78±0.04	0.12±0.02	0.01±0.01	0.00±0.01	85
Cd	47.14±0.00	24.16±0.01	39.97±0.01	59.84±0.00	31.16±0.06	42.41±0.01	0.00±0.00	0.00±0.00	0.00±0.00	0.8
Cr	42.40±0.12	21.09±0.06	15.92±0.00	51.18±0.06	29.81±0.06	22.11±0.02	0.20±0.00	0.01±0.01	0.01±0.01	100
As	78.40±0.01	64.81±0.23	68.40±0.02	91.09±0.06	76.02±0.00	71.60±0.06	0.00±0.00	0.00±0.00	0.00±0.00	0.2
Zn	35.15±9.01	22.85±0.00	17.70±0.01	43.72±0.01	31.64±0.06	14.11±0.23	16.18±0.17	1.41±0.17	1.01±0.17	50
Cu	32.11±0.00	21.50±0.06	16.25±0.00	38.81±0.00	35.54±0.00	12.05±0.12	0.00±0.00	0.00±0.00	0.00±0.00	36
Ni	50.69±0.03	34.16±0.23	27.58±0.01	82.53±0.00	41.87±0.06	33.81±0.05	0.06±0.00	0.01±0.00	0.01±0.00	35
Co	38.06±0.00	23.90±0.17	13.32±0.02	43.26±0.01	24.72±0.23	18.32±0.02	0.04±0.00	0.00±0.00	0.00±0.00	5

Values represent mean ± SEM at n= 3 and $p \leq 0.05$; *WHO permissible limits for heavy metals in soil

All the heavy metals being investigated were found on site. Lead (Pb), has mean values of 56.24±0.01 mg/kg, 35.4±0.02 mg/kg and 38.71±0.04 mg/kg at top, middle and bottom depths (0-15 cm, 45 cm and 90 cm) respectively for sample point one, while point two has 56.71±0.0 mg/kg, 43.18±0.00 mg/kg and 22.78±0.06 mg/kg at the specified depths respectively. The above values are considerably higher than the soil got from the control site but are however within the World Health Organization (WHO) permissible limit. It was also observed that on average, the heavy metal concentration in the soil decreases as the depth increases. This is obvious as it is the ultimate first point of contact illegal refining operations. It may also be as a result of many factors like type of soil, permeability, rainwater leaching (Mohammed and Folorunsho, 2015). Cadmium (Cd) has mean values of 47.14±0.00 mg/kg, 24.16±0.01 mg/kg and 39.97±0.01 mg/kg at 15 cm, 45 cm and 90 cm depth respectively for Point one of the Site, while Point Two has 59.84±0.00 mg/kg, 31.16±0.06 mg/kg and 42.41±0.02 mg/kg at the various depths. The mean values for Chromium (Cr) are 42.4±0.12 mg/kg, 21.09±0.06 mg/kg, 15.92±0.00 mg/kg and 51.18±0.06 mg/kg, 29.81±0.06 mg/kg, 22.11±0.01 mg/kg respectively for points One and Two at the stipulated various depths and are below the WHO permissible limits, while Arsenic (As) content was 78.4±0.01 mg/kg, 64.81±0.23 mg/kg, 68.4±0.02

mg/kg and 91.09±0.06 mg/kg, 76.02±0.00 mg/kg, 71.6±0.06 mg/kg for points one and two respectively at various depths which are far above the WHO permissible limit. The mean values for Zinc (Zn) are 35.15±9.01 mg/kg, 22.85±0.00 mg/kg, 17.7±0.01 mg/kg and 43.72±0.01 mg/kg, 31.64±0.06 mg/kg, 14.11±0.23 mg/kg for points one and two at various depths respectively and are below the WHO standard, while Copper is 32.11±0.00 mg/kg, 21.5±0.06 mg/kg, 16.25±0.00 mg/kg for point one and 38.81±0.00 mg/kg, 35.54±0.00 mg/kg, 12.05±0.12 mg/kg for point two at various depths. The mean value of Cu for point two is slightly higher than the WHO standard of 35 mg/kg at 15 cm and 45 cm depth even though there was no Cu in the control soil. The mean values for Nickel (Ni) were 50.69±0.03 mg/kg, 34.16±0.23 mg/kg, 27.58±0.01 mg/kg and 82.53±0.00 mg/kg, 41.87±0.06 mg/kg, 33.81±0.05 mg/kg for points one and two at various depths respectively, however, the point one at depth 15 cm and point two at depth 15 cm and 45 cm are higher than the standard the values generally higher than the control. Cobalt (Co) has mean values of 38.06±0.00 mg/kg, 23.9±0.17 mg/kg, 13.32±0.02 mg/kg and 43.26±0.01 mg/kg, 24.72±0.23 mg/kg, 18.32±0.02 mg/kg for points one and two at various depths respectively. The values are higher than the WHO permissible limits and also higher than the control values.

