ISSN 2350-1049

International Journal of Recent Research in Interdisciplinary Sciences (IJRRIS)
Vol. 10, Issue 1, pp: (23-30), Month: January - March 2023, Available at: www.paperpublications.org

Contamination Profile of Hydrocarbons and Heavy Metals in Soil from an Artisanal Refining Site, K-Dere South-South Nigeria

[1]Sibe, L., [2]Onwugbuta, G. C.

Biochemistry/Chemistry Technology (Option), School of Science Laboratory Technology,
PMB 5323 East-West Road, Choba, Port Harcourt, Rivers State, Nigeria.

DOI: https://doi.org/10.5281/zenodo.7721799

Published Date: 11-March-2023

Abstract: **This study aims at the assessment of heavy metals (Fe, Pb, Cd, Cr, Zn, Ni, As, and V), TPH and PAHs in soils from K-Dere artisanal refining site and Nwinua mangrove forest Kono (control site), Ogoni Rivers State. Hydrocarbons were analysed with gas chromatography; heavy metals were analysed using AAS. The study showed that there were spatial, temporal and significantly statistical variations ($P<0.05$) of TPH, total PAHs and heavy metals between study areas. Concentration of TPH peaked at 250,602mg/kg was found in intertidal soil sample where artisanal refining activities are carried out against 78.00mg/kg found in the control site in Kono. These values are well above EGASPIN target value of 1mgkg-1 in soil. The observed concentration of PAHs at the study areas varied both temporally and spatially in the soil samples analysed. The maximum mean PAHs concentration (68.85 ± 53.59mgkg^{-1}) and the lowest mean (8.50 ± 7.15mgkg^{-1}) was recorded in August and September 2018 at the artisanal refining site while the highest mean (21.99mgkg^{-1}) were recorded in May 2019 at the control site. These values are far higher than the Department of Petroleum Resources (DPR, 2002) target value for PAHs in soil 1mgkg-1 and also higher than the limit set by World Health Organization (WHO) (0.1mg/kg), thus raising concern of human exposure to cancer through food chain. High levels of heavy metals Fe (219 – 13, 234mgkg^{-1}), Pb (2.66 ± 0.39 – 3.15 ± 0.45mgkg^{-1}), Cr (BDL – 89.21mgkg^{-1}), Zn (23.00 – 111.10mgkg^{-1}), Cd (7.25 ± 1.11 – 8.06 ± 1.21mgkg^{-1}) were observed in soil samples from the artisanal refining site. These values are all indicators of pollution, and environmental degradation. Therefore, it is recommended that crops should not be planted at areas proximate to artisanal refining site as this may have effect on human through food chain. It is also recommended that artisanal refining activities in the area should be discouraged to avoid further contamination in the area.**

Keywords: **Soil, artisanal refinery, heavy metals, PAHs and TPH.**

I. INTRODUCTION

The soil an ecosystem of its own is directly affected with the discharge of wastewater containing hydrocarbons, residual crude oil spillages from source of the crude and resultant spilling of both crude oil and refined products during production and transportation. This causes various effects on both plants and microorganism that are dependent on the nutrients inherent in the soil for survival, it retards plants growth (Anoliefo et al., 1994), reduces aeration by blocking pores between soil particles hence create condition of anaerobiosis (Rossel and Tarradellas, 1991).

The term non-conventional refining plant in the context and scope of this study will be referred to as a setup which involves the use of drums and pipes fitted together and mounted on a heat source so as to heat or distil the crude oil inside the drum to a certain temperature in order to produce some petroleum products. Amangbara and Njoku (2012) described it as artisanal refining and ‘‘Kpo Fire’’ by the locals.

“Kpofire” also known as illegal refinery or makeshift refinery is a slang used to describe illegal distillation of crude oil obtained through bunkering. A business that is common in K-Dere, Ogoniland and other parts of Niger Delta region.

“Kpo-fire” is coined from the explosive sound produced when fuel is poured on the fire underneath the drums. Waste from this “kpo-fire” are been discharged into our water bodies and mainland. The waste generally consists of heavy metals, polycyclic aromatic hydrocarbons, total petroleum hydrocarbons, inorganic complexes and other non-biodegradable substances (Ferre-Huguet et al., 2009). The untreated industrial waste disposal into environment affects quality of soil and well-thought-out as detrimental for soil use (Qazilbash, et al., 2006). These pollutants not only change the quality of soil but also pose severe problems (Karthikeyan et al., 2010). There is increasing sense of global resolution concerning the environmental pollution by chemicals arrangement used in various activities. Wastewater produced from industrial treatment plant comprises significant metal pollutants. Their concentration must be condensed to levels that are conventional before being unconfined into the environment. Fast development has led to the rise of heavy metal disposal into the environment (Shipra et al., 2014). The ever-increasing activities associated with the local refining of petroleum products have inundated most environments with heavy metal, polycyclic aromatic hydrocarbons and total petroleum hydrocarbons. Pollution by these pollutants could be associated with considerable damage to the public health and environment because of their non-biodegradability, less solubility and toxicity for having carcinogenic and mutagenic effects. The contamination of heavy metals, PAHs and TPH in the soil is becoming worrisome and giving a warning signal to the world. Moreover, it is also creating avenues for debate on food security and its safety all around the globe (Al Saad et al., 2019). This study was therefore aimed at evaluating the concentration of heavy metals, PAHs and TPH from artisanal crude oil refinery (Kpo-Fire) impacted soil in K-Dere, Rivers State, South-South Nigeria.

