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Impact of Hydrocarbons and Heavy Metals on Coastal Interstitial Water Quality from an Artisanal Refining Site, K-Dere Ogoni, Nigeria

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Abstract: **The existence of heavy metals, PAHs and TPH in Artisanal refinery impacted water creates significant risks to human health and the ecosystem. In this study the concentration of heavy metals (Fe, Pb, Cd, Cr, Zn, Ni, As, and V), TPH and PAHs in interstitial water from K-Dere artisanal refining site and Nwinua mangrove forest Kono (control site), in Ogoniland Rivers State were evaluated. Determination of PAHs and TPH in interstitial water was analyzed using Gas Chromatography (GC)-FID (USEPA 8015-GC/FID), heavy metals were analyzed using Atomic Absorption Spectrophotometer (AAS; SensAA GBC Scientific) in accordance with ASTM (1999) and US EPA (2019) analytical methods. The results showed that total petroleum hydrocarbon concentration (TPH) in interstitial water at K/Dere peaked at 5633mg/l against 66.00mg/lat the Control site. Statistical analysis showed no significant difference between (P>0.05) during the entire period of study. The lowest mean concentration (1341.08± 664.87mg/l) was recorded in April, 2019 and peaked in May, 2019 (1515.29 ± 803.77mg/l). PAHs analysis showed that PAHs were below detectable limit during the entire period of this study. The comparison of levels of heavy metals in water samples from K-Dere and Kono gave the following results Fe (0.01-35.34mg/l), Pb (BDL-5.30mg/l), Cr (0.02-0.78), Zn (BDL-0.80mg/l), Cd (BDL-0.30mg/l) Ni (0.01-0.65mg/l). Results for all parameters analysed were above DPR compliance limits indicating that artisanal refining operations have increased the natural background concentrations of metals at K-Dere. Based on these findings, relevant governmental and regulatory bodies in the region should collaborate with local instruments to enforce bans on activities of these Illegal artisans and introduce appropriate strategies, programmes in place to integrate them into responsible means of livelihood.**

Keywords: **Interstitial water, Artisanal refinery, heavy metals, PAHs and TPHs.**

1. INTRODUCTION

Water is an essential natural resource required for sustaining life on earth. Water on earth can be said to be enormous in quantity, with about 72% of the earth covered by it, yet, fresh potable water free from harmful heavy metals, polycyclic aromatic hydrocarbons and total petroleum hydrocarbons is not always available at the right time or the right place for human or ecosystem use (Imoobe and Okoye, 2011; Chinedu et al., 2011). Pollution of the aquatic environment is a serious and growing problem. Increasing numbers and amounts of pollutant discharged into the aquatic environment have led to various deleterious effects on aquatic organisms. Aquatic organisms, including fish, accumulate pollutants directly from contaminated water and indirectly via the food chain (Hammer, 2004; Mohammed, 2009). The contamination of aquatic resources has become a daily occurrence especially in developing nations like Nigeria where immense wastes are generated without proper waste management practices and technology to treat such wastes effectively (Howard, 2004). These wastes are basically a result of the increased rate and technology utilized in the extraction of economically valued resources such as petroleum. The processes of production, refining and marketing of these mineral resources result in the discharge of

enormous wastes, either in gaseous, liquid and/or solid forms. Waste assimilation and transportation capabilities of most environmental systems have simply been overstretched. This is as a result of the unregulated and continuous discharge of urban, agricultural and industrial wastes into these systems. Most of these wastes generated include chemical toxicants such as polyaromatic hydrocarbons (PAHs), total petroleum hydrocarbons and heavy metals, which persist in the general environment and are ultimately transported into the aquatic environment and hence, bioaccumulate in aquatic resources (Custodio et al., 2021). To add to this dilemma of improper waste management, Tanee and Yabrade (2016), Howard et al., (2007) in their various studies concluded that the unwholesome use of stolen crude oil by balkanizing crude oil facilities for pecuniary gains through the use of crude refining methods and discharge of petroleum products and crude oil into the environment with outright disregard for the safety of the environment and its host is another burden. This irresponsible act of national theft endangers not only the natural resource base of the area but also the livelihood of the natives who depend on the aquatic resources for their daily survival. It is, therefore, of immense importance to monitor, assess and safeguard the contamination of water resources through indiscriminate discharges of wastes (Avishai et al., 2002).