The study showed that heavy metals are distributed in the soil in the following patterns and order As> Pb>Ni > Cd> Cr> Co> Zn> Cu at Site as a result of Illegal refinery activities. The highest concentrations were found in As, Pb, Ni, Cd, Cr and the lowest were Co, Zn and Cu. It also showed that as the depth in the soil increases, the concentration of the heavy metals decreases from Top < Middle <Bottom soils. This may be as a result of type of soil, soil particle size, rate of absorption, climatic/weathering conditions, geological structures and other factors. This agrees with the reports of Iwegbue, *et al*., (2006) and Ezejiofor *et al.,* (2013) in their various studies. Ogundele *et al.,* (2015) reported that from the analysis of atmospheric deposits found on top soil and dusts in cities, revealed heavy metals as contaminants which are from industries and weathered materials that ultimately affect and impact their levels in soils generally. This research results therefore conform to the impact of petroleum industries as materials like drilling muds, bentonite and other chemical materials for petroleum drilling and the illegal refinery operations influence heavy metals concentration in the soil samples which are all anthropogenic. Also, the research location is predominantly a farming area that make use of herbicides, insecticides and other agrochemicals that contain Arsenic which eventually are left in the soil. Heavy metals have been implicated in the toxic and harmful involvement of enzymatic disorder and metabolic problems in humans in low concentrations as for As, Pb, Cd, Ni, Cr and Co amongst orders, while Cu, Zn constitute essential part of the metabolism and detoxification proteins (WHO, 1996; Carpenter, 2001; Ezejiofor *et al*, 2013)

The study also made use of the average mean concentration of metals collected from the top soil of the two points; this is as a result of various authors reporting that most staple food crops like cassava grow on top soil with an average root depth of about 16.59 cm and with known facts that from this study, the pollution decreases as the soil depth increases (Gbado and Egbe-Okpenge, 2018). Table 3 shows the mean metal concentration, contamination factor and contamination/pollution index of the heavy metals from the illegal refinery site.

Table 3: Mean metal concentration, contamination factor and contamination/pollution index of heavy metals from oshika illegal refinery site

	Oshika illegal refinery site			Control	
Metals	Metal concentration (mg/kg)	Cf	C/P	Metal concentration (mg/kg)	DPR Value
Pb	56.48±0.01	0.66	0.26	0.12±0.02	85
Cd	53.49±0.00	67.00	26.00	0.04±0.00	0.8
Cr	46.79±0.12	0.47	0.18	0.20±0.00	100
As	84.75±0.01	85.00	33.00	0.08±0.00	1.0
Zn	39.44±9.01	0.28	0.11	16.18±0.17	140
Cu	35.46±0.00	0.99	0.38	0.09±0.00	36
Ni	66.61±0.03	1.90	0.74	0.06±0.00	35
Co	40.66±0.00	2.00	0.79	0.04±0.00	20
PI	2.60				

The contamination factor calculated showed that the soil was mostly contaminated with Arsenic (AS) with CF of 85, followed by Cadmium (Cd) 67, Cobalt (Co) 2.0, Nickel (Ni) 1.9, Cupper (Cu) 0.99, Lead (Pb) 0.66, Chromium (Cr) 0.47 and Zinc (Zn) 0.28. The individual heavy metal contamination factors recorded in this study are by far higher than that of Osakwe and Okoli, (2015); Nweke and Ukpai, (2016); Marcus *et al*., (2017); Edori and Kpee, (2017); Veria *et al*., (2017) and Sor *et al*., (2020) who researched from similar Niger Delta region but from different operational environment involving slight spillages, dumpsites, abattoir and agricultural lands. Relatively, the study site was heavily contaminated by Arsenic and Cadmium which are highly toxic and have been implicated in several health problems to human beings.