II. MATERIAL AND METHODS

Study Area:

Bon-Ngyia is located within Bomu oilfield (Figure 1) in Kegbara Dere (N04o38`21.7” and E007o14`30.4), one of the largest and populous communities in Gokana local government Area of Ogoni land. Ogoni land is situated in South-Eastern region of Rivers State, South-South of Nigeria (Figure 1). Ogoniland covers an estimated 1,000km2 of the Niger Delta basin. According to the 2006 census, the population of the Ogonis was about 832,000 people and maybe over a million and a half presently. While in operation in Ogoni land, SPDC built 12 oilfields and drilled 116 oil wells of which about 52 is in Bomu Oilfield (K-Dere) networked to 2 flow stations (UNEP, 2011). Although oil production ceased in Ogoni in 1993, there are numerous pipelines still carrying crude across the rivers and lands of K-Dere which serve as a source of oil for artisanal refining. Hence, refinery sites are commonly located at the riverbanks, wetlands, coasts and in the mangrove zones bordering the river and creeks in the area to enable easy access to crude oil from pipelines, wellheads and well as to aid the transportation of both raw crude and refined fractions. Several artisanal refineries are located within the riverbanks of Bon-Ngyia and their potential impacts on the environment are cumulative.

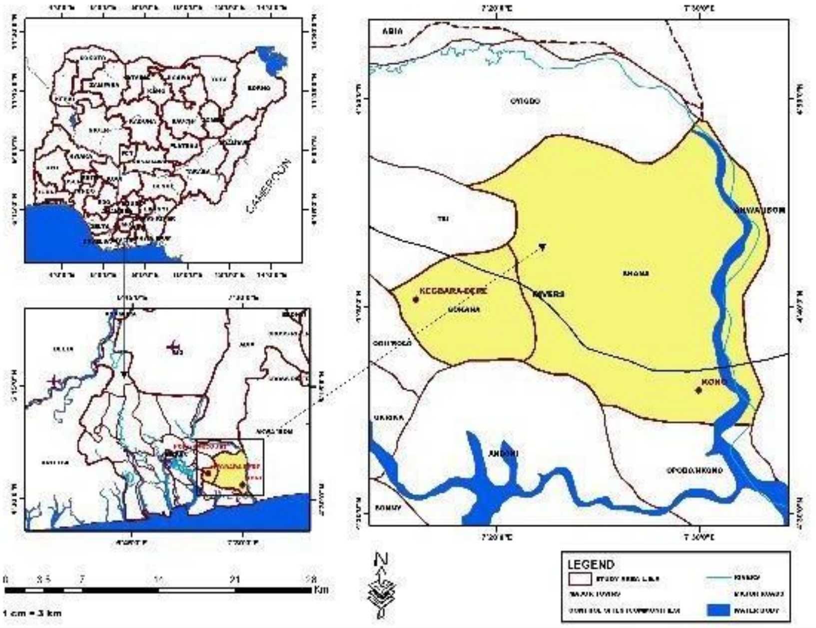

Figure 1: Map of Ogoni showing K.Dere and Kono in Ogoni Rivers State, Nigeria.

Field Study

Samples were collected from three zones at Bon- Ngyia artisanal refining site in K-Dere coastal region. Three (3) composite soil samples were collected 100m apart and at a depth of 3m i.e. from High intertidal (N04°38`21.7” and E007 °14`30.4”, N04°38`21.9” and 70 E007°14`31.8”, N04°38`26.0” and E007°14`32.7”), Mid intertidal (N04°38.331` and E007°14’54.0”, N04°38’34.1” and E007°14’56.1”, N04°38’39.5”and E007°14’56.5”) and Low Intertidal zones (N04°38’34.2” and E007°14’53.1”, N04°38’37.3” and E007°14’54.3”, N04°38’39.1” and E007°14’53.3”). Only one (1) composite soil samples were collected from each zone at Nwinua Protected Mangrove Forest in Kono, (N04°34.51.3” and E007°30’63.0”, N04°34’49.7” and E007°30’64.8”, N04°34’47.9” and E007°30’65.7” which was chosen as the control station. Both study areas (K-Dere and Kono), are located in Ogoni in Southern-Eastern Nigeria.