In K-Dere, Ogoniland and Niger Delta at large, illegal oil bunkering and artisanal refining are on the rise, worsening the environmental challenges and ecological destruction of land and surface water bodies in the region, and the social conflict caused by the oil industry. On the average, typical artisanal refinery produces about forty to sixty drums of refined products a day. Severe damage is done to the environment as a result of artisanal refining. The refining process leads to a significant quantity of wastage being dumped in rivers and streams or on land; two drums of crude oil translate into one drum of product once refined (Obenade and Amangabara, 2014). According to Ogbuagu, et al,. (2011), it has been reported that petroleum refining contributes solid, liquid and gaseous wastes in the environment. Some of these wastes could contain toxic components such as the polynuclear aromatic hydrocarbons (PAHs), which have been reported to be the real contaminants of oil and most abundant of the main hydrocarbons found in the crude oil mixture (El-Deed and Emara, 2005).

The local refining of crude oil has become a lucrative but disturbing business in the Niger Delta region of Nigeria. Deep inside the forest of the Niger Delta, camps are built and used for local refining of crude oil. The economic benefits this brings to the refiners are clear, however the host communities are severely hit by the activities of the local crude oil refiners. Rivers have been destroyed and fishing settlement evacuated as a result of pollution of the rivers and estuaries. These pollutant (PAHs, TPH and heavy metals) if found at high concentration are non-essential for the growth of plants, animals, and humans and are shown to pose potential deleterious effects on a range of aquatic organisms. They are listed in the category of carcinogenic and toxic contaminants found in aquatic ecosystems (King et al., 2007; Adeniji et al., 2019) and have adverse health effects; oral intake of PAHs and TPH through food, inhalation, and dermal interaction causes a significant risk to human health. They pose a serious threat to the health of aquatic organisms and human life through bioaccumulation within short periods of exposure (ATSDR, 2005; Olatunji et al., 2014).

A number of studies have been carried out in Niger Delta Rivers to investigate the environmental impact of artisanal refining of crude oil. However, there has not been any study targeted at the determination of heavy metals, PAHs and TPH impact of the rampant illegal oil refining activities on the water quality of K-Dere River, Rivers State. This study has become imperative due to the operations of illegal refineries in the upper reaches of the river and the surrounding creeks, where illegally acquired crude oil is refined to petroleum products.

2. MATERIALS AND METHODS

2.1 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 1,000km^2 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 over 60 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.