The pollution index from the site was calculated to be 2.6, while the individual heavy metal contamination/pollution index recorded As 33, Cd 26, Co 0.79, Ni 0.74, Cu 0.38, Pb 0.26, Cr 0.18 and Zn 0.11. Using the significance of Contamination/Pollution index in Table 1, As and Cd fell under Excessive Pollution, while Co and Ni fell under Very Severe Contamination and Severe Contamination respectively. Cu and Pb fall under Moderate Contamination, while Cr and Zn fall under Slight Contamination.

The values of geo-accumulation index of the metals from the study is recorded in Table 4. Cadmium (Cd) recorded the highest value of 6.89, followed by Arsenic (As) 2.11. Lead (Pb) and Cobalt (Co) showed calculated values of 0.91 and 0.51 respectively. Nickel (-0.61), Cupper (Cu) -0.93, Chromium (Cr) -1.53 and Zinc (Zn) 1.85. When analyzed by the classification adopted by Birch, (2022); Cd with 6.89 is placed on open class which is higher than extremely contaminated, while As with 2.11 is placed in class 3 which is moderately to heavily contaminated. Pb and Co with values of 0.91 and 0.51 respectively are placed in class1 which is uncontaminated to moderately contaminated. Ni, Cu, Cr and Zn are all placed in class 0 which is practically uncontaminated.

Table 4: Mean metal concentration and geo-accumulation index

Oshika illegal refinery site			Control	
Metals	Metal concentration (mg/kg)	Igeo	Metal concentration (mg/kg)	Background value
Pb	56.48±0.01	0.91	0.12±0.02	20
Cd	53.49±0.00	6.89	0.04±0.00	0.3
Cr	46.79±0.12	-1.53	0.20±0.00	90
As	84.75±0.01	2.11	0.08±0.00	13
Zn	39.44±9.01	-1.85	16.18±0.17	95
Cu	35.46±0.00	- 0.93	0.09±0.00	45
Ni	66.61±0.03	- 0.61	0.06±0.00	68
Co	40.66±0.00	0.51	0.04±0.00	19

All the index models used showed that the soil at the site was heavily contaminated and polluted by Cd and As while the soil indicated uncontaminated and unpolluted by Pb, Co, Ni, Cu, Cr and Zn. This finding is in agreement with Sor et al, 2020 that found that their study in selected oil bearing communities in Kogana, Rivers State was severely polluted with Cd but were uncontaminated with other metals. However, the finding of class 0 and other low pollution indices is not surprising as factors like high soil particle size, rate of absorption, climatic/weathering conditions, geological structures, rate of chemical degradation and other factors which have been found in several other studies. Another reason for low pollution indices may arise as a result of frequent remediation of the area as a result of cleanup arising from various spillages; as it has been recorded that oil spillage has been occurring from the 14 inch Okordia-Rumuekpe pipeline at Oshika community since 1983 when about 5000 barrels of oil spilled the lakes and swamp forest of the community (Muhammed, 2021) before the advent of the illegal refinery.

4. CONCLUSION

The study showed that the activities of illegal petroleum crude oil refineries increased the concentration of heavy metals in the soil which impacted negatively to the environment. The values are higher than the control and specifically increased the contamination and pollution indices of Cadmium and Arsenic which are very toxic despite all the remediation being carried out in the region. Hence there is need to discourage the activities of illegal refiners by publicizing its adverse effects and formulating a new policy of integrating them into modular refinery scheme with adequate provision of standard operation practice and guidelines, training and well standardized equipment.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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