Physico-Chemical Alterations of Interstitial Water Quality by Artisanal Refining Operations at K-Dere Coastal Plain, South-Eastern Nigeria

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ABSTRACT-The Physico-Chemical parameters of Interstitial water from the intertidal zone of Bon-Ngyia creek in K-Dere where artisanal refining activities involving constant disposal of both unrefined crude oil and bottom hydrocarbons fractions were investigated. In-situ measurements of some fast changing parameters, such as pH, Temperature, Conductivity, Dissolved Oxygen, Total Dissolved Solids and Turbidity in the water samples collected were immediately carried out with the aid of pH meter,/Conductivity meter/TDS meter/Turbidity meter and /DO meter respectively. BOD, Alkalinity, and Sulphates were determined using titrimetric methods while Phosphates, Nitrates and Ammonia were evaluated by Spectroscopic techniques. Results were compared with a Control study carried out at Nwinua Protected Mangrove Forest in Kono for 6 months. Temperature and pH fluctuates temporally 6.0-8.2 and 27° - 32°C respectively. TDS (1845 – 7655mgl-1) falls within the US EPA range (3000 – 10,000mgl-1) for highly saline water. EC and TDS (238 - 7885µS/cm and 1845 – 7655mgl-1) also varied temporally and spatially between study areas. Significant statistical variations ($P<0.05$) were observed in months for DO (0.25 – 2.30mgl-1) and BOD (2.97 – 8.60mgl-1). These values disagreed with 5 – 6mgl-1 DO and 4.00mgl-1 BOD for warm water biota (EPA, 1986). Alkalinity showed no significant difference ($P>0.05$) in sample means between study locations. All other parameters: Nitrates, Phosphates, and Ammonia showed temporal and spatial variations. Activities of Artisanal (illegal) refining have significantly impacted water quality in K-Dere creeks and may affect biodiversity and the survival of biota.

Index Terms: Artisanal refining, Interstitial water, Temporal, Spatial, Variation, Biota, Physico-Chemical, Significant, K-Dere, Kono

1.0 INTRODUCTION

Ogoniland represents an area covering about 1000km2 of South-Eastern region of Nigeria with a population of 850,000 people (UNPO, 2017). It is situated in the Oil-rich Niger Delta region where oil exploitation has its seat. Although Multinational drilling companies (SPDC and Chevron) seized operation in the area, some major oil pipelines containing crude such as 24-inch and 28-inch Bomu to Bonny trunk line, etc. are still passing through K-Dere. UNEP (2011) observed several defunct SPDC oil wells which are located in the Ogoniland creeks. These wells contain oil and are self-flowing such that by operating the well-valves; crude oil (along with gas and water) can be produced providing an easy source of crude oil for local Artisanal refining operation.

After several years of incompliance to the demands of the Ogoni people as enshrined in the Ogoni Bill of Right (OBR) by the Nigerian government and SPDC, the youths of Ogoniland eventually resorted to join her counterparts in the Niger Delta to engage in oil bunkering and artisanal refining operations in order to secure a living from the wealth of her natural resource. Artisanal refining is a process that describes the illegitimate distillation of crude oil in locally constructed stills. This activity has drastically aggravated the extent of environmental pollution and degradation caused by oil exploration and exploitation. The Artisanal refinery is often located on the coastline of creeks, lakes, seas, etc., thereby destroying the biodiversity and causing ecological imbalance. In Bodo West, in Bonny LGA, an increase in Artisanal refining between 2007 and 2011 has been accompanied by a 10% loss of healthy Mangrove cover, or 307,381 m2 (UNEP, 2011).

Crude oil is released into the sea, creeks during bunkering, transportation to site and during the refining operations. Bunkered oil is transported in canoe commonly with leakages allowing seepages into the river. However, the major source of hydrocarbon contamination from Artisanal refining is from accidental disposal of crude oil, refined fractions and indiscriminate storage of the heavy and bottom fractions of petroleum refining. The refinery facilities cannot process the heavier fractions such as lubricating oil and bitumen. Hence, they are usually stored or disposed of in pits around the site of the refinery. According to Attah (2012), the inefficiency of the process is so high such that it is most likely that as much as 80% of the bottom fractions of the crude oil cannot be refined and are just discharged into the environment. These are eventually washed into the sea, river or lake at high tide and are deposited at the foreshore and seabed. The intertidal zones of the tidal brackish and tidal freshwater are noted for organisms that depend on the diurnal tidal cycle (Aminayanaba *et al.*, 2013). These organisms are mainly macrofauna and may be heavily impacted by hydrocarbon exposure.

2.0 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 Ogoniland. Ogoniland 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 (UNEP, 2011). According to the 2006 census, the population of the Ogonis was

837,239 people (City population, and NPCN, 2006) and maybe over a million and a half presently. While in operation in Ogoniland, SPDC built 12 Oilfields and drilled 116 Oil wells of which about 52 is in Bomu Oilfield (K-Dere) networked to 2 flow stations. Illegal 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 inter alia trading of both raw crude and refined fractions. Bon-Ngyia serves as one of the numerous local seaports for fishermen and other sea businesses in K-Dere (Plate 1). Several Artisanal refineries are located within the coasts of Bon-Ngyia and their potential impact on the environment is cumulative.

