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ORIGINAL RESEARCH

The Impact of Makeshift Oil Refining Activities on the Physico-Chemical Parameters of the Interstitial Water of the Nun River Estuary, Niger Delta, Nigeria

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ABSTRACT
Sampling was done in six sampling stations for one year (August, 2014- July, 2015) to investigate the impacts of makeshift oil refineries physico- chemistry of the interstitial water of the Nun River estuary of the Nun River estuary in the Niger Delta region of Nigeria after over 3 years of chronic pollution of this estuary by the makeshift refinery activities. The results of the analysis revealed that the Total Hydrocarbon Content (THC) of the estuary was exceptionally high (ranged from 632.4mg/l - 1996.5mg/l), the pH was acidic (ranged from 5.27 to 6.56), the DO was very low (ranged from 0.59 mg/l to 2.76mg/l), the BOD was high (ranged from 8.66 mg/l to 10.37 mg/l), and the sulphate, phosphate, and nitrate concentrations were high- ranging from 214.7mg/l to 935.87mg/l, 0.03mg/l to 1.65mg/l, and 0.12mg/l- 2.08mg/l, respectively. Temperature, salinity, pH, DO, BOD, SO_4, PO_3^-, NO^- exhibited significant differences between stations and between months- P< 0.5. However, THC had significant difference of between stations (P< 0.05) but no significant difference between months (P>0.05).

KEY WORDS: *Physico- chemistry, pollution, makeshift oil refineries, interstitial water.*

Introduction

The mangrove ecosystem consists of the whole complex of swamp terrain, mudflats, mangrove trees, creeks, drain canals, the invertebrate and vertebrate fauna and micro-organisms, and the interacting physico-chemical factors such as temperature, salinity, and tides associated with the system (Moses, 1985). For several decades, the Niger Delta mangrove wetland has been consistently subjected to ecological abuse as a result of crude oil exploration and exploitation, which has resulted in the reduction of habitat quality and loss of biodiversity. Pollution from crude oil especially light crude gives rise to poor water and sediment quality and is a major threat to mangroves (Hanley, 1992; Kadam, 1992; Tarn and Wong, 1995).

The water quality in an aquatic environment is very important for the survival of its flora and fauna. This is usually assessed by physico-chemical parameters such as temperature, pH, salinity, dissolved oxygen (DO), Biological (Biochemical) oxygen Demand, phosphates, sulphates, nitrates in the water, which are key parameters in many ecological studies. The quality of interstitial water has impacts on species composition, assemblages and distribution of benthos (Hart and Zabbey, 2005). Thus, the range of physico- chemical parameters in an environment is

used to detect the impacts of pollution (RPI, 1985).

The physico- chemical properties of interstitial water are very important to benthic animals and these primarily depend on the sediment characteristics (Knox, 2001). The physico-chemistry of the interstitial water and overlying water column are mutually inclusive (Sikoki and Zabbey, 2006), and there may be fluxes in the parameters across the sediment- water interface according to differential ambient conditions (Spiff and Horsfall, 2004; Zabbey, 2011).

The aim of this project was to determine the impacts of makeshift oil refining activities, including their dispersants and spills on the physico- chemical parameters of the interstitial water of the Nun River estuary, in the Niger Delta, Nigeria, in comparison with less or non- impacted locations. The specific objective of this research is to determine the levels of some physico-chemical variables of the interstitial water of the estuary on a monthly basis, as a means of ascertaining seasonal range and mean values of the system.

Materials and Methods

Description of Study Area

The study area is the Nun River Estuary in Akassa kingdom in Brass Local Government Area in Bayelsa State situated in the Niger Delta Region of Nigeria.

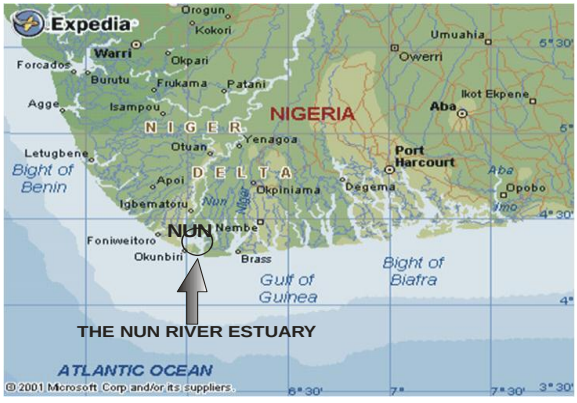

Figure 1: Map of the Niger Delta, Nigeria, showing the Nun River Estuary.

Akassa kingdom occupies an area of 120km2 and is situated on both sides of the Nun River estuary. Akassa kingdom has a population of over 280,000 people who are inhabitants of 21 major towns and several fishing settlements that make up the kingdom. The mother tongue of the Akassa people is the Izon (Ijaw) language. The Estuary is located on latitude of 40: 20" and 40: 17"N longitude of 60: 49" and 40:55"E (Knight et al., 2000). The rainy season spans from April to November, while the short dry season spans from December to March.

The Estuary is interconnected with several creaks, inlets, and canals which serve as navigational routes and drainages in the area. It is also connected to other estuaries through these channels. The Nun River estuary is bordered to the east by the Brass river estuary and to the west by the Sangana river estuary. It opens up into the Atlantic Ocean at its southern part.

Makeshift oil refineries (Kpo fire) also abound in the area. Makeshift oil refineries are local means of processing crude oil for sale in the black market. Makeshift refiners of crude oil employ indigenous technology used to distil locally made alcohol (gin or ogogoro or kaikai) to refine the crude oil into various petroleum products such as diesel and kerosene. The basic materials typically include metal pipes and drums welded together- in which crude oil is boiled and the resultant fumes are collected, cooled and condensed in tanks to be used locally for lighting, energy or transport.

The makeshift (local) oil refineries or Kpo fire have been in operation since 2011 and abated gradually early 2015. Thus the Nun River Estuary was subjected to heavy aquatic pollution from crude oil spills, which have caused severe damages to the flora (especially, mangrove) and the fauna (especially, the benthic organisms). The study area was chosen because; in spite of its vulnerability to environmental degradation, no environmental impact assessment has been done in the area, especially, on the macro benthic intertidal invertebrates.

Designation of Sampling Stations

Sampling Station 1 (Apparanbie makeshift Refinery Camp 1):

Sampling station 1 was established on one of the makeshift oil refineries in Apparanbie Creek; a tributary of the Nun River Estuary. The site is supposed to have red mangrove vegetation.

Sampling Station 2 (Apparanbie 2):

This sampling station has both red and black mangrove species and an inhabited area that is without mangrove vegetation. This area is less polluted and some macro-zoobenthos were also collected. This area was designated "impacted".

Sampling Station 3 (Apparanbia Makeshift Refinery Camp 2):

It was established on one of the makeshift oil refineries in Apparanbie Creek; a tributary of the Nun River Estuary. The

site is supposed to have red mangrove vegetation. The site is highly polluted by crude oil and mangroves are massively destroyed. The soil was completely laden with crude oil, both at the surface and absorbed by the sediments.

Sampling Station 4 (Akahapolo):

This sampling station corresponds to station 1 of the baseline study that was conducted earlier in 2010 in the same estuary. This sampling station is characterized by mangrove vegetation and a relatively short intertidal zone. The vegetation consists mainly of red mangroves.

Sampling Station 5 (Erewei- kongho):

Sampling station 5 corresponds to sampling station 2 of the baseline study that was conducted earlier in 2010 in this same estuary. This station is around Erewei- kongho community. In this station the low intertidal zone is muddy, the middle intertidal zone is a mixture of sand and clay and the high intertidal zone is sandy. This station does not have mangrove vegetation. The fringes of this station are dominated by grasses.

Sampling Station 6 (Ogbokiri):

Sampling station 6 corresponds to station 3 of the baseline study that was conducted earlier in 2010 in the Nun River estuary. The station is situated on a mud flat. It has vegetation that is dominated by the white mangroves.

Note: Only temperature, salinity, and pH were analyzed during the baseline study. The remaining parameters are compared between stations.

Field Sampling and Laboratory Analysis

Levels of nine variables were determined in interstitial water samples collected monthly at the six sampling stations for one year (August, 2014 to July, 2015). The parameters that were monitored include Salinity, Temperature, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), pH, Nitrates, Sulphates, Phosphates, and Total Hydrocarbon Content (THC). Atmospheric temperatures were measured in situ with the mercury in glass thermometer. The Salinity, Temperature, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), and pH of the water samples were measured in situ with Horiba water checker, Model U-10. The biochemical oxygen demand (BOD) was measured by measuring the dissolved oxygen (DO) in situ with the Horiba water checker, Model U-10. The same samples were fixed with 2ml Winkler's reagent in the DO bottle and taken to the laboratory and kept in the dark for five days after which the dissolved oxygen (DO) was measured again and the difference was recorded as the biochemical oxygen demand (BOD). Water Samples for the analysis of Phosphates, Sulphates and Nitrates were collected with collection bottles and taken to the laboratory for analysis. The samples for total hydrocarbon content (THC) analysis were placed in pre-labelled glass containers and sealed with aluminium foil. The samples were then transported to the central laboratory of the department of chemical sciences for analysis.

Statistical Analysis

The variations in physico- chemical parameters between stations, months and seasons were analyzed as randomized block design using the Statistical Parkage for Social Sciences (SPSS) at 95% confidence interval and means separated using Duncan's - Multiple range Test (DMRT). Significant differences were recorded. Mean separation was carried out at the 5% probability level using least significant differences (LSD) for between stations and Seasons and the New Duncan's Multiple Range Test (DNMRT) for differences between months.

Results

The results of the physico- chemical parameters of the interstitial water of the polluted Nun River Estuary are presented in Tables 1 and 2. The means and standard deviations of the physico- chemical parameters in each of the sampling stations are presented in Table 1, and while the monthly means of the physico- chemical parameters of interstitial water of the Nun River Estuary (August 2014- July, 2015) are presented in Table 2.

The outcome of the analysis of the physico- chemistry of the interstitial water of the Nun River estuary revealed that the Total Hydrocarbon Content (THC) of the estuary was exceptionally high (ranged from 632.4mg/l - 1996.5mg/l), the pH was acidic (ranged from 5.27 to 6.56), the DO was very low (ranged from 0.59 mg/l to 2.76mg/l), the BOD was high (ranged from 8.66 mg/l to 10.37 mg/l), and the sulphate, phosphate, and nitrate concentrations were high- ranging from 214.7mg/l to 935.87mg/l, 0.03mg/l to 1.65mg/l, and 0.12mg/l- 2.08mg/l, respectively. Temperature, salinity, pH, DO, BOD, SO4, PO3-, NO- exhibited significant differences between stations and between months- $P< 0.5$. However, THC had significant difference of between stations ($P< 0.05$) but no significant difference between months ($P>0.05$).

Table 1: Mean and Standard Deviation of physico- chemical parameters of the Six Stations (September, 2014- July, 2015)

PARAMETER	SAMPLING STATIONS					
	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6
Temp. (°C)	28.83±2.09[a]	28.68±2.11[a]	28.73±2.06[a]	29.05±2.45[bc]	29.22±2.43[c]	28.83±2.52[ab]
Salinity (‰)	7.865±4.29[a]	7.9±4.3[a]	7.92±4.11[a]	8.36±4.28[b]	8.55±4.2[c]	8.66±4.22[c]
pH	5.54±5.63[a]	5.47±0.13[a]	5.47±0.13[a]	6.07±0.24[b]	6.17±0.21[b]	6.25±0.21[c]
DO (mg/l)	0.9±0.07[a]	0.79±0.15[a]	0.68±0.08[a]	1.42±0.27[a]	1.85±0.44[b]	1.83±0.28[b]
BOD (mg/l)	11.19±1.41[e]	9.96±1.43[d]	11.55±1.69[f]	8.26±1.39[c]	7.72±0.66[b]	6.84±0.76[a]
THC (mg/l)	1881.79±82.33[a]	1810.43±94.36[b]	1907.89±85.78[c]	1356.8±227.06[d]	1194.58±325.3[e]	1122.69±203.02[f]
PO_3^- (mg/l)	0.06±0.02[a]	0.15±0.07[b]	0.18±0.3[c]	0.32±0.3[d]	0.4±0.39[e]	0.43±0.45[e]
SO_4 (mg/l)	366.64±120.93[a]	424.57±112.44[b]	391.06±126.90[c]	468.60±134.93[d]	519.79±149.07[e]	556.75±190.28[f]
NO^- (mg/l)	0.28±0.07[a]	0.33±0.07[a]	0.28±0.05[a]	1.35±0.46[b]	1.36±0.58[b]	1.09±0.43[b]

Keys: Temp.: Temperature; DO: Dissolved Oxygen; BOD: Biochemical Oxygen Demand; THC: Total Hydrocarbon Content; mg/l: Milligrams per litre; ‰: Parts per thousand; °C: Degrees Celsius; PO_3^-: Phosphates; SO_4: Sulphates; NO^-: Nitrates

Table 2: Monthly mean of physico- chemical parameters of interstitial water of the Nun River Estuary (August 2014- July, 2015)

Month/ Year	Temperature (°C)	Salinity (‰)	pH	DO (mg/l)	BOD (mg/l)	THC (mg/l)	PO_3^- (mg/l)	SO_4 (mg/l)	NO^- (mg/l)
Aug	25.98	6.52	5.71	1.33	10.37	1766.74	0.69	343.12	0.63
Sept	25.1	0.36	5.82	1.44	9.08	1720.72	0.61	268.11	0.69
Oct.	29.2	1.29	5.85	1.41	10.1	1588.97	0.16	333.78	0.78
Nov	30.28	5.52	5.73	1.3	8.67	1629.28	0.17	470.43	0.91
Dec.	30.4	9.27	5.76	1.12	8.74	1579.67	0.17	567.42	1.01
Jan	28.32	11.71	5.84	1.12	8.95	1532.95	0.17	573.08	0.88
Feb	31.5	12.67	5.9	0.93	8.97	1453.76	0.18	677.8	0.99
Mar	31.08	12.83	5.81	1.16	9.12	1546.46	0.16	613.98	0.85
Apr.	31.23	12.36	5.92	1.18	9.24	1428.38	0.12	494.38	0.84
May	29.59	10.3	6.03	1.22	8.66	1499.03	0.11	405.12	0.64
June	27.95	8.59	5.93	1.31	10.08	1438.87	0.29	374.41	0.73
July	26.02	7.13	5.95	1.42	9.31	1363.55	0.28	333.23	0.45

Discussion

Temperature

The temperature of the interstitial water of the Nun River estuary ranged from 28.68°C- 29.22°C during the current study while that of the baseline study ranged from 27.8°C-31.9°C. The results obtained in this study corroborates with the results of other studies that were conducted in the Niger Delta, Nigeria. Temperatures between 28°C and 30°C have been reported in the lower Bonny estuary by Aleleye-Wokoma and Hart (1999). Zabbey *et al.* (2002) recorded temperatures between 25.8- 30.4 °C of subsurface water in Woji creek in Rivers state, Nigeria. Also, Zabbey (2011) recorded temperatures between 25- 33°C in Bodo in the Niger Delta, Nigeria. Eremasi *et al.,* (2015), also reported temperature values between 27.75 °C and 31.7°C in Kolo Creek, Imiringi, Bayelsa State. Davies *et al.*, 2006, also reported that the temperature ranged between 28 and 31.5°C. Furthermore, Okon (2005) also recorded mean temperature values ranging from 22.5°C to 29.0°C.

The results revealed the mean temperatures varied both spatially and temporally. Spatially, station 5 (which corresponds to station 2 in the baseline study) had the highest mean Temperature (29.22°C) while the lowest mean temperature (28.68°C) was recorded in station 2 (Table 1). Station 5 along with 6 (which corresponds to stations 2 and 3 in the baseline study) had the highest temperature of 29.7°C during the baseline study too. Thus, the results indicated that the temperature of this station remained unchanged even

after exposure to frequent crude oil pollution. The mean temperature that was recorded in station 4 (which corresponds to station 1 in the baseline study) during this current study was 29.05^{o}C against 29.98^{o}C that was recorded during the baseline study. Station 6 (previously, station 3) had mean temperature of 28.83^{o}C, which was lower than the temperature of the baseline study (29.67^{o}C). The results obtained during this study corroborates with temperature values reported by other researches in the Niger Delta. Woke (2004), also reported that mean values of temperature varied from one station to another. Davies *et al.* (2006) also reported that the temperature values varied between the four stations that were sampled. Zabbey (2011), also reported that mean temperatures varied significantly (AVOVA= 3.57> P) throughout the study between stations. Temporally, the temperature of the interstitial water was higher in the dry season than the rainy season. The highest mean value of temperature (31.5^{o}C) of the interstitial was recorded in February, 2015 while the lowest mean (25.1^{o}C) was recorded in September, 2014. The one year monthly temperatures are in conformity with the seasonal pattern in the Niger Delta. Frequent rainfall characterizes the Niger Delta, creating a long rainy season from March to November which is usually broken by a short spell of dry period known as August break (Odokuma and Okpokwasili, 1996). Beginning from August, 2014, the temperature of the Nun river estuary generally declined from 25.98^{o}C to 25.1^{o}C in September (the lowest mean temperature), during which rainfall is usually at its peak. The temperature of the interstitial water gradually and progressively increased from October to December, 2014 (dry season) and declined a bit in January, 2015 and got to its peak in February, 2015 and remained high till April, 2015. The temperature values declined in May, 2015, and continued to decline from June, 2015 to August, 2015 (rainy season), during which the research was concluded. The least temperature was recorded in September, 2014 (the peak of the rainy season). The current study of the interstitial water of the Nun River estuary had its lowest temperature in September, 2014, while the highest temperature was recorded in February, 2015, similar to the results of the baseline study that was conducted earlier in this estuary. During the baseline study conducted by Gijo (2011), the lowest mean temperature (20.5^{o}C) was recorded in September, 2009 (rainy season) as well while the highest mean temperature (30^{o}C) was, however, recorded in January, 2010 (dry season). This progressive decline in temperature of water bodies agrees with similar studies conducted in the Niger Delta. Zabbey (2011), also recorded temporal differences in temperature, during his study of community ecology of intertidal macro zoobenthos at Bodo Creek, Nigeria. Moslen *et al.*, 2006 reported that the surface temperature ranged from 26- 30^{o}C and that there were minimal variations in temperature from September to January, while the highest temperature values were recorded in February at all sites. Similarly, Okon (2005) recorded the lowest mean temperature value (22.5^{o}C) in June, 2001 (rainy season) while the highest mean temperature of his study (29.0^{o}C) was recorded in February, 2001 (dry season). The high temperature values recorded in the dry season are expected since the heat from the sun can increase the temperature of the interstitial water. Eremasi *et al.,* (2015), also reported that Temperature showed significant differences between the wet and dry seasons. Alagoa (2012) also observed similar reduction in temperature in Taylor creek during the rainy season.

Salinity

The salinity of the interstitial water of the Nun River estuary that was recorded during this study varied a little from the baseline study in concentration, spatially, and temporally. Salinity was at its peak (12.83%o) in March, 2015 while the lowest mean value (0.36%o) was recorded in September, 2014. During the baseline study, the highest mean value of salinity was 9.25%o (against 12.83%o that was recorded in the current study) and this was recorded in January (instead of March, as in the current study). On the other hand, the lowest mean value of salinity that was recorded during the baseline study was 0.19%o (Lesser than 0.36%o that was recorded during the current study) and this was recorded in September just like this current study. The differences recorded during this current study could be as a result of differences in the dilution by rain and the concentration by evaporation between the time period of the baseline study and that of the current study. Knox (2001) reported the salinity of interstitial water as representing a balancing between the overlying seawater and fresh water seeping out from the land. Furthermore, he also stressed that salinity variations are greatest on tidal flats due to dilution by rain and concentration by evaporation. There was significant

variation in salinity in each of the months throughout the duration of the study and among the different sampling stations. Station 1 had the lowest mean salinity (0.26±1.09%o) in September and the highest mean (13.1±0.15%o) was recorded in station 6 in March, 2015. Unlike the baseline study, there was a progressive increase in salinity from station 1 to station 6 (from the upper reaches down to the lower reaches) during this current study in almost all the months.

The results of the current study corroborates with the usual situation of estuarine waters whereby salt concentration increases downstream due to the flow of oceanic waters and the decreasing influence of river and run off derived from fresh water sources. Zabbey (2011), during his study, however, reported that the salinity gradient of the mudflats deviated from this usual situation (the increase in salt concentration downstream), just like the baseline study. However, Ogbeibu and Oribhabor (2008) monitored salinity in Buguma Creek and noted significant spatial trend. Snowden and Ekeozor (1990) also reported that the annual mean salinity increased rapidly down the estuary from Iwofe (7.5%o) to Port Harcourt (21%o), but only gradually over the remaining 40km to the mouth at Bonny (26%o). They further reported that salinity was higher during the dry season (December to February) than during the rainy season (April to November). Moslen *et al.* (2006) reported that there were clear patterns of salinity spatially and temporally. They further reported that salinity increased from one of the stations (station OA) to another (OD) in the Obufe creek and then from another (AA) to yet another (AD) at the Azuabie creek. Furthermore, Davies *et al.* (2006) reported that the salinity of the creek ranged between 14.5 %o and 21.2 %o and spatial variation was also evident. Okon (2005) also reported that salinity values varied between stations. He reported that salinity values ranged from 2.29%o to 11.37%o.

pH (Hydrogen Ion Concentration)

Spatial and temporal variations were also observed in the pH values of the interstitial water of the Nun River Estuary. The highest mean pH (6.03) was observed in May, 2015 while the lowest mean (5.73) was recorded in November, 2014. Furthermore, the mean pH values of stations 1, 2, and 3 were much lower than that of stations 4, 5, and 6 in all the months and all the pH values were acidic, < 7. The pH values of the interstitial water of the current study are more acidic than the baseline study. During the current study, mean pH values ranged from 5.27 to 6.56, unlike the pH values of the Baseline study that ranged from 6.06 to 7.83. However, it is also noteworthy that a pH range of 5.5- 7.9 has been reported in the Niger Delta. Zabbey (2011) reported that the pH of Bodo creek fluctuated between mild acidic and alkalinity. Davies *et al.* (2006) recorded pH values of 7.2, 7.3, and 7.4, respectively. Okon (2005) recorded pH values ranging from 7.3- 8.1. Puyate and Rim-Rukeh (2008) recorded pH values of 4.5 to 6.5.

The pH of the current study, when compared to the baseline study seems to show that water quality deteriorated over the years as a result of the consistent massive pollution of the estuary as a result of the illegal crude oil refining activities in the Nun river estuary. Emuedo *et al.,* (2014), in their study on oil pollution and water quality in the Niger Delta: implications for the sustainability of the mangrove ecosystem, which was conducted in Nembe, Okrika, and Okpare also, recorded low (acidic) pH. They reported that the pH of the water samples was acidic, ranging from 5.03 in Nembe to 5.6 at Okpare with a mean of 5.29±0.29. They also stated that the low pH observed in the water samples would seem to indicate the unhealthy nature of water in the Niger Delta region. The pH of their study, when compared to a baseline study report RPI (1985): 7.50-7.80; and Dublin-Green (1990): 6.90-7.60, seems to show that water quality deteriorated over the years in the Niger Delta. The pH values obtained in this study are slightly outside the 6.00 to 9.00 range, which were suggested for optimal fish production (Onuoha and Nwadukwe, 1987). The results obtained from this study and others revealed that crude oil may be responsible for the reduction of the pH of the interstitial water.

Spatially, the pH values of stations 1, 2, and three were higher than those of stations 4, 5, and 6. The lowest mean pH (5.31) was observed in station 1 in December, 2014 while the highest mean (6.45) was recorded in station 4 in June, 2015. Moslen *et al.*, (2006) recorded highest pH of 7.5 in October while the lowest of 6.4 was recorded in December. They also reported that there was significant temporal difference ($p < 0.001$) in pH but no significant spatial difference (between locations). However, Egborge (1994) recorded low pH values during the rainy season in Warri

River, and attributed this to the inflow of humic runoff and accumulation of free carbon dioxide due to little photosynthetic activities.

Dissolved Oxygen (DO)

The results revealed that there was significant seasonal and spatial variation in the amount of DO of the interstitial water. DO values also varied tidally. The dissolved oxygen values of the interstitial water ranged from 0.59 mg/l to 2.76mg/l. The lowest monthly mean value (0.93 mg/l) was recorded in February, 2015 (dry season) while the highest monthly mean DO value (1.44 mg/l) was recorded in September, 2014-rainy season. The DO values increased from August, 2014 and got to its peak 1.44 mg/l) in September, 2014 and then declined gradually and got to the lowest value (0.62 mg/l) in February, 2015, and then gradually increased till July, 2015. Also, the DO values for stations 1, 2, and 3 were lower than those of stations 4, 5, and 6. The lowest mean value of DO (0.59 mg/l) was recorded in stations 2 and 3 in November, 2014 while the highest mean value (2.55 mg/l) was recorded in station 5 in July, 2015. The low DO concentration in stations 1, 2, and 3 may be as a result of the crude oil pollution, which could cause oxygen deterioration through the reduction in gaseous diffusion through the surface film of oil. This, in turn, could have far reaching effects on the flora and fauna of the affected area (Osuji *et al.,* 2004).

The results of this study corroborate with the findings of other researches in the Niger Delta, especially on interstitial water. Zabbey (2011) reported DO values of interstitial water ranging from 0mg/l to 4.8 mg/l and the maximum DO values were recorded in September while the lowest DO values were recorded in April. Moslen *et al.,* (2006), reported that DO showed significant difference between locations and periods. Furthermore, DO was highest in September and lowest in February. They reported that high value in September was attributable to surface water agitation and turbulence effects which coincides with periods of heavy rain falls in the Niger Delta. Also, Emuedo *et al.,* (2014) reported DO values of 5.38, 5.75, and 6.07 mg/l, in Nembe, Okrika, Okpare, respectively.

Biological Oxygen Demand (BOD_5)

The BOD_5 values of the interstitial water of the Nun River estuary varied spatially and temporally. The lowest mean value of BOD_5 (8.66 mg/l) was recorded in May, 2015 while the highest mean BOD_5 value (10.37 mg/l) was recorded in August, 2014. Also, the BOD_5 values for stations 1, 2, and 3 are higher than those of stations 4, 5, and 6. The lowest mean value of BOD_5 (5.68±0.42 mg/l) was recorded in Stations 6 in October, 2014 while the highest mean value (13.79±1.54 mg/l) was recorded in station 4 in August, 2014. Similar results on BOD_5 values have been published with regard to some water bodies in the Niger Delta, Nigeria. Ekweozor and Agbozu (2001) recorded BOD_5 values ranging from 9.54- 13.44 mg/l in the surface water near Etelebou oil field in Bayelsa state. The relatively high BOD_5 values in Etelebou oil field were ascribed to the degradation associated with continuous discharges of partially treaded effluents from the oil field. Similarly, the BOD_5 values of the current study at the Nun revealed that Stations 1 and 3 (the illegal oil refinery camps) had the highest BOD_5 values, followed by station 2 (adjacent to an illegal oil refinery), and then the BOD_5 values gradually declined from stations 3 to 6 (which had lesser input of polycyclic aromatic hydrocarbons). This is an indication that the polycyclic aromatic hydrocarbons (PAHs) increases BOD_5, reduces DO, and also reduces pH (making the water and sediments to be acidic). This may be why the flora (mangroves) and the fauna (especially, the intertidal benthic macro invertebrates) were destroyed in stations 1 and 3, and reduced in stations 2, 4, 5, and 6.

Sulphates (SO_4)

The results of the sulphate concentration of the interstitial water collected from the six sampling stations of the Nun River estuary showed that the sulphate concentration of the estuary ranged from 214.7mg/l to 935.87mg/l. The lowest mean value of sulphates (214.7mg/l) was recorded in station 1 in October, 2014 while the highest mean value (935.87mg/l) was recorded in station 3 in March, 2015. The sulphate concentrations recorded during this study are in line with the reports of other studies that were conducted in the Niger Delta, Nigeria. Depending on local, natural and anthropogenic conditions sulphates concentrations in the river systems in the Niger Delta differ. High sulphate concentrations (ranging from 1815mg/l to 3197mg/l) were recorded in the Bonny River (Chindah, 2004). High sulphate values were also recorded in Elechi creek (Ogamba *et al.,* 2005). Zabbey (2011) also reported sulphate concentrations ranging from 55.04 mg/l to 1169.6 mg/l in the interstitial water of Bodo creek. The high sulphate content of the Elechi

creek has been attributed to sea water supplies from Bonny River and leachates from marginal dump sites, industrial outfalls and municipal inputs through run- offs (Ogamba *et al.,* 2004). Izonfuo and Bariweni (2001), however, recorded very low values (0.3- 6.27 mg/l) in Epie creek. Obunwo *et al.* (2004) also recorded relatively low sulphate contents (36.7mg/l- 92.92.9mgl) in Minichida Stream in Port Harcourt. The results also indicated that the mean sulphate concentrations of stations 1, 2, and 3 (which are stations that were sited on and around the illegal oil refinery camps) were lower than those of stations 4, 5, and 6- which are a little distant from the illegal oil refinery camps. Sampling station 1 had the least mean sulphate concentration (366±120.9), followed by station 3 (391.06±126.90), then stations 2 (424.57±112.44), 4 (468.60±134.93), 5 (519.79±149.07), and 6 (556.75±190.28), respectively. These results corroborate with the results of other researches that were conducted in oil polluted sites in the Niger Delta. Ekweozor and Agbozu (2001) also recorded low sulphate concentrations (3.35-10.20) in surface waters around Etelebou Oil Field. Puyate and Rim-Rukeh (2008) recorded sulphate values ranging from 0.8 to 13.6mg/l after analyzing the physico-chemical characteristics of water samples taken from ten (10) selected river bodies in the Niger Delta region. The relatively high sulphate concentration at stations 2, 4, 5, and 6 may be attributed to local geochemical richness or anthropogenic inputs from the neighboring communities.

Phosphate (PO_3^-)

Phosphate (PO_3^-) values ranging from 0.03mg/l to 1.65mg/l were recorded during this study. The PO_3^- values that were obtained during the current study are within the range of values that were obtained by other researchers in the Niger Delta, Nigeria. Zabbey (2011) recorded phosphate values ranging from 0.004mg/l to 1.815mg/l. Emuedo *et al.* (2014) also recorded PO_3^-(mg/l) values of 1.41±0.03, 1.25±0.06, and 0.83±0.10 mg/l. The concentrations of phosphate seldom exceed 0.02mg/l (Chapman, 1996).

The lowest mean value of PO_3^- (0.11mg/l) was recorded in May, 2015 while the highest mean PO_3^- value (0.61mg/l) was recorded in August, 2014. It was also observed that the PO_3^- values progressively increased from station 1 to 6. Cooney (1984) stated that rivers can be nutrient poor at the source, but generally become nutrient- rich downstream after receiving domestic and industrial effluents and agricultural run- offs. Zabbey (2011) reported that the interstitial values of nitrates and phosphates were significantly higher than the concentrations of the overlaying water. Temporally, the lowest mean values of PO_3^- (0.03±3.05mg/l and 0.03±0.10 mg/l) were observed in November 2014, and January and March, 2015 (dry season) respectively in Station 1 while the highest mean value (1.51±0.16mg/l) was recorded in station 6 in August, 2014- rainy season.

Nitrates (NO^-)

Nitrate (NO^-) and phosphate (PO_3^-) concentrations are taken to represent the inorganic nitrogen and phosphorus present in the interstitial waters. For instance, nitrate comprises 84% of dissolved inorganic nitrogen in surface waters (Allan, 1995). The results of the concentration of Nitrates (NO^-) in the interstitial water of the Nun River estuary revealed that the nitrate concentration of the estuary ranged from 0.12mg/l- 2.08mg/l. Similar ranges of values have been obtained by other researchers in the Niger Delta and elsewhere. For instance, Nyananyo *et al.* (2007), recorded mean nitrate values ranging from 0.185mg/l- 0.252mg/l at the Amassoma axis of the River Nun. Years later, Ogamba *et al.,* 2015 recorded nitrate values ranging from 0.117±0.005mg/l - 0.394±0.033mg/l in the same river. Puyate and Rim-Rukeh (2008) recorded nitrate values ranging from 0.71 to 1.82 mg/l. Also, Kaizer and Osakwe (2010) recorded nitrate values of 1.43±0.14mg/l, 1.45±0.26mg/l, 0.61±0.07mg/l, 3.88±0.39mg/l, and 1.81±0.07mg/l at Ase River, Agbarho River, Ethiope River, Ekakpamre River, and Afiesere River, respectively, all in the Niger Delta. Furthermore, Eremasi *et al.* (2015) recorded nitrate values between the ranges of 1.62±0.97mg/l to 3.60±2.93mg/l.

Temporal and spatial variations of nitrate concentrations were also observed. The least monthly mean value of NO^- (0.45mg/l) was recorded in July, 2015 while the monthly mean NO^- value (1.01mg/l) got to its peak in December. Very low NO^- values were recorded in station 1, 2, and 3, compared to stations 4, 5, and 6. The lowest mean value of NO^- (0.12±0.08mg/l) was recorded in Station 1 in April, 2015, while the highest mean value (2.40±0.08mg/l) was recorded in station 6 in December, 2014.

Total Hydrocarbon Content (THC)

The results of the analysis of the Total Hydrocarbon Content (THC) of the interstitial water of the Nun river estuary

indicated that the estuary was highly polluted. THC values of the Nun river estuary ranged from 632.4mg/l - 1996.5mg/l. The lowest mean value (632.4mg/l) was recorded at the mid intertidal level of station 6 in June, 2015 while the highest mean value (1996.5mg/l) was recorded in station 3 (one of the illegal oil refinery camps) in August 2014. The mean (and standard deviations) of the THC values of stations 1, 2, 3, 4, 5, and 6 were 1881.79±82.33, 1810.43±94.36, 1907.89±85.78, 1356.8±227.06, 1194.58±325.3, and 1122.69±203.02, respectively. The highest mean monthly value of THC (which was recorded in August, 2014) was 1766.74mg/l while the lowest monthly mean value of THC (which was recorded in July, 2015) was 1363.55mg/l. Furthermore, sampling stations 1, 2, and 3 in the current study had higher THC values than those of stations 4, 5, and 6. Sampling station 3 (which is an illegal oil refinery camp) had the highest mean THC value (1987.9±13.59 mg/l) in June, 2015 while lowest mean value of THC (856.37±121.97 mg/l) was recorded in Stations 6 in April, 2015.

The THC values that were obtained during this study are higher than those reported by other researchers in the Niger Delta. Okon (2005), reported THC values ranging from 1.48mg/l (in June- July) to 2.19mg/l. Also, Emuedo *et al.* (2014) recorded THC values of 1741.5±22.78 mg/l, 1883.75±24.13 mg/l, and 1883.75±24.13 mg/l, respectively. Wokoma (2014) recorded mean THC values in surface water ranging from 15.60±1.56mg/l to 23.40±2.55mg/l. Uzoekwe and Oghosanine (2011) reported THC values of 8.81mg/l, 2.85mg/l and 2.83mg/l at the point of discharge, downstream and upstream of the point of discharge the same Polluted tidal creek, in Bonny River. Wokoma and Upadhi (2012) reported THC values ranging from 0- 1.87mg/l in Elechi Creek- an area far removed from oil and oil related activities. Howard *et al.* (2012) reported mean concentration of THC in water ranging from 0.5- 36.7mg/l. Ibigoni *et al.* (2009) reported mean concentration of THC in water which varied from 4.07±1.44- 45.71±8.86mg/l with a mean of 23. 60±4.37. Eja and Ogri (2003) recorded mean THC value of 149±81.11mg/l in the coastal areas of South Eastern Nigeria. Similarly, Otokunefor and Obiukwu (2005) it is also higher than the reported values of oil and grease in the waste waters from the Port Harcourt Refinery. Elsewere, Mohd. Tahir *et al.* (1997) also recorded a low THC range of 1.4-21.8mg/l in the coastal waters of Malaysia. This could be attributed to the fact that water samples for this investigation were collected shortly after the oil spill incidence, when the bulk of the petroleum product are still suspended in the water column.

Furthermore, it was also observed the THC of the sampling stations seem to have some relationship with the pH, dissolved oxygen (DO), biochemical oxygen demand (BOD_5), Posphates (PO^{-3}), sulphates (SO_4), nitrates (NO^-) and also the soil Total Organic Carbon (TOC) - Table 4.1 and Figures 4.3 and 4.4. The sampling stations that had high THC (stations 1, 2, and 3) had lower (acidic) pH, DO, SO_4, PO^{-3}, and NO^-, but higher BOD_5 and soil TOC. Thus, it can be said that the crude oil and related dispersants of polycyclic aromatic hydrocarbons affects the physico-chemistry of the interstitial water of the Nun River estuary by reducing the pH