Sample Preparation and Analysis

Determination of Total Petroleum Hydrocarbons

10g of the soil sample was accurately weighed using a precision analytical weighing balance (Shimadzu ATY) into a clean 50ml extraction bottle. This was followed by the addition of 20-40ml dichloromethane (extraction solvent) into the bottle. The sample mixture was stirred for 2 minutes and then the extract was allowed to settle for few minutes. The extracted mixture was passed through a filter paper containing 5g of activated silica gel and 5g of sodium sulphate (Na_2SO_4) and transferred into the vial and subsequently injected into the GC for analysis. The total petroleum hydrocarbons present in intertidal soil samples were determined using a Gas Chromatograph (GC, Agilent Technologies 7890A, Auto sampler) equipped with a flame ionization detector.

Determination of Polycyclic Aromatic Hydrocarbons

10g of the soil sample was accurately weighed using a precision analytical weighing balance (Shimadzu ATY) into a clean 50ml extraction bottle. This was followed by the addition of 40ml dichloromethane (extraction solvent) into the bottle. The sample mixture was agitated by shaking for 2minutes and then the extract was allowed to settle for few minutes. The extracted mixture was passed through a filter paper containing 5g of activated silica gel and 5g of sodium sulphate (Na_2SO4) and transferred into the vial and subsequently injected into the GC for analysis. The total petroleum hydrocarbons present in intertidal soil samples were determined using a Gas Chromatograph (GC, Agilent Technologies 7890A, Auto sampler) equipped with a flame ionization detector. The samples were first extracted and diluted before analysed (where sample extract is relatively dark or thickly concentrated).

Determination of Heavy Metals

The intertidal soil samples were mixed and accurately homogenized and then dried at a temperature <60°C in an oven. Samples were brought from the oven and allowed to cool then finely ground and sieved through a 20mm/10mesh sieve. 0.5g of the soil samples were accurately weighed to the nearest milligram using a high precision weighing balance and introduced into a 125ml beaker. This was followed by the addition of 100ml distilled water, 0.5ml HNO_3 and 5ml HCl to the beaker. The digestion was finalized by heating the sample mixture on a steam bath in a well-ventilated hood until the volume was reduced to 15 to 20ml while ensuring that the sample did not boil. The solution was brought down and allowed to cool. The digested sample was then filtered with a WHATMAN filter paper and washed to remove solids and diluted with distilled water to 100ml mark. The digested sample was assayed using Atomic Absorption Spectrophotometer (AAS; SensAA GBC Scientific) atomized by using an air–acetylene flame and external standards in accordance with ASTM (1999) and US EPA (2019) analytical methods.

III. RESULTS AND DISCUSSION

Table 1 shows result obtained from the analysis of PAHs, TPH and heavy metals (Fe, Pb, Cr, Cd, Zn, Ni, As and V), in intertidal soil sample of hydrocarbon polluted environment were artisanal refining is ongoing and a control site with no evidence of illegal refining activities.

Table 1: Range and Mean Concentration (Mean±SEM; mg/kg) of Hydrocarbons and Heavy metals in Soil from two Study areas (K/Dere and Kono, Nigeria) studied July 2018-June, 2019.