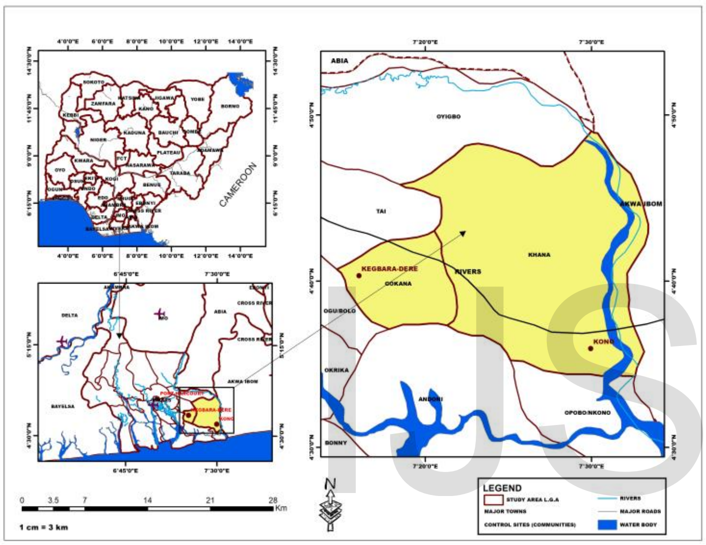

Figure. 1: Map of Ogoni showing two (2) study areas in Rivers State

Plate 1: Bon-Ngyia Local Seaports for Fishermen and Other Sea Businesses in K-Dere

2.2 Sample Collection, Preservation and Storage

Samples were collected from three intertidal zones at Bon-Ngyia Artisanal refining site in K-Dere coastal region. Three (3) samples were collected 100M apart and at a depth of 3m from high intertidal (N04o38`21.7" and E007 o14`30.4", N04o38`21.9" and E007o14`31.8", N04o38`26.0" and E007o14`32.7"), mid intertidal (N04o38.331` and E007o14.540`, N04o38.341` and E007o14.561`, N04o38. 395`and E007o14. 565`) and low intertidal zones (N04o38.342` and E007o14.531`, N04o38.373` and E007o14.543`, N04o38.391` and E007o14.533`). One (1) interstitial water sample were collected in the same manner from each zone at Nwinua Protected Mangrove Forest in Kono (N04o34.513` and E007o30.630`, N04o34.497` and E007o30.648`, N04o34.479` and E007o30.6570`) which was chosen as the control station.

All samples were taken in plastic and glass bottles, stored in an Ice Chest at 4oC and immediately transported to the laboratory for analysis. All samplings were carried out for 6 months from July 2018-June 2019.

2.3 Sample Analysis

In situ measurements were carried out using portable electronic instruments to determine the pH, Temperature, Turbidity, Electrical Conductivity (EC), Total Dissolved Solids (TDS) and Dissolved Oxygen (DO) of interstitial water samples. BOD, Alkalinity, and Sulphates were determined using titrimetric methods while Phosphates and Nitrates were evaluated by spectroscopic techniques.

3.0 RESULTS AND DISCUSSION

3.1 RESULTS

The results of physico-chemical alterations of Interstitial water from two Locations (K/Dere and Kono, Nigeria) July 2018-June 2019 are presented in Tables 1 and 2.The lowest interstitial water temperature of both the Study site and Control site is 27 oC with a peak of 32 oC and 29.17oC respectively. T-test showed statistically significant variation (P<0.05) in all months analyzed except in May 2019 when the temperature shows no statistically significant variation t (15.852) = -0.762, P(0.46) > 0.05. Also, the lowest pH value recorded at both sites is 6.0 with a peak of 8.2 and 8.0 respectively. The recorded TDS concentration at the Artisanal Refining site (K-Dere) were in the range of 1845 – 7655mgl-1 against 1258 – 5643mgl-1 recorded at the control site (Kono). T-test Statistic of TDS from the two study areas show that is statistically significant difference between sample means in all months during the study period. DO was found in the range of 25 – 2.30mgl-1 and 1.00 – 4.80mgl-1, BOD of 2.97 – 8.60mgl-1 and 2.22mgl-1 -

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4.89mgl-1, Turbidity of 10- 64.00NTU and 11.00 – 22.00NTU, Alkalinity of 16- 83mgl-1 and 19 - 54 mgl-1 of 0.60mg/l - 6.60mg/l and 0.90mg/l – 5.70mg/l, Ammonia of 0.19mg/l – 8.00mg/l at the Artisanal refining and Control Site respectively. The concentration of ammonia in interstitial water showed no significant statistical difference (P >0.05) between study areas during Sulphates of 21.00 - 87.00mgl-1 and 20-65 mgl-1, Phosphates of 0.20 - 4.00mg/l and 0.20 -3.00 mg/l, Nitrates the period of this study. Similarly, alkalinity did not any significant difference except in the months of July 2018 and June 2019 when significant differences were observed at levels of t (11.695) = -2.788, P (0.01) <0.05 and t(13.999) = -4.271, P (<0.01) <0.05 respectively.

Table 1. Range and mean concentration (Mean±SEM) of Physico-chemical alterations of Interstitial water from two Locations (K/Dere and Kono, Nigeria) July, 2018-June, 2019.