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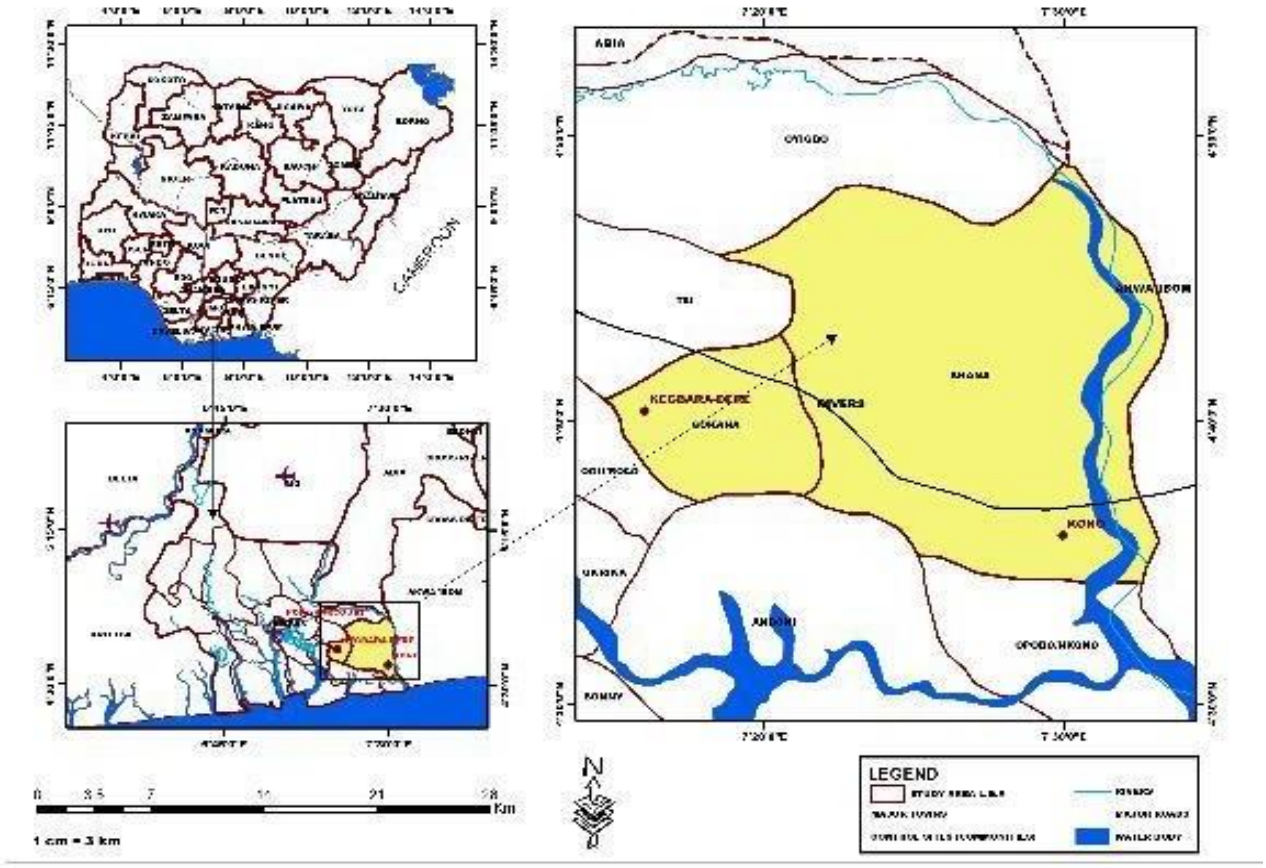

Figure 1: Map of Ogoni showing K.Dere and Kono in Ogoni Rivers State, Nigeria.

2.2 Field Study

Samples were collected from three zones at Bon- Ngyia artisanal refining site in K-Dere coastal region. Three composite interstitial water samples were collected from the respective sampling points in the different zones. Only one (1) composite interstitial water samples were collected from each zone at Nwinua Protected Mangrove Forest in Kono, (N04^{O}34.513` and E007$^{O}$30.630`, N04^{O}34.497` and E007$^{O}$30.648`, N04^{O}34.479` and E007$^{O}$30.6570`) which was chosen as the control station. Both study areas (K-Dere and Kono), are located in Ogoni in Southern Nigeria

2.3 Sample Preparation and Analysis

2.3.1 Determination of Total Petroleum Hydrocarbons (TPH).

100ml of each interstitial water sample was poured into a separatory funnel and followed by the addition of 40 - 100ml of dichloromethane. The sample mixture was shaken for about 2mins and the organic layer was allowed to separate. 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.

2.3.2 Determination of Polycyclic Aromatic Hydrocarbons (PAHs)

Extraction of PAHs in interstitial water sample was carried out by pouring 1L of the sample into a separatory funnel. This was followed by the addition of 40 - 100ml of dichloromethane. The sample mixture was shaken for about 2mins and the organic layer was allowed to separate. The extracted mixture was passed through a filter paper containing 5g of activated silica gel and 5g of sodium sulphate (Na_2SO4) and subsequently transferred into the vial for injection into the GC for analysis.

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2.3.3 Determination of Heavy metals

100ml of well-mixed interstitial water samples were measured into a 125ml beaker. 0.5ml of Concentrated Trioxonitrate (V) acid (HNO_3) was added while well-mixed and homogenized. 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.

3. RESULTS AND DISCUSSION

3.1 Total Petroleum Hydrocarbon (TPH) in Interstitial Waters

The Total Petroleum Hydrocarbon concentration (TPH) in interstitial water at K/Dere peaked at 5633mg/l against 66.00mg/lat the control site(Table 1.0). Statistical analysis showed no significant difference between ($P>0.05$) during the entire period of study.

The lowest mean concentration (1341.08 $\pm$ 664.87mg/l) was recorded in April, 2019 and peaked in May, 2019 (1515.29 $\pm$ 803.77mg/l) (Table 1.0). The observed concentrations at the artisanal refining site are within the range of TPH reported by Gijo et al., (2016) as TPH in the range of 1122.69 $\pm$ 203.02 – 1907.89 $\pm$ 85.78 at Station 6 and 3 respectively. The low TPH concentration at the control site (ND – 15.74 $\pm$ 6.64mg/l) can be attributed to drippings from boats during transportation of crude oil, refined products and spillages from upstream which may have been eventually washed down to non-artisanal refining sites by tidal flow, etc.

Notably, low levels of TPH is expected in water bodies, since heavier ends of petroleum hydrocarbons are not usually found in water due to their lipophilic and hydrophobic nature. For example, PAHs are long – chain and heavy weight hydrocarbons and are mostly bond to sediments, intertidal zones and on surfaces of phytoplanktons as well as on stems of mangrove trees.

3.2 Polycyclic Aromatic Hydrocarbons (PAHs) in Interstitial Waters.

The result from Table 1 showed that polycyclic aromatic hydrocarbons were below detectable limit in all sample of interstitial water sampled during the period of carrying out this research.

Table 1: Range, Mean ±Standard error mean (mg/L) of Hydrocarbons and Heavy metals in Interstitial waters from K/Dere and Kono (July 2018-June 2019).

	MONTH/YEAR	A	B	C	D	E	F	STD
LOCATION	PARAMATERS							
K-DERE	TPHs	0.00 - 4401 1364 ± 673	4.63 - 4814 1353 ± 666	3.89 - 4752 1364 ± 2919	0.20-4443 1341± 2874	0.00 - 5633 1515± 3368	0.00 - 4988 1484± 3210	10*
	PAHs	°BDL	°BDL	°BDL	°BDL	°BDL	°BDL	
	Fe	8.1- 34.30 23.47±3.52	10.31-31 20.34±2.33	12.21-35 22.51 ± 2.49	7.80-44 25.80 ± 4.25	11.12-32 21.72± 2.65	13.56-35 24.7± 2.8	1.0*
	Pb	0.00-3.10 1.58±0.30	0.00-0.97 0.49 ±0.11	0.51-5.30 1.68 ± 0.48	ND-3.11 1.69 ± 0.34	0.01-0.97 0.50 ±0.11	0.61-4.90 1.65± 0.43	0.05*
	Cr	0.15-0.68 0.45 ±0.67	0.07-0.46 0.26±0.04	0.07-0.52 0.24 ±0.05	0.15-0.78 0.41±0.07	0.07-0.45 0.28±0.05	0.08-0.51 0.24±0.05	0.3*
	Zn	0.08-0.45 0.19 ±0.04	0.00-0.14 0.06±0.02	0.01-0.28 0.12 ±0.03	0.09- 0.45 0.21±0.04	ND-0.80 0.16 ± 0.08	0.07- 0.22 0.11 ± 0.02	1.0*

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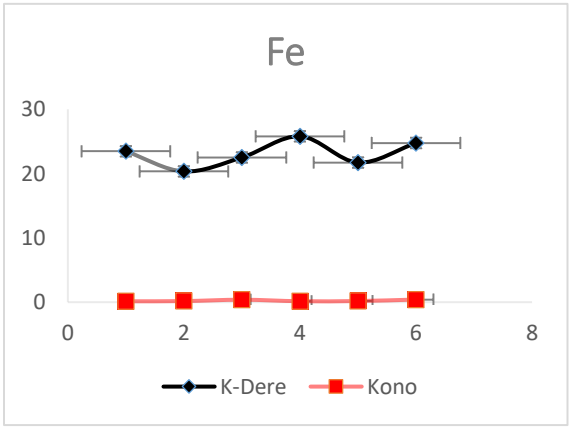
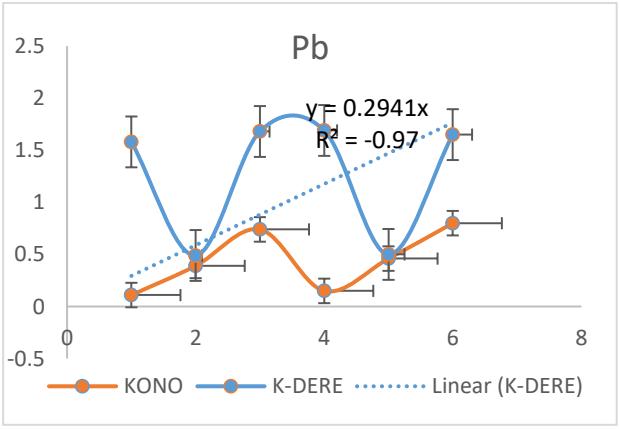
	Cd	0.11-0.22 0.17 ± 0.01	0.09 – 0.16 0.13 ± 0.01	0.07 – 0.17 0.11 ± 0.01	0.11 – 0.30 0.18 ±0.02	0.01 – 0.17 0.12 ± 0.02	0.07 – 0.2 0.11 ± 0.01	
	Ni	0.25-0.50 0.35±0.03	0.27-0.45 0.37±0.02	0.12-0.40 0.29±0.03	0.26-0.59 0.39±0.04	0.30-0.65 0.43±0.05	0.12-0.40 0.31±0.03	
	As	°BDL	°BDL	°BDL	°BDL	°BDL	°BDL	
	V	°BDL	°BDL	°BDL	°BDL	°BDL	°BDL	
KONO	**TPHs**	4.80– 16.20 8.88±1.83	0.001- 0.001 .001 ± 0.00	0.001- 0.001 0.001± 0.00	4.00 -66 15.74 ± 6.63	2.00 - 44 12.23± 22.4	2.00 - 31.00 12.13 ± 19.8	
	PAHs	BDL	BDL	BDL	BDL	BDL	BDL	
	Fe	0.10-0.22 0.14 ± 0.1	0.14-0.19 0.17 ± 0.01	0.04-0.67 0.38±0.09	0.10-0.22 0.15 ±0.02	0.12-0.22 0.18±0.01	0.04-0.67 0.41± 0.08	
	Pb	0.09 - 0.13 0.11 ± 0.00	0.08-1.01 0.39± 0.15	0.00-2.71 0.74 ±0.14	0.09-0.35 0.15 ±0.03	0.02-1.01 0.46 ±0.16	ND -2.91 0.80 ±0.20	
	Cr	0.23-0.57 0.44±0.40	0.29-0. 35 0.32±0.01	0.13-0.28 0.20± 0.02	0.23- 0.68 0.48 ± 0.05	0.22-0.44 0.33 ± 0.02	0.11-0.28 0.19 ± 0.02	
	Zn	0.07-0.17 0.11 ± 0.02	1.0 – 0.12 0.04 ± 0.02	0.10- 0.22 0.16 ± 0.02	0.02- 0.17 0.09 ± 0.02	ND – 0.13 0.07 ± 0.02	0.10-0.22 0.16 ±0.02	
	Cd	0.12- 0.13 0.13 ± 0.00	0.12-0.14 0.13 ± 0.00	0.07 – 0.12 0.10 ± 0.01	0.07-0.24 0.13 ± 0.01	0.12- 0.16 0.13 ± 0.00	0.07- 0.17 0.11 ± 0.01	
	Ni	0.37- 0.43 0.39±0.01	0.20-0.46 0.34±0.04	0.12-0.33 0.25±0.03	0.24-0.56 0.38±0.03	0.20-0.43 0.28±0.03	0.12-0.32 0.21±0.03	
	As	°BDL	°BDL	°BDL	°BDL	°BDL	°BDL	
	V	°BDL	°BDL	°BDL	°BDL	°BDL	°BDL	

- = DPR DISCHARGE LIMITATIONS FOR TREATED PETROLEUM REFINERY (FUEL OIL/GASOLINE/LUBE OIL CATEGORY) WASTE WATER

°BDL = Below Detectable Limit. STD =STANDARD/REGULATION





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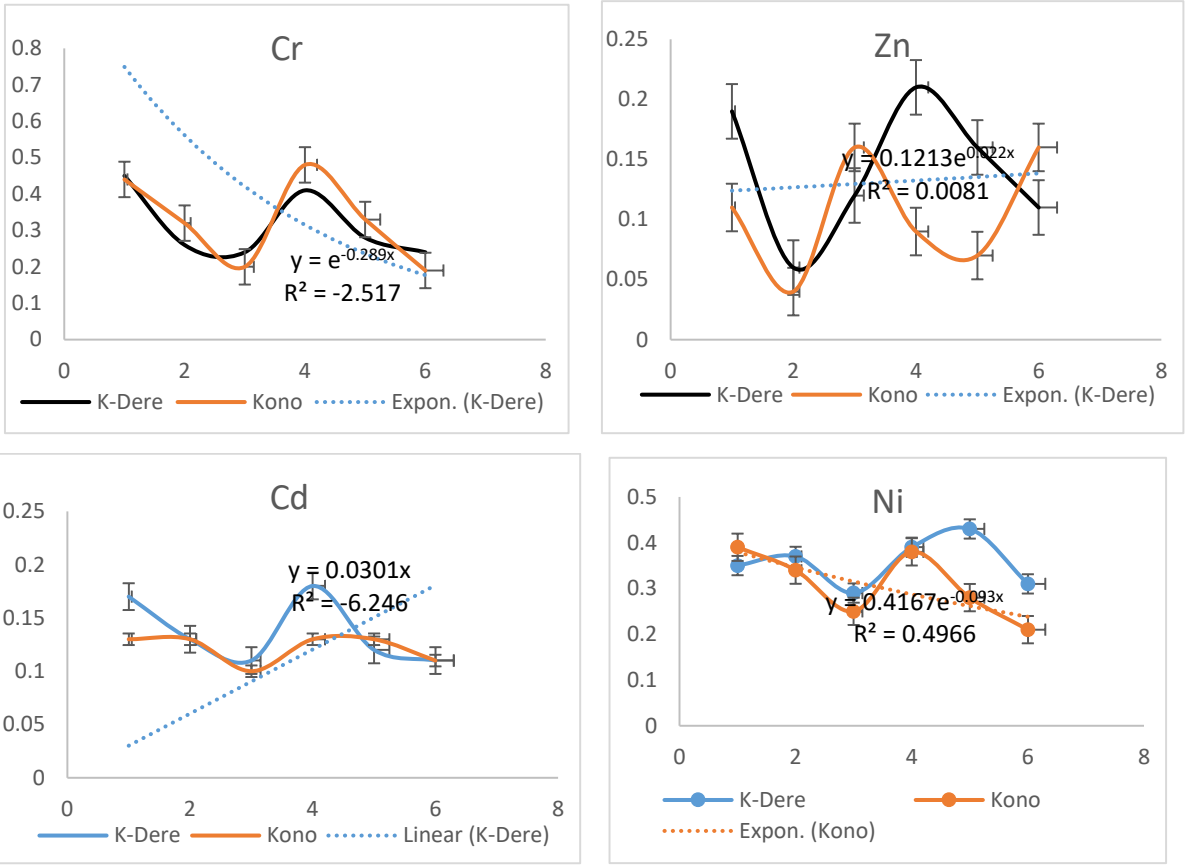

Figure 2. Mean monthly concentrations of heavy metals (mg/kg) in interstitial water (July 2018-June 2019) from Bon-Ngyia Artisanal refining site, K-Dere and a Control site, Kono in Ogoniland, Rivers State, Nigeria

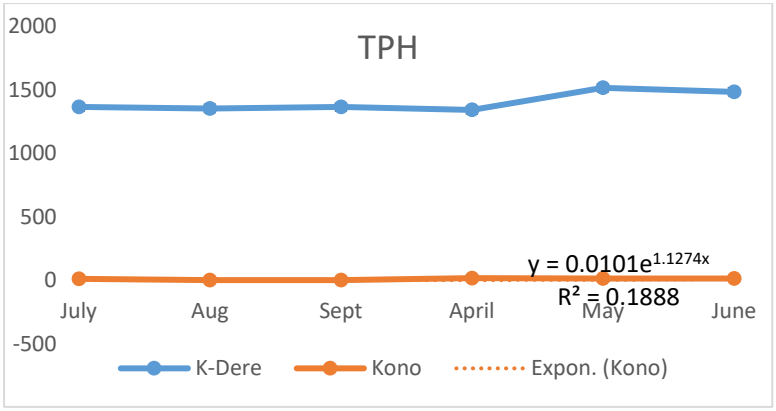

Figure 3. Mean monthly concentrations of TPH (mg/kg) in interstitial water (July 2018-June 2019) from Bon-Ngyia Artisanal refining site, K-Dere and a Control site, Kono in Ogoniland, Rivers State, Nigeria

3.3 Heavy Metals in Interstitial Waters

From Table 1.0, the heavy metals analyzed in interstitial water of the artisanal refining site and in K/Dere and the Nwinua protected mangrove forest include Fe, Pb, Cd, Cr, Zn, Ni, As and V. Arsenic (As) and Vanadium (V) were both present in undetectable (ND) amounts throughout the period of this research. The amount of Iron (Fe) in interstitial water of K/Dere Artisanal refining site and Kono Nwinua protected mangrove forest are presented in Table 1. Iron was found in the range of 7.80mgl^{-1} to 44.00mgl^{-1} in April, 2019 (25.80 $\pm$ 4.25mgl^{-1}) in K/Dere and 0.10 – 0.67mgl^{-1} (0.15 $\pm$ 0.02 and 0.41 $\pm$ 0.08mgl^{-1}) in April and June, 2019 respectively. The results showed very low levels of Fe ranging from 0.04 mgl^{-1} – 0.67 (0.41± 0.08) at Kono in June,2019. The observed concentrations of iron (Fe) in both areas of study showed a strong statistical

significance (P<0.05) when the means of the two populations were compared, during the entire period of this research. The mean concentrations of iron at the control site falls fairly within US EPA (0.20mgl^{-1}) and WHO (0.30mgl^{-1}) recommendation in surface water while the values of Fe found in interstitial water at the refining site were above both drinking, surface water limit values and DPR (1.0mg/l) discharge limitation for petroleum refineries. Although, iron (Fe) is a natural constituent of soils, it is only mostly found in low concentration water in its soluble form (Fe^{2+}) following oxidation in air (US EPA, 2001). These levels are often insignificant to impact any health impact. The observed colour of interstitial water in this study was not brown or reddish. This indicates that the concentration of Fe in water may be the nonoxidized specie (Fe^{2+}) and not the brownish oxidized specie (Fe^{3+}). This study however, was limited to assessment of metal concentration in sample matrixes and not speciation of heavy metals.

The concentration of Lead (Pb) in interstitial water analyzed during the period of this research was observed with few variations. Mean lead concentration was lowest (0.50 ± 0.11mg/l) in May, 2019 and peaked at 1.69 ± 0.34mgl^{-1} in April, 2019 at K/Dere while the minimum mean concentration (0.11 ± 0.00mgl^{-1}) at Kono was recorded in July, 2018 and the maximum in 0.80 + 0.20mgl^{-1} was recorded in June, 2019. During the study period, only two months July 2018 and April 2019 showed significant variation lead (Pb) concentration. The US EPA (1991) recommends a maximum level of 0.015mgl^{-1} in drinking water while WHO (2002) guideline puts it at 0.01mgl^{-1}. The observed levels of Pb in water at the artisanal refining site may have been introduced from the use of leaded pipe, solders, plumbeous metals, etc. in the activities of refining during construction/welding of pipes used as stills.

Mean concentration of chromium ranged from 0.24 ± 0.05mg/l in September, 2018 and June, 2019 to 0.45 ± 0.67 in July, 2018 at the refining site and ranged from 0.19 ± 0.02mgl^{-1} in June, 2019 to 0.48 ± 0.05mgl^{-1} in April, 2019 at the control site (Table 1.0). The independent sample T-test carried out showed no significant variation (P>0.05) between sample means from the two study areas. Both US EPA and WHO (2003) have a uniform provisional guideline of 0.05mgl^{-1} Cr in drinking and surface water. The observed concentrations of Cr in this study are above the regulatory limits for drinking water. The measured values of Chromium in this study may arise from soil, the crude oil and petroleum products disposed on the environment during artisanal refining. Chromium has been found and reported in crude oil samples taken from NNPC in the range of 0.48 – 0.54ppm (Khmad *et al*,2010).

The concentration of zinc analyzed in this study from both areas of study were found in the ranges of not detectable (ND) – 0.80mg/l and ND – 0.20mg/l in the interstitial waters of K/Dere artisanal refining site and Kono Nwinua protected mangrove forest respectively. The lowest mean concentration (0.06 ± 0.02mgl^{-1}) was recorded in August, 2018 at the refining site against 0.04 ± 0.02mg/l at the control site in the same month. However, the peak mean concentration(0.21±0.04mgl^{-1})attherefiningsitewasrecordedatthecontrolsiteinboth September, 2018 and June, 2019 (Table 1.0). The observed mean concentration of zinc in the study falls within the natural background concentration (<10mgl^{-1}) often encountered in natural waters (IZA, 2014) and fairly below the recommended limits of (5mgl^{-1}) in drinking water set by US EPA (1994a) and <3.0mgl^{-1} by WHO (2013).

Independent sample T-test showed no statistical significant difference (P>0.05) in all the months of this study except in April, 2019 when there was an observable significant variation (P<0.05) between study locations. This data shows that the observed levels of zinc in the environment of study may not significantly originate from anthropogenic sources but instead, zinc is present at natural background concentration in the areas of study.

MeanconcentrationofCadmium(Cd)rangedfrom0.11±0.01mg/linJune,2019to0.18±0.02mg/linApriland0.10±0.01inSeptember,2018to0.13±0.00mg/linApril,2019at K/Dere and Kono respectively (Table 1.0) T-test showed no statistical significant variation(P>0.05) in all the months of analysis except in July, 2018 when a difference in means of the sample population was observed (t (8.098 = 2.802), P (0.02)<0.05.The observed level of cadmium was high when compared to the JECFA (2000) guideline value for drinking water (0.003mgl^{-1}) but below the European Commission recommendation for Cadmium in Estuary (0.5mgl^{-1}) and DPR (0.3mg/l) discharge limitation for petroleum refinery. The observed lack of significant

variation in concentration of Cd indicated lack of major pollution byCadmium.

This research found that the concentration of Nickel in interstitial water at K/Dere ranged from0.12to0.59mgl^{-1}.Themeanconcentrationwaslowest(0.29±0.03mg/l)inSeptember, 2018 and peaked at 0.43 ± 0.05mg/l in May, 2019 at K/Dere while at Kono, Ni had a range of 0.21mg/l- 0.56mg/l with the lowest concentration of 0.21 ± 0.03mgl^{-1} which was recorded in June, 2019 and highest concentration of 0.39 ± 0.01mgl^{-1} in June 2018. There werestatistical significant difference (t (13.727) = 2.613, P (0.02) <0.05 between sample means of the two populations compared.

The WHO guideline for Nickel in drinking water is 0.07mgl^{-1}. The result obtained in this study is above this guideline but falls within limits set for Nickel in Estuaries. The observed significant levels of Nickel measured between the artisanal site and the control site shows that the presence of Nickel in the environment in the areas of study is predominantly the natural background concentration and less of anthropogenic source. There is no evidence of the use of nickel or nickel containing pipes and fittings in the artisanal refining stills that may contribute significantly to its occurrence in the areas ofstudy.

4. CONCLUSION

The interstitial water samples studied in this work were obtained from the intertidal zones of two study areas (K-Dere and Kono) and analyzed for heavy metals TPH and PAHs. Results obtained from the artisanal refining area (K-Dere) were compared to results from the control site (Kono) and with relevant recommended standards. It was observed from the data obtained that the artisanal refining environment is severely polluted by hydrocarbon. The total petroleum hydrocarbon concentration (TPH) in interstitial water at K/Dere peaked at 5633mg/l against 66.00mg/lat the control site. From the result it was observed that PAHs were below detectable limit at the period of carrying out this work. The comparison of levels of heavy metals in water samples from K-Dere and Kono gave the following results Fe (0.01-35.34mg/l), Pb (BDL-5.30mg/l), Cr (0.02-0.78), Zn (BDL-0.80mg/l), Cd (BDL-0.30mg/l) Ni (0.01-0.65mg/l) these values showed that artisanal refining operations have increased the natural background concentrations of metals at K-Dere. Generally, activities of artisanal refining have drastically impacted the environment of K-Dere.

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