Month /Year	Sampling Location	TPH	PAHs	Fe	Pb	Cr	Zn	Cd	Ni	As	V
July, 2018	K/Dere	84.00– 250600 40098.22 ± 26960	24.85 – 37.31 30.41 ± 1.38	219.00–12284 3460.22± 1533	1.30 – 5.36 2.94 ± 0.46	27.53 – 89.21 62.37 ± 6.73	27.39 – 87.54 56.12 ± 6.33	2.11 – 12.45 7.55 ± 1.27	36.74– 105.9 76.51 ± 6.82	ND	ND
	Kono	24.00 – 78.00 46.89 ± 8.34	11.05 – 33.07 21.33 ± 2.55	23.33 – 77.76 54.07 ± 6.84	ND – 0.31 0.10 ± 0.05	ND – 6.57 2.19 ± 1.09	101.00-131.0 118.89 ± 3.68	1.23 – 3.69 2.82 ± 0.27	17.15 – 34.85 24.61 ± 2.27	ND	ND
August, 2018	K/Dere	0.001– 135600 18348± 14765	0.001 – 485.00 68.85 ± 53.59	421 – 13012 4377.56± 1549	1.44 – 4.60 2.67 ± 0.34	38.62 – 88.50 62.05 ± 6.07	38.24 – 69.26 51.55 ± 3.39	2.31 – 11.18 7.25 ± 1.11	40.67 – 88.62 71.47 ± 4.53	ND	ND
	Kono	0.001 – 0.001 0.001 ± 0.00	0.001 – 0.001 0.001 ± 0.00	46.55 – 83.64 68.34 ± 5.59	0.001 – 0.20 0.07 ± 0.03	ND ND ± ND	93.11– 122.6 106.5 ± 4.31	0.04 – 3.47 1.78 ± 0.49	20.05-28.13 23.54 ± 1.19	ND	ND
September, 2018	K/Dere	ND – 19184.00 2852.44± 2102.3	ND – 65.52 8.50 ± 7.16	199.00 – 12534 3684.89±1646.4	1.30 – 5.34 2.66 ± 0.39	21.67 – 66.90 50.86 ± 4.29	22.58 –103.01 64.49 ± 8.32	1.34 – 14.06 8.06 ± 1.21	40.42 – 91.89 63.93 ± 6.02	ND	ND
	Kono	ND – ND ND ± ND	ND – 0.23 0.77 ± 0.04	30.06 – 76.03 60.52 ± 7.61	1.21 – 4.64 3.23 ± 0.52	2.86 – 8.99 4.96 ± 1.00	80.54–117.19 97.62 ± 5.28	2.90 – 7.22 4.57 ± 0.67	60.47 – 68.51 63.41 ± 1.28	ND	ND
April, 2019	K/Dere	84.00–250600.00 43939.22±27133.7	24.85 – 44.54 32.08 ± 2.12	219 – 12284 3655.78±1593.30	1.77 – 5.36 3.15 ± 0.45	33.33 – 87.82 65.04 ± 5.72	24 – 67.87 52.59 ± 4.70	2.11 – 12.45 7.56 ± 1.30	44.12–108.42 76.49 ± 6.57	ND	DN
	Kono	22 – 78 43.43 ± 7.39	10.06 – 44.54 21.99 ± 2.93	33.33 – 87.82 56.65 ± 5.95	ND – 0.33 0.11 ± 0.05	ND – 6.57 1.88 ± 0.93	101 – 138 120.67 ± 3.72	2.11 – 3.69 2.79 ± 0.17	17.15 – 42.10 25.69 ± 2.74	ND	ND
May, 2019	K/Dere	ND – 168300.00 20645 ± 1846.87	ND – 485.00 56.96 ± 53.51	454.00–8673.00 6431.67±1952.9	1.36 – 5.34 2.69 ± 0.42	38.62 – 88.50 62.54 ± 6.37	38.24 – 69.26 51.24 ± 3.04	2.78 – 11.20 7.60 ± 1.07	44.60 – 84.50 69.81 ± 4.64	ND	ND
	Kono	ND ND ± 0.00	ND ND ± 0.00	45.65 – 86.33 16.93 ± 5.64	ND – 0.40 0.15 ± 0.04	ND ND	88.40–132.20 107.45 ± 5.27	0.04 – 3.47 1.76 ± 0.41	20.05 – 28.13 23.48 ± 1.12	ND	ND
June, 2019	K/Dere	ND – 46876 6646.78± 5064.27	ND – 89.50 13.08 ± 9.59	238 – 13234 4060.5± 749.82	1.30 – 5.36 2.79 ± 0.38	22.00 – 57.20 43.90 ± 3.52	23 – 111.10 65.21 ± 8.76	1.34 – 14.06 8.05 ± 1.17	40.42 – 92.12 61.45 ± 5.67	ND	ND
	Kono	ND ND	ND – 0.23 0.03 ± 0.03	30.06 – 77.03 59.34 ± 7.21	1.21 – 5.01 2.97 ± 0.50	2.33 – 8.99 5.18 ± 0.99	34.00–117.23 89.8 ± 9.20	1.92 – 6.78 4.08 ± 0.57	45.6 – 72.10 63.15 ± 2.59	ND	ND

Heavy metals in Intertidal Soil

The results of the heavy metals in soils from the two locations or stations are shown in Table 1. The concentrations iron (Fe) in the soil of the examined stations showed spatial variation in Fe concentrations between sampling locations. In a recent study by Okon and Ogba (2018) on the impacts of crude oil exploitation on soil in Ogoni, Fe concentration was reported in the ranges of 426.11 – 6701.04mgkg^{-1} and 262.06 – 6626.11mgkg^{-1} in surface and sub-surface soils respectively. In another study conducted by Nduka and Aigberaa (2018) recorded Iron (Fe) concentration in the range of 572.71858.8mgkg^{-1} in soils from the banks of effluent retention pits. These results when compared with present study, shows that the increase in concentration of Fe in soil is aggravated by anthropogenic activities such as the activities of artisanal refining. The use of metallic stills and of iron pipes (unprotected) eventually results to rusting and corrosion of the metals. These amongst other things can increase the concentration of Iron in soils. Results from this study show that the concentration of iron (Fe) was higher in soils than in interstitial water. It is possible that the species of iron found in soil at the study sites were predominantly the water insoluble iron (III) compounds (Fe^{3+}) while the water soluble iron(II) compounds may be present in water.

The mean concentration of Lead (Pb) recorded in soils from Bon-Ngyia artisanal refining site (K/Dere) were in the range of 2.66 ± 0.39 and 3.15 ± 0.45mgkg^{-1} (Table 1) in the months of September 2018 and April 2019 respectively. However, results obtained from the control site in Kono varies both temporally and spatially with a minimum mean concentration of 0.07 ± 0.03mgkg^{-1} in August 2018 and a peak concentration of 3.23 ± 0.52 in September. The data obtained shows non-statistical significant difference ($P > 0.05$) only during the months of September, 2018 and June, 2019 between the two study areas. The results obtained in this study were within the range of values reported in soils within the Niger Delta region of Nigeria. Tanee and Albert (2013) reported the mean concentration of Pb in the range of 2.69 ± 0.74 – 6.92 ± 2.51mgkg^{-1} in soil samples taken along some major roads in Ogoni known for receiving vehicular emissions. The observed lead (Pb) concentrations (Table 1) are all below EGASPIN target (85mgkg^{-1}) and intervention (530mg/kg) values of Pb in soil and sediments. Therefore, environmental pollution due to Pb may be insignificant to impact the soil within the studied location.

The results for Cr in soil samples Bon-Gyia Artisanal refining site (K/Dere) and the control Station (Kono) are with the following ranges: not detectable (ND) – 89.21mgkg^{-1} in K/Dere and not detectable (ND) – 8.99mg/kg in Kono. The lowest and maximum mean concentrations were 43.90 ± 3.52 in June 2019 and 65.04 ± 5.72mg/kg in April 2019 at K/Dere while 5.18 ± 0.99mg/kg mean concentration was observed as the highest level of Cr at Kono. There were both temporal and spatial statistical variations in Cr levels between the two Stations. Independent sample T-test also show uniform significant statistical difference ($P < 0.05$) throughout the period of the study. Chukwuma et al (2019) in a recent study of heavy metals in a hydrocarbon polluted soil in Ogoni reported mean Chromium concentration of 143.66mg/kg and 71.50mgkg in soil from a polluted agricultural land and unpolluted land respectively. Okon and Ogba (2018) reported mean concentration of 1.70, 1.71, 1.862 and 2.16mg/kg in sub-surface soils from Khana, Gokana, Eleme and Tai Local Government Areas in Ogoni. These levels of Cr are in agreement with other results from similar studies conducted within the region. However, all the levels of Cr found in soils within Ogoni and environs are below EGASPIN intervention value for Cr in soil (380mg/kg). The observed values in this study (max. 89.21mgkg^{-1}) are below both the target value (100mgkg^{-1}) for chromium in soil for healthy functionality of living organisms (DPR, 2002). Therefore, the ecology of K/Dere and Kono may not be impacted due to chromium pollution. However, it is possible that chemical reaction such as complexation may have altered the geochemistry of the study environment and may deplete the natural background concentration of heavy metals originally in place.

Zinc concentrations reported in this study were in the range of 23.00 – 111.10mgkg^{-1} at the Artisanal refining site and 34.00 – 138mgkg^{-1} at the Control station (Table 1). The mean minimum concentration was 51.24 ± 3.04mgkg^{-1} was recorded in May, 2019 at the artisanal refining site while maximum mean value 65.21 ± 8.76mgkg^{-1} was recorded in June, 2019. The observed values at the control site was different temporally and spatially, the lowest mean zinc concentration was 89.8 ± 9.00mgkg^{-1} and a peak value of 120.67 ± 3.72mgkg^{-1} in the months of June and April, 2019 respectively. There existed significant statistically variation (T-test, $P < 0.05$) during all the months of this study except June, 2019 (T-test, P (0.07) >0.05). In a recent study, Chukwuma et al (2019) had reported 158.94 and 55.85mgkg^{-1} Zn in both polluted and unpolluted soils. Similarly, 58.89 and 58.82mgkg^{-1} Zn concentration were detected and recorded at a depth of 0 – 15cm and 15 – 30cm respectively in soil samples from an oil spill land in K/Dere (Digha *et al*, 2017). Okon and Ogba (2018) also reported mean Zinc concentrations of 27.41, 13.30, 23.82 and 8.34mgkg^{-1} in hydrocarbon polluted areas of Khana, Gokana, Eleme and Tai L.G.As of Ogoni. The observed levels of Zinc in this study and other reported studies in polluted site within Ogoni and Rivers are generally lower when compared to levels of Zn found in intertidal soil of the control site where there is no evidence of artisanal refining practices. In addition, the concentrations of Zinc (Zn) found in this study are also below the target value (140mgkg^{-1}) and intervention value (720mgkg^{-1}) set by DPR (2002). Zinc is an essential element needed by animals and plants for survival. Therefore, inadequate amount may affect the ecosystem and ultimately the survival of humans.

The mean concentrations of Cadmium (Cd) found in this study at K/Dere, Bon-Ngyia Artisanal refining site were lowest (7.25 ± 1.11mg/kg) during the month of August 2018 and highest (8.00±1.21mg/kg) in the month of September 2018. In contrast, the minimum concentration of Cd (1.76 ± 0.41mg/kg) was observed in May 2019 and peaked at September, 2018 as 4.57 ± 0.67mg/kg at the control station (Kono). Temporal variations were observed between and within the study areas. T-test statistics showed significant difference ($P < 0.05$) in sample means between Stations. The results for Cadmium obtained in this study do not deviate from the range of Cd levels commonly encountered in the Niger Delta. for example, Chukwuma et al (2019) recently recorded concentrations of 6.27 and 3.21 mg/kg in crude oil polluted agricultural land, Bodo in Ogoni and a control Station respectively. Mean concentrations of 2.13 and 1.59mg/kg Cd were reported in Khana as against 1.64 and 1.53mg/kg found in Gokana (Ogba & Okon, 2018). Results reported in relatively non-hydrocarbon polluted soil samples taken from roadsides in Eleme LGA, Rivers state showed lower levels of Cd (0.16 ± 0.01 to 0.26 ±0.04mg/kg) (Tanen & Albert, 2013). These results indicate that despite Cadmium's trace concentration in surface soils, it can be increased by anthropogenic practices such as artisanal refining. Some Cd may get into the environment from Cadmium-containing solders which are used in joining metallic pipes used in the artisanal refining stills. The levels of Cd found in this study are well above EGASPIN target value (0.8mg/kg) but below the intervention value (12mg/kg), (DPR, 2002).

The concentration of Nickel found in this study varied both temporally and spatially within and between study areas. The concentration at the artisanal refining site varied from 36.74mg/kg July 2018 to 108.42mg/kg in April 2019 with a peak mean concentration of 76.51 ± 6.82mg/kg in July, 2018. Lower levels of Ni were observed at the Control Station in the range of 17.15mg/kg – 72.10mg/kg with a peak mean value of 63.15 ± 2.59mgkg^{-1}. There was marked statistical deviation ($P < 0.05$) in sample means between sampling locations during the period of this study. A mean level of 22.70mg/kg and 17.24mgkg^{1} were reported in surface and sub-surface soils in Khana L.G.A against 17.55mg/kg and 15.18mg/kg in Gokana L.G.A. both in Ogoniland (Okon & Ogba, 2018). These values of Ni are within the target value (35mg/kg) and intervention value (210mg/kg) for nickel in soil and sediment (DPR 2002). Osuji and Onojake (2004) also observed significant levels ($P < 0.05$) of nickel in soils Ebocha – 8 oil spillage. In another study, the concentration of nickel as reported in the range of 0.15 – 1.65mg/kg with significant variation ($P < 0.05$) at surface and sub-surface levels (Osuji & Adesiyan, 2005). The results show a trend in increase in amounts of heavy metals in the environment following proliferation of artisanal refining and other related practices that releases hydrocarbon into the soil. Earlier studies show lower concentrations as against the present levels of contaminants recorded in this study.

Figure 2. Mean concentrations of heavy metals (Fe, Pb, Cr, Cd, Zn, Ni in mg/kg) in intertidal soils from Bon-Ngyia Artisanal refining site, K-Dere and a Control site, Kono in Ogoniland, Rivers State, Nigeria.

Total Petroleum Hydrocarbon in Intertidal Soil.

The observed maximum concentration of TPH in this study (250, 602mg/kg) is extremely above 63,600mg/kg reported by UNEP (2011) at Bomu Manifold site in the same community where this research was carried out. Similar study conducted in the Niger Delta area recorded spatial variation in Total Hydrocarbon Content (THC) between the artisanal refining site (1325 ± 95 to 2785 ± 57.6 mg/kg) against 175 ± 25mgkg^{-1} at the control site (Tanee and Yabrade, 2016). These values were higher when compared to the level of TPH recorded in sediment of the Aznabic creek, at the upper reaches of Bonny estuary, in the range of 5.7 – 819.5µg. The elevated TPH concentration is likely due to the direct activities of artisanal refining at the area, K/Dere. Although, environmental pollution had been reported in the area prior to this study which was eventually followed by an assessment carried by UNEP on the extent of degradation done to the environment, the report presented by UNEP was not complete since there were site-access hindrances by the locals, etc. Hence, the concentration of TPH reported in this study should not be used to quantify the levels of hydrocarbons introduced into the environment via artisanal refining; but as a record of the extent of pollution that has been aggravated by artisanal refining and its attendant practices – pipeline vandalism, etc. Although, hydrocarbons are naturally occurring, they are not expected in surface soils since they are only mined thousands of feet below the earth's surface. It therefore translates that sampling points where hydrocarbons were undetectable indicates lack of pollution by crude oil. In such points, like the high-intertidal-zones, small amount of crude oil or products disposal may not contribute significantly to hydrocarbon pollution due to steep-sloping and the constant washing by rainfall and high tidal flows. Biodegradation processes may also reduce the amount of hydrogen spilt on the environment.

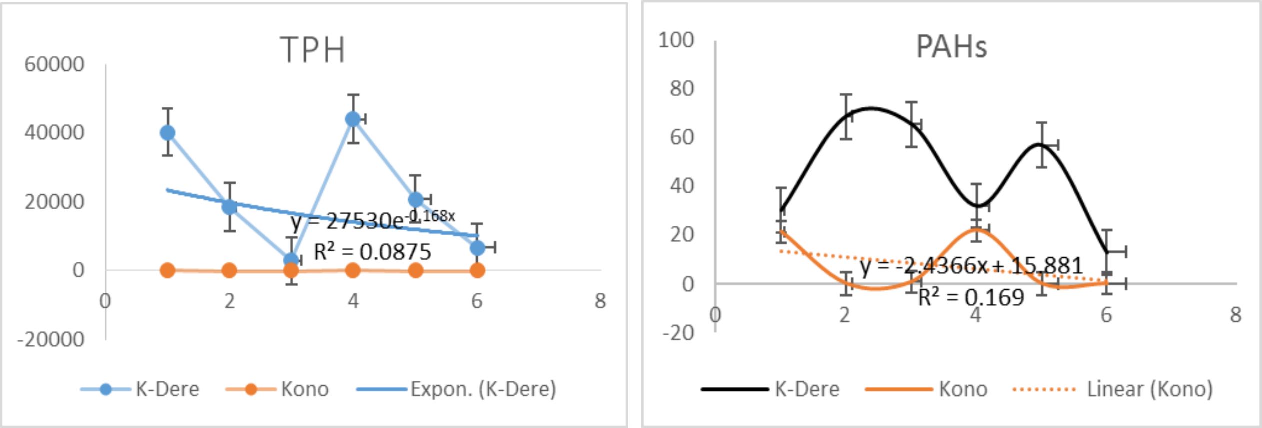

Figure 3. Mean monthly concentrations of TPH and PAHs (mg/kg) in intertidal soils (July 2018-June 2019) from Bon-Ngyia Artisanal refining site, K-Dere and a Control site, Kono in Ogoniland, Rivers State, Nigeria.

Polycyclic Aromatic Hydrocarbons in Intertidal Soil.

The observed concentrations of PAHs at the study areas varied both temporally and spatially in the soil samples analyzed. The maximum mean PAHs concentration (68.85± 53.59mgkg^{-1}) and the lowest mean (8.50 ± 7.15mgkg^{-1}) was recorded in August and September 2018 at the artisanal refining site while the highest mean (21.99mgkg-1) were recorded in May 2019 at the Control site. In an earlier study conducted by Okparanma et al (2014), lower concentrations of PAHs. (1-16-1.95mgkg^{-1}) were reported in soil samples from polluted sites in Ogoniland. The Department of Petroleum Resources (DPR, 2002) target value for PAHs in soil is 1mgkg^{-1}. It is therefore, inferred that hydrocarbon pollution in Ogoniland is pandemic. Ocean current, rivers flows can transport hydrocarbon to creeks and soils which are not receiving direct pollution from activities of artisanal refining. Oil sheens have been seen on creeks surfaces arising from boat leakages and sometimes accidental disposal or unintentional disposal due to conflicts during vandalism and occasional encounter with security operatives.

IV. CONCLUSION

Concentrations of TPH peaked at 250,602mgkg^{-1} was found in intertidal soil sample where artisanal refining activities are carried out against 78.00mgkg-1 found at the control site in Kono. In addition, PAHs peaked at 68.85 ± 53.59mgkg^{-1} as against EGASPIN target value of 1mgkg^{-1} in soil. High levels of heavy metals Fe (219 – 13, 234mgkg^{-1}), Pb (2.66 ± 0.39 – 3.15 ± 0.45mgkg^{-1}), Cr (BDL – 89.21mgkg^{-1}), Zn (23.00 – 111.10mgkg^{-1}), Cd (7.25 ± 1.11 8.06 ± 1.21mgkg^{-1}) were observed in soil samples from the artisanal refining site. These values are all indicators of pollution, and environmental degradation. Generally, there is an indication that soil quality has been extremely compromised.

REFERENCES

[1] Al Saad, M. A., Hatem, A. M. A., Hanan, A. E. E., Muhammad, N. J. & Nada, A. (2019). Estimation and bio-availability of toxic metals between soils and plants. *Polish Journal of Environmental Studies*, *28*(1), 15-24.

[2] Amangabara, G. T., & John, D.N. (2012). Assessing groundwater vulnerability to the activities of artisinal refining in Bolo and environs, Ogu/Bolo local government area, Rivers State, *Nigeria. British Journal of Environment and Climate Change*, *2*(1): 28 – 36.

[3] Anoliefo, G.O., & Nwiko, O.F. (1994). Effects of spent oil lubricating oil on the growth of *Capsicum annum.L and Lycopersiconesculatummiller* in Delta State. *Environmental Pollution, 88*, 361-374

[4] ASTM Standards (1999). Water and Environment Technology, West Conshohocken, USA.

[5] Chukwuma, C.C., Onuah, C. L., & Monanu, M.O. (2019). Human health risk assessment of heavy metals from a crude oil polluted agricultural soil in Ogoniland, Nigeria. *Brazilian Journal of Biological Science*, *6*(12), 297 - 309.

[6] Digha, O. N., Ambah, B. & Jacob, E. N. (2017). The effects of crude oil spillage on farmland in Gokana local government area of Rivers State. *European Journal of Basic and Applied Sciences, 4* (1), 1-8

[7] DPR (2002) Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) Revised Edition

[8] Ferre-Huguet, N.C., Bosch, C., Lourencetti, M., Nadal, M., Schuhmacher, J.O., & Grimalt, D.J. (2009). Human health risk assessment of environmental exposure to organochlorine compounds in the Catalan stretch of the Ebro River, Spain. *Bulletin of Environmental Contamination and Toxicology*, *83*,662-667.

[9] Karthikeyan, K., Chandran, C., Kulothungan, S. (2010). Biodegradation of oil sludge of petroleum waste from automobile service station using selected fungi. Journal of *Ecotoxicology and Environmental Monitoring*, 20, 225-230.

[10] Nduka, J. O. & Aigberua, A. O. (2018) Heavy metals and physicochemical characteristics of soils from the banks of effluent wastewater retention pits in the Niger Delta, Nigeria. *Biotechnological Research*, *4*(1), 48-53

[11] 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*, 5: e4297. https://doi.org/10.4236/oalib.1104297.

[12] Okparanma, R. N., Coulon, F. & Mouazen, A. M. (2014). Analysis of petroleum- contaminated soils by diffuse reflectance spectroscopy and sequential ultrasonic solvent extraction–gas chromatography, *Environmental Pollution*, *184*, 298-305.

[13] Osuji, L. C. & Adesiyan, S. O. (2005). Extractable hydrocarbons, nickel and vanadium contents of Ogbodo-Isiokpo oil spill polluted soils in Niger Delta, Nigeria. *Environmental Monitoring and Assessment*, *110* (1–3), 129–139.

[14] Qazilbash, A., Faryal, R., Naqvi, K., Ahmad, S., & Hameed, A. (2006). Efficacy of indigenous Bacillus species in the removal of chromium from industrial effluent. *Biotechnology*, *5*, 12-20.

[15] Rossel, D., & Tarradellas, J. (1991). Dehydrogenase activity of soil microflora, significance in ecotoxilogical test. *Environmental toxicology*, *6*, 17-21.

[16] Shipra, J., Ritu, C., & Dikshit, S. (2014). Fungal biomass as biosorbent for removal of heavy metals from industrial wastewater effluent. *Asian Journal of Plant Science*, *13* (2), 93-97.

[17] Tanee, F. B. G. & Albert, E. (2013)**.** Heavy metals contamination of roadside soils and plants along three major roads in Eleme, Rivers State of Nigeria. *Journal of Biological Sciences*, *13*(4), 264 -270.

[18] Tanee, F. B. G. & Yabrade, F. N. (2016). Assessing the impact of artisanal petroleum refining on vegetation and soil quality: A Case Study of Warri South West salt wetland of Delta State, Nigeria. *Research Journal of Environmental Toxicology*, *10*, 205.212.

[19] UNEP (2011) Environmental Assessment of Ogoniland, ISBN: 978-92-807-3130-9, Job No.: DEP/1337/GE, UNEPPup, Nairobi, Kenya.

[20] US EPA (2019). National Primary Drinking Water Regulations: Inorganic Chemicals: Chemical Contaminant Rules Summaryhttps://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Inorganic