Month/ Year	Sampling Location	PH	TEMP	TDS	EC	DO	BOD
July, 2018	K/Dere	6.0 – 7.5 6.9 + 0.41	28.0 – 32 0 29.77 + 0.43	2148.00 – 4100.00 3196.00 + 272.96	1012.00 – 7885.00 5030.89 + 1033.27	0.25 – 1.95 1.14 + 0.16	3.58 – 7.88 4.89 + 0.54
	Kono	7.1 – 7.4 7.2 + 0.08	28.10 – 29.00 28.47 + 0.14	1583.00 – 1876.00 1711.00 + 43.29	3044.00 – 3608.00 3290.33 + 83.34	2.84 – 2.86 2.85 + 0.00	2.49 – 3.41 3.90 + 0.15
August, 2018	K/Dere	6.40 – 7.30 6.91 + 0.08	29.00 – 30.30 29.63 + 0.17	1845.00 – 4012.00 3135.89 + 288.98	2440.00 – 5307.00 4148.11 + 382.29	1.28 – 2.72 1.59 + 0.16	2.97 – 7.63 4.35 + 0.59
	Kono	7.20 – 7.30 7.23 + 0.02	28.80 – 29.00 28.93 + 0.03	1628.00 – 1886.00 1751.67 + 37.33	2153.00 – 2495.00 2317.00 + 49.49	3.82 – 4.80 4.17 + 0.16	2.32 – 2.58 2.45 + 0.04
September, 2018	K/Dere	6.60 – 7.30 6.94 + 0.09	29.00 – 30.20 29.58 + 0.17	2031.00 – 3985.00 3246.00 + 252.46	2687.00 – 5271.00 4293.78 + 333.92	1.13 – 1.43 1.25 + 0.04	4.00 – 7.40 5.39 + 0.47
	Kono	7.10 – 7.20 7.13 + 0.02	29.00 _ 29.30 29.17 + 0.04	1828.00 – 2033.00 1942.00 + 30.14	2418.00 – 2689.00 2568.67 + 39.84	2.34 – 2.85 2.6 + 0.07	3.00 – 3.90 3.30 + 0.15
April, 2019	K/Dere	6.70 – 7.70 7.08 + 0.12	27.00 – 31.00 29.33 + 0.50	2345.00 – 3400.00 2838.00 + 139.89	2345.00 – 7856.00 5475.00 + 700.53	0.90 – 2.30 1.76 + 0.16	3.68 – 8.60 5.73 + 0.55
	Kono	6.80 – 7.60 7.21 + 0.10	27.00 – 28.00 27.33 + 0.17	1675.00 – 2220.00 1822.44 + 53.87	2348.00 – 7654.00 4758.56 + 531.74	1.90 – 3.00 2.64 + 0.11	2.89 – 4.89 3.62 + 0.21
May, 2019	K/Dere	6.00 – 8.00 6.76 + 0.22	27.00 – 30.00 28.44 + 0.29	2134.00 – 4532.00 3426.78 + 258.58	238.00 – 7821.00 4700.44 + 820.79	0.34 – 1.88 1.20 + 0.15	3.58 – 7.89 4.96 + 0.52
	Kono	6.00 – 8.00 7.30 + 0.13	27.00 – 30.00 28.77 + 0.32	1258.00 – 2542.00 1785.56 + 139.10	2884.00 – 3608.00 3247.22 + 74.18	1.00 – 2.30 1.61 + 0.17	2.22 – 3.54 3.04 + 0.12
June, 2019	K/Dere	6.70 – 8.20 7.50 + 0.18	27.00 – 30.00 28.00 + 0.37	3245.00 – 7655.00 5766.11 + 505.71	2356.00 – 5432.00 3693.11 + 372.96	0.33 – 1.77 0.88 + 0.15	3.33 – 8.56 5.33 + 0.63
	Kono	6.50 – 7.50 6.98 + 0.09	26.00 – 28.00 27.00 + 0.24	2984.00 – 5643.00 3554.56 + 295.21	1265.00 – 3777.00 2162.33 + 299.49	1.00 – 2.20 1.72 + 0.15	2.44 – 3.99 3.32 + 0.17

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Table 2. Range and mean concentration (Mean±SEM) of Physico-chemical alterations of Interstitial water from two study areas (K/Dere and Kono, Nigeria) July 2018-June, 2019

Month/ Year	Location	Turbidity	Alkalinity	Sulphate	Phosphate	Nitrates	Ammonia
July, 2018	K/Dere	13.60–4.00 29.22+ 3.38	16.00– 4.00 30.22 + 4.86	21.00– 82.00 54.56 + 7.47	0.30 – 2.80 1.56 + 0.28	3.70 – 6.20 4.69 + 0.30	0.20 – 3.10 0.92 + 0.29
	Kono	13.60– 8.20 15.27 + 0.74	36.00–52.00 45.33 + 2.40	21.00– 33.00 28.97 + 1.99	0.20 – 1.00 0.70 + 0.13	1.40 – 5.70 3.50 + 0.62	0.10 – 4.00 1.57 + 0.61
August, 2018	K/Dere	20.60–41.80 31.00 + 2.24	18.00– 0.00 28.44 + 4.38	44.00– 81.00 65.78 + 4.24	0.52 – 2.11 1.34 + 0.19	3.10 – 4.80 3.90 + 0.19	0.20 – 1.10 0.59 + 0.09
	Kono	14.10 15.20 14.70 + 0.16	22.00–36.00 31.33 + 2.33	52.00– 56.00 54.00 + 0.58	0.25 – 0.61 0.46 + 0.05	3.10 – 3.80 3.37 + 0.11	0.20 – 1.00 0.53 + 0.12
Septem ber, 2018	K/Dere	10.00– 1.00 22.11 + 3.79	16.00– 8.00 24.67 + 3.32	28.00– 73.00 50.00 + 5.47	0.60 – 4.00 1.96 + 0.39	0.70 – 3.10 1.48 + 0.24	0.19 – 1.44 0.53 + 0.12
	Kono	11.00–14.00 12.00 + 0.50	22.00– 0.00 25.33 + 1.20	20.00– 24.00 21.67 + 0.60	0.60 – 2.10 1.43 + 0.22	0.90 – 1.50 1.13 + 0.09	0.42 – 0.69 0.53 + 0.04
April, 2019	K/Dere	15.70– 8.80 29.48 + 2.97	16.00–55.00 29.33 + 3.94	42.00– 87.00 63.44 + 4.52	0.20 – 2.10 1.49 + 0.20	3.00 – 6.60 4.92 + 0.39	0.50 – 8.00 1.62 + 0.81
	Kono	13.60–18.40 15.41 + 0.59	19.00– 54.0 39.67 + 3.79	33.00– 65.00 41.56 + 3.82	0.20 – 3.00 0.89 + 0.30	1.20 – 4.20 2.68 + 0.29	0.10 – 4.00 1.46 + 0.49
May, 2019	K/Dere	15.00– 4.00 34.03 + 4.24	22.00– 83.0 38.22 + 6.72	22.00– 76.00 53.89 + 5.76	0.67 – 4.00 1.75 + 0.33	4.00 – 5.50 4.67 + 1.92	0.70 – 2.20 1.04 + 0.15
	Kono	11.00– 2.00 14.84 + 1.32	29.00– 48.0 40.44 + 2.25	22.00– 54.00 34.33 + 3.46	000 – 2.10 1.16 + 0.23	1.70 – 5.50 2.96 + 0.43	0.10 – 2.70 0.19 + 0.30
June, 2019	K/Dere	21.00–45.00 32.22 + 3.21	21.00– 45.0 30.22 + 2.59	26.00– 76.00 55.67 + 5.39	0.80 – 3.60 1.69 + 0.29	3.90 – 5.20 4.43 + 0.17	0.60 – 1.90 0.98 + 0.14
	Kono	11.00–18.00 13.57 + 0.96	31.00– 49.0 43.56 + 1.74	22.00– 54.00 34.89 + 3.20	0.60 – 2.20 1.22 + 0.21	1.70 – 5.00 2.76 + 0.37	0.20 – 2.40 0.96 + 0.26

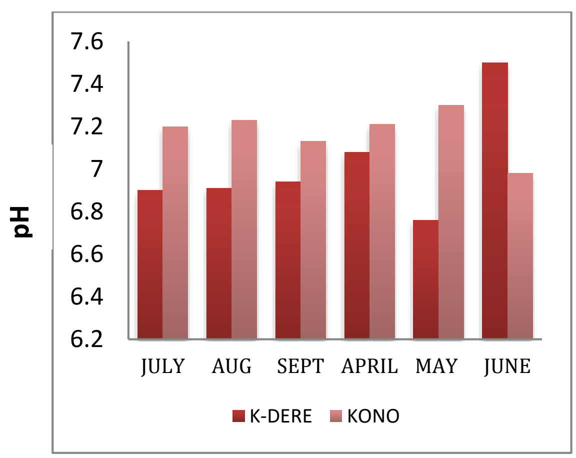
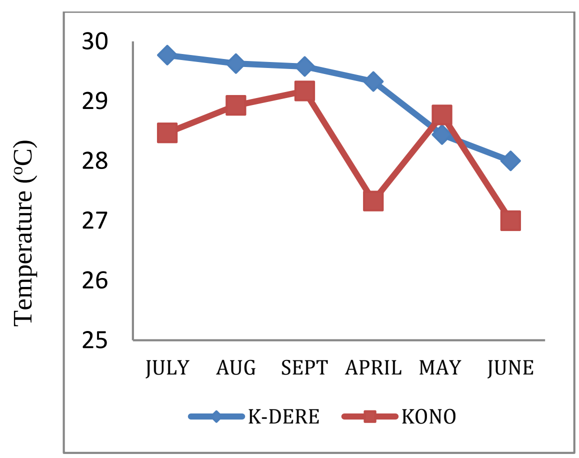


Figure 1



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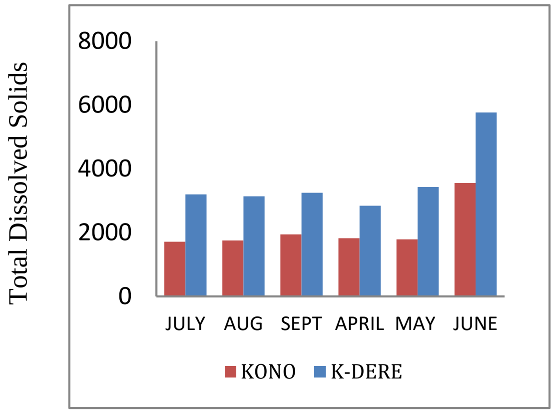

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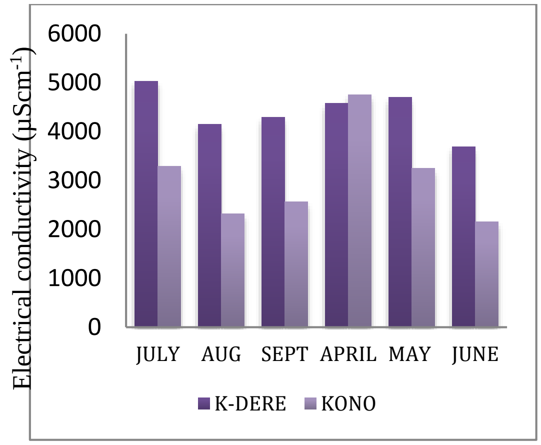

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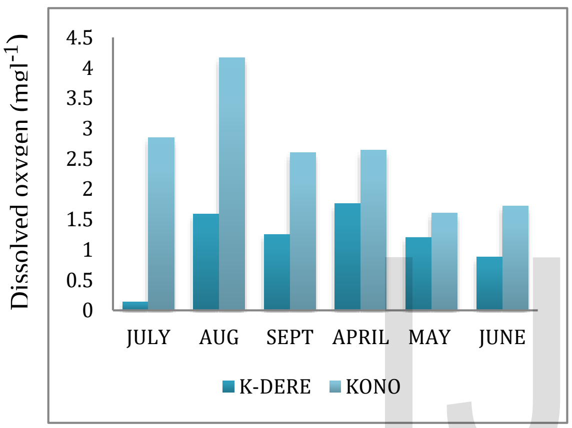

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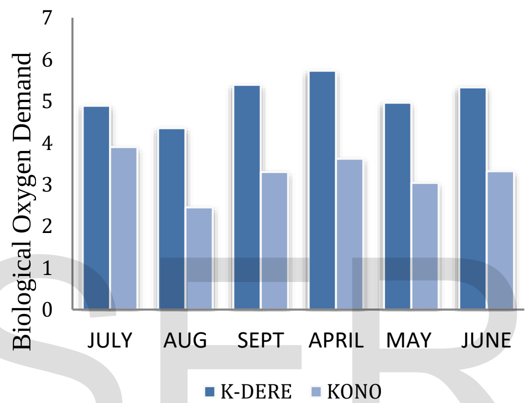

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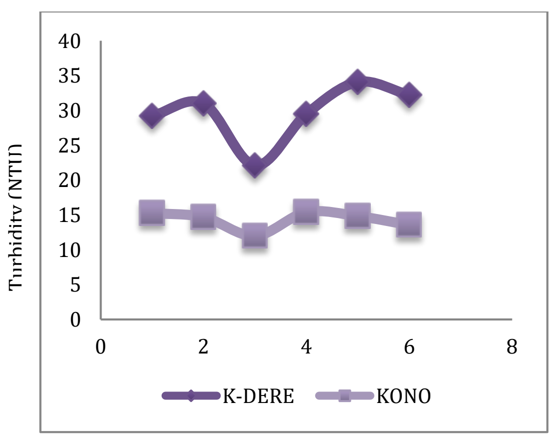

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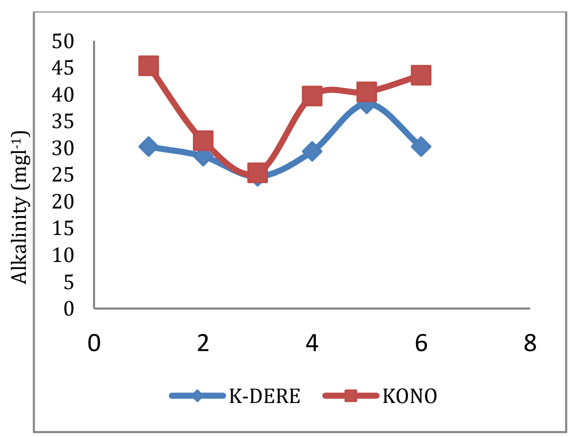

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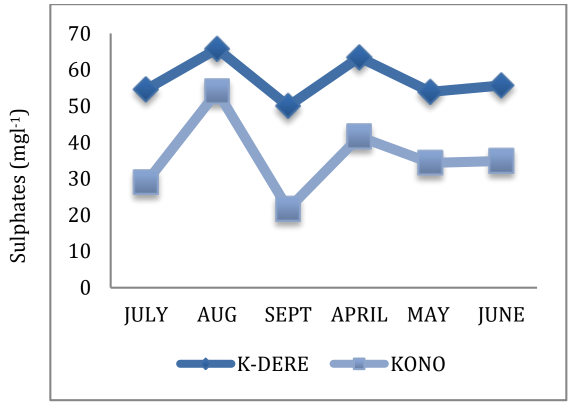

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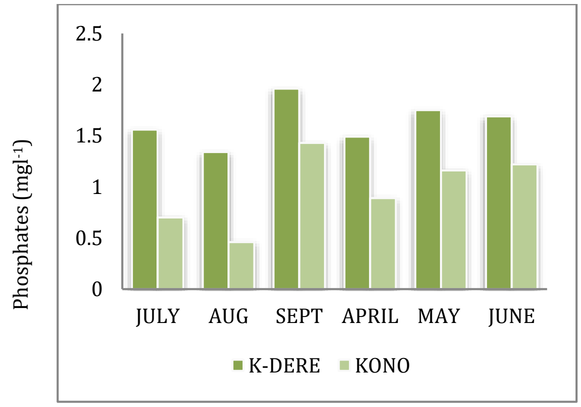

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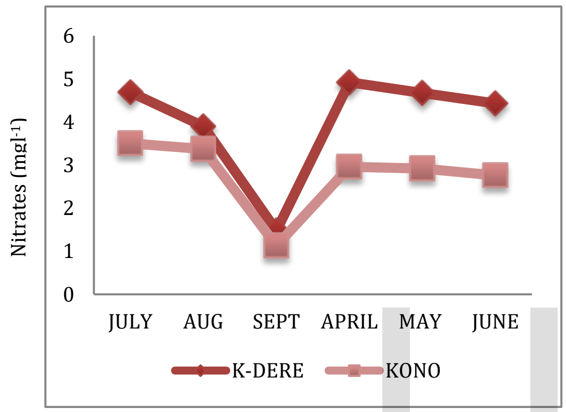

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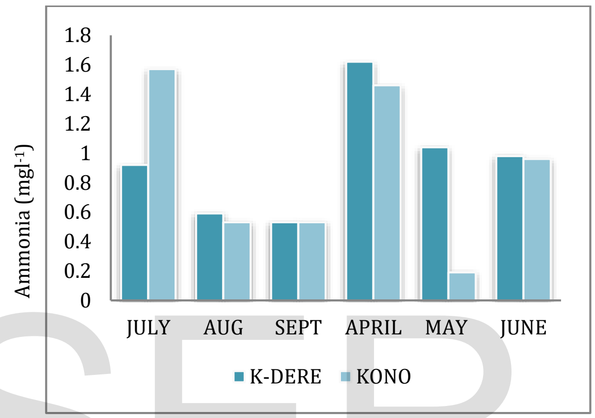

Figure 12

Figure. 1-12 Showing mean monthly physico-chemical properties of Interstitial studied at K-Dere and Kono (July 2018-June 2019), Ogoni Nigeria

3.2 DISCUSSION

This study found that the pH of interstitial water at the Artisanal refining state, K/Dere ranged from 6.0 – 8.2 while that obtained at the control site in Kono ranged from 6.0 – 8.0 (Table 4.1). Independent sample T–test carried out to compare the sample means showed statistically significant variation of pH of interstitial water during July – August, 2018 and June, 2019. However, no statistically significant variations were recorded in pH value during September, 2018, April and May 2019.During the study, the highest mean pH of was observed in May, 2019, at the Artisanal refining site and the lowest value of 6.9 in June, 2019 at the control site (Kono). The result obtained from this study falls within the acceptable range of 6.5 – 8.5 (USEPA 1986) for sea water and aquatic life survival. Similar pH range of 6.4 – 8.10 were reported in Bodo Creek, notable for Artisanal refining activities (Zabbey and Hart, 2011). However, Gijo *et al.,* (2016) reported mean pH between 5.27 and 6.56 which also agrees with a recent study by Nwankwoala *et al.,* (2017) on the impacts of Artisanal refining activities on soils and water quality in Okrika and Ogu-Bolo, Rivers State. This study reported mean pH value in the range of 5.70 – 6.50. Notably, this slight variation may be due to pollution history, incessant activities of Artisanal refining as against temporal and intermittent cessation of Artisanal refining activities in Ogoni.

Temperature

The temperature measured in interstitial water at the Artisanal refining site (K/Dere) ranged from 27.0oC – 32.0^{o}C (Figure 2) while that of the Control Site was 26.0 oC -30.0 ^{o}C (Table 1). Independent sample T-test carried out to compare the mean temperature of interstitial water at the Artisanal refining site and the control site varied significantly ($P<0.05$) in all months analyzed except in May, 2019 when the temperature shows no statistically significant variation $t(15.852) = -0.762$, $P(0.46) > 0.05$.
The highest mean temperature (29.77^{o}C) was recorded in July, 2018 and the lowest (28.00oC) was recorded in June

2019 at the Artisanal refining site while the maximum temperature of interstitial water at the control site was measured in September 2018 as 29.17^{o}C and a minimum of 27.00^{o}C. The observed drop in temperature during the early month of June, 2019 may be due to a heavy down pour experienced during that month against the high temperature already experienced in the summer of July, 2018. Also, the higher temperature values recorded at the Artisanal refining site (K/Dere) is due to direct heating of sunlight on the tidal flat as a result of death of mangrove and lack of cover. Whereby, the intertidal flat of Kono is thickly covered by fresh and shady vegetation significantly the mangrove and Nipa palm trees (figure).

The observed temperature values in this study is notably similar to those recorded by Gijo *et al.,(*2016) in the range of 28.68oC – 29.22oC in a similar study of Nun – River Estuary, and Zabbey (2011) at Bodo Creek in the range of 25 – 34^{o}C. This consistent rise in temperature at Artisanal refining sites can be attributed to constant exposure of the tidal flat cum foreshore to high temperature due to the total destruction of vegetation that could not withstand the continual exposure to heavy ends of crude oil disposed-off on the environment and eventually settling on the stems, etc, of vegetation and inhibiting normal respiratory as well as transpiration and other processes occurring in a plant's life.

Rivers State is characterized by variable and non-seasonal rainfall. Although, the heaviest down pour occurs through April – September, climate change has been known to affect the rate of precipitation. Hence, the amount of rainfall in any particular month of the year is not always constant when compared to other years. This characteristic climate of Rivers State makes the temperature of the state to be relatively constant (Wikipedia, 2019).

Total Dissolved Solids (TDS)

The results from the analysis of interstitial water at the Artisanal refining site in K/Dere showed concentration of TDS in the range of 1845 – 7655mgl-1 against the range of 1258 – 5643mgl-1 recorded at the control site (Kono) (Table 4.1). Independent sample T-test used to compare the sample means of TDS from the two study areas showed that there was statistically significant difference between sample means in all months during the study period. The highest mean TDS concentration (5766.11+ 505.71) at the Artisanal reefing site was observed during the month of June, 2019 and the lowest (2838.00 + 139.89mgl-1) was found in the month of April 2019 (Figure 3) while the maximum mean TDS level in interstitial water at Kono (3554.56 + 295.21mgl-1) was also found in June, 2019 but the minimum level (1711.00 + 43.29mgl-1) was recorded in July, 2018 (Table 1). The observed values of Total dissolved solids (TDS)in this study are well-above WHO's is and USEPA maximum contamination level of 500mgl-1 in potable water in both study areas, but falls within the range of 1000 – 3000mgl-1 as classified for moderately saline water and 3000 – 10,000mgl-1 for very saline water (USEPA, 1994 & Heath, 1983).

The amount of salts called salinity represents the TDS of fresh water (EPA, 1994) but these usually include organic solutes in contaminated and waste water. High TDS concentrations are known to cause adverse effect to aquatic life (Pasquero, 2008).

The mean concentration of TDS obtained from this study at the Artisanal refining site falls within the range of highly saline water and may affect the life and development of macrofauna. The polluted Artisanal refining site lacks the presence of natural organisms such as fauna and flora (biota). For example, the area which was natural habitat for mudskippers (Periopthalmus papilio), oysters, mud, crab, hermit crab, etc. is now like a dessert, saturated by foreign hydrocarbon substances (Plate).

Electrical Conductivity (EC)

The electrical conductivity measured during the study at the Artisanal refining site, K/Dere was recorded in the range of 238 - 7885µS/cm while that recorded at Kono is in the range of 1265 - 7654 µS/cm. The maximum mean EC of interstitial water at K/Dere was in the month of April, 2019 (5475 + 700.53 µS/cm; mean + SEM) and the lowest value for EC was observed in the month of June, 2019 (3693.11 + 372.96 µS/cm). Similarly, the maximum of (4758.56 + 531.74 µS/cm) and minimum value of 2162.33 + 299.49 µS/cm was recorded in Kono in the months of April and June, 2019 respectively (Table 1). The results show statistically significant variation in electrical conductivity for three months (August, September 2018 and June, 2019), $t(8.268) = 4.750$, $p (<0.01) <0.05$, $t(8.228) =5.130$, $P (<0.01) <0.05$ and $t(15.287) = 3.200$, $p (0.01) <0.05$ respectively while the other three months (July, 2018 and April, May 2019) showed no statistically significant variation in electrical conductivity between the two stations.

When EC value of the Artisanal refining site is compared with TDS, the concentration of TDS varies unproportionately within the month of April and June. This observation implies that the measured TDS in interstitial water at the Artisanal refining site is not a function of the ionic dissolved salts alone as obtainable in fresh water but shows the presence of soluble organic compounds introduced into the environment arising from Artisanal refining practices. The value of electrical conductivities of interstitial water reported in this study is similar to those reported by Zabbey (2011) in the range of 6980 - 44300 µS/cm at Bodo Creek, Niger Delta Nigeria. The fluctuations of the value of conductivity may also be due to temperature. EC is known to increase with increasing temperature of water (EPA, 2019).

Dissolved Oxygen (DO)

Analysis of interstitial water at the polluted site in K/Dere for Dissolved Oxygen (DO) found the concentration in the range of 0.25 – 2.30mgl-1 in the months of July, 2018 and April, 2019 respectively. While the control site at Kono ranged from 1.00 – 4.80mgl-1 in the months of May, June, 2019 and August, 2018 respectively (Table 1). T-test statistics showed significant difference (P <0.05) in DO in all the months between the two sampling locations except in the month of May, 2019 when no statistically significant difference was observed (T (15.810) = -1.804, P (0.09) >0.05. During the study period (July 2018 – June, 2019) the highest mean concentration of DO was recorded in April (1.76 + 0.16) at the polluted site and the lowest concentration (0.88 + 0.15mgl-1) was recorded in June, 2019 (Figure 4.5). This is against the result at the control site where the maximum mean concentration of DO (4.17 + 0.16mgl-1) was recorded in August, 2018 and the minimum mean value (1.61 + 0.17mgl-1) was recorded in May, 2019.

The observed Dissolved Oxygen concentration at Artisanal refinery site is below USEPA recommended concentration of 5 – 6mgl-1 for warm water biota (USEPA, 1986). Although, the DO level at the Artisanal refinery site is generally low, the higher mean concentration recorded (1.76mgl-1) may be attributed to low temperature and light precipitation encountered during sampling as against other months when samples were taken during calm whether condition. It is obvious that sensitive aquatic organisms as well as fin fishes and other interstitial organisms cannot survive long at this low concentration. Zabbey (2011) reported very low level (0.00 – 3.50) and 0.66 + 1.27 at Bodo Creek in a study carried out at Bodo which shares boundary on the south of K/Dere, the location of this present study. These represent serious level of pollution as both towns are notable for Artisanal refining activities. In a similar study, Gijo *et al.*, (2016) reported a mean concentration of 0.9 + 0.07, 0.79 + 0.15, 0.68 + 0.08, 0.42 + 0.27, 1.85 + 0.44 and 1.83 + 0.28mgl-1 DO in stations 1 – 6 respectively where studies were carried out. These low value of DO oxygen among other things is caused by heavy ends of petroleum disposed on the environment, flushed by tidal water and deposited on sediments, foreshore (figure)at the Artisanal refinery sites. This blocks pores of soils, etc. and prevents aeration as well as gaseous exchange with the surrounding.

Biological Oxygen Demand (BOD)

The amount of oxygen required by microorganisms in interstitial water studied at the Artisanal refining site ranged from 2.97 – 8.60mgl-1 recorded during the months of August, 2018 and April, 2019 respectively. In contrast, BOD measured in interstitial water at Kono ranged from 2.22mgl-1 - 4.89mgl-1 for the months May and April, 2019 respectively (Figure 4.6). From the statistical analysis there were sharp variations in Biological Oxygen Demand (BOD) levels in interstitial water of K/Dere Artisanal refining site and that of Nwinua protected mangrove forest. The observed high level of BOD at the Artisanal refining site during the month of April (8.60mgl-1) agrees with the fact that a high BOD level depletes the available dissolved oxygen (1.76 + 0.16 mgl-1, Table 1). During the period of this investigation, the BOD level measured for all samples from KONO agrees favourably with the guidelines of 4.00mgl-1 for BOD measured at 20 – 30oC (EPA, 1986) while results from the Artisanal refining site was found to be fairly above (Table 1) the standard. Zabbey and Arimoro (2017) recently studied in environmental forcing of interstitial benthic macrofauna of Bodo Creek and reported a peak BODs level of 14.64mgl-1 at station 3 during the period of the study. However, on earlier study conducted reported BODs in the range of 0.64 – 32.00mgl-1 (Zabbey and Hart, 2011). Gijo et al (2016) had reported BODs mean concentration within the range of 8.66 – 10.37mgl-1 in interstitial water of the Nun River estuary. Vincent Akpu et al (2015) observed spatial variation in BOD in the range of 13 – 19mgl-1 with a mean and standard deviation of 15 + 6, 19 + 4, and 13 + 2 in stations 1, 2 and 3 in Bodo Creek respectively.

Turbidity

Results from the analysis of turbidity of interstitial water sampled from artisanal refining site of K/Dere showed turbidity in the range of 10.00 – 64.00 NTU, in the months of September, 2018 and July, 2018 respectively with a mean and standard mean error 22.11 + 3.79 and 29.22 + 3.38 (Table 2). The highest mean Turbidity (34.03 + 4.24 NTU) was recorded in May, 2019. In contrast, the highest mean Turbidity (15.41 + 0.59) was recorded in April at the control station (Kono). The control station generally, showed low levels of Turbidity in the range of 11.00 – 22.00NTU as against 10.00 – 64.00NTU at the Artisanal refining site. The observed mean values at K/Dere are generally above the EGASPIN standard (15NTU) for the discharge of effluents and waste waters onto the environment (DPR, 2002).

The presence and ubiquity of detritus of mangrove and other dead organic matter including macrofauna may contribute sharply to the high level of turbidity of the interstitial water at the refining site.

Alkalinity ($CaCO_3$)

The levels of alkalinity of interstitial water found in interstitial water from the Artisanal refining site ranged from 16mgl-1 and peaked at 83mgl-1 in May, 2019 while the maximum concentration observed at Kono (54mgl-1) was recorded in April, 2019, the lowest mean concentration (24.67 + 3.32mgl-1) and the highest mean concentration (38.22 + 6.72mgl-1) were found in September, 2018 and May, 2019 respectively at the Artisanal site against the lowest mean concentration of 25.33 + 1.20mgl-1 and the highest mean level of 45.33 + 2.40mgl-1 observed at Kono in the month of September, 2018 and July, 2018 respectively. There were no statistically significant difference in the levels of alkalinity between the two study areas except in July, 2018 and June, 2019 when significant

differences were observed at levels of t (11.695) = -2.788, P (0.01) <0.05 and t (13.999) = -4.271, P (<0.01) <0.05 respectively. This implies that the alkalinity of the studied area during the period of study were fairly normal to neutralize any prevailing acidity of the interstitial water.
Zabbey and Francis (2017) reported fluctuations in alkalinity of interstitial water of Bodo Creek studied May 2006 – April, 2007. They reported a minimum value of 7.46mgl-1 at Station 2 with no significant statistical difference in sample means (P>0.05). The observed alkalinity values in these studies are within 30 – 90mgl-1 often encountered in fresh water and below 116mgl-1 common reported in seawater (EPA, 2006).

Sulphate

The concentration of sulphate ions (SO42-) from K/Dere ranged between 21.00mgl-1 and 87.00mgl-1 in the months of July, 2018 and April, 2019 respectively. The highest mean concentration (65.78 + 4.28mgl-1) and the lowest mean concentration (50.00 + 5.47mgl-1) were recorded during the months of August 2018 and September, 2018 respectively (Table 2). The level of Sulphate in Kono interstitial water was generally lower as a minimum mean concentration of 21.67 + 0.60 was observed in September, 2018 and this peaked at 54.00 + 0.58mgl-1 (Table 2, Figure 9) in August, 2018. Statistical significant differences (P<0.05) were observed between study areas in all months studied during the period of this research. Although the observed sulphate concentrations were below values reported in similar studies in Ogoni in the Niger Delta, they are still above the range of 3 – 30mg/l often encountered in freshwater (EPA, 2003). Recent studies on effects of Artisanal refining had reported higher concentrations of sulphate. Howard et al (2017) had reported a mean concentration of 279.8mg/kg in sediments. Gijo et al (2016) reported sulphate level in the range of 214.7mg/l – 935.87mg/l in interstitial water of the Nun River Estuary. Similarly, Zabbey (2017) reported 381.8, 484.6, 468.8 and 430.4mgl-1 in Stations 1, 2, 3 and 4 respectively. There is no available data on the geological characteristics of soil in the area of study. It can be deduced that the crude oil used in the activities of Artisanal refining in the study area may contain low sulphur which is about 0.14% (Crossroad oil, 2019).

Phosphates

The concentrations of phosphates in interstitial water at the Artisanal refining site were found in the range of 0.20mg/l - 4.00mg/l against 0.20mg/l - 3.00 mg/l at the Control site (Table 2, Figure 10). Statistically, there were insignificant differences in all months of the study except in the months of July and August 2018 when significant variations t (11.147) = 2.804, P(0.01) <0.05 and t (9.377) = 4.526, P(<0.01) <0.05 were observed in phosphate concentration respectively. Other studies conducted within Ogoni and the Niger Delta reported similar phosphate concentrations. Zabbey and Francis (2017) recorded a peak level of 0.34mgl-1 PO4 – P in interstitial water of Bodo Creek, and observed monthly non-significant difference between sampling stations P (2.56)>0.05. Gijo et al (2016) had also reported low concentrations of Phosphate in the range of 0.03mg/l - 1.65mgl-1. Phosphorous-containing compounds (PO42-) are known to get into water commonly through surface run-offs from agricultural lands (USGS, 2019). Phosphate levels 8.23 – 9.05 mgl-1 were reported by Williams and Money (2017) from a study of two Rivers in Ogoni known for receiving inorganic fertilizers input by surface run-offs.

Nitrates (NO_3^-)

Mean concentration of Nitrates (NO3-) in interstitial water of K/Dere Artisanal refining site ranged between 1.48 + 0.24mgl-1 in September, 2018 and peaked at 4.92 + 0.39mgl-1 in April, 2019, while that of Kono ranged from 1.13 + 0.09mg/l in September, 2018 to 3.50 + 0.62mgl-1 in July, 2018 (Table 4.2, Figure 4.11). During the period of study, nitrate concentrations varied significantly between study areas except in July, 2018 and September, 2018 during which no significant variations (t (11.632) = 1.719, P (0.11) >0.05 and t (10.262) = 1.318, P (0.21) >0.05) were recorded. The observed nitrate concentration in the present study, were in agreement with levels recorded in similar research within Ogoni and the Niger Delta Region. In Bodo Creek, Zabbey and Francis (2017) reported non-significant variations and low levels of nitrates between sampling stations studied. Similarly, Gijo *et al.,* (2016) reported concentration in the range of 0.12mgl-1 – 2.08mgl-1 in the interstitial water of the Nun Rivers. The observed nitrate concentrations reported in all studies within Ogoni in surface water and interstitial water falls below the EPA (2001) recommended limit values for drinking and surface water (50mgl-1).

Ammonia

The level of ammonia found in interstitial water in this study ranged from 0.19mg/l in September, 2018 – 8.00mg/l in April, 2019 at the Artisanal refining sampling with a mean and standard mean error (mean + SEM) of 0.53 + 0.12mg/l and 1.62 + 0.81mg/l respectively, while the lowest concentration was observed in the months of August and September, 2018 (0.53 + 0.12mg/l and 0.53 + 0.04mg/l) and peaked at 0.96 + 0.26mg/l in June, 2019 (Table 2, Figure 12) at the control site in Kono, Nwinua protected mangrove forest. There were no significant statistical variation in ammonia concentration when sample means of both study areas were compared (P > 0.05). The levels of ammonia found in interstitial water at both study areas (K/Dere and Kono) are above the reported level (0.2mg/l) commonly present in groundwater and surface water (WHO, 2003). However, there is currently no health based guideline for ammonia since it is often oxidized to nitrite and nitrates and thus, poses no immediate significant health impact. The presence of ammonia in interstitial water cannot be attributes to agricultural run-offs since there are no close farmlands within study areas. The habitat (intertidal zones) is constantly being washed into the Creeks by tidal flows. Hence, this level of ammonia may most significantly arise from decomposition of dead mangroves, micro and macro fauna that have been killed by noxious constituents of crude oil which is constantly being disposed into the environment as the activities of artisanal refining persists.

4.0 CONCLUSION

This study was carried out to determine the level of water quality alteration resulting from the disposal of hydrocarbon and other indiscriminate activities of artisanal refining at the coastal region of K-Dere. The study found temporal and spatial variations in water physical and chemical properties of interstitial water between study locations. Dissolved oxygen levels were generally low while nitrate levels were high which indicates that nitrogen utilizes the DO in oxidation reactions. As a result, the BOD levels at the artisanal refining site were higher than levels at the control site. Statistical significant differences observed in TDS, EC, Turbidity, etc., indicates contamination of the interstitial water at Artisanal refining site at K-Dere which may be detrimental to the survival of macrafuana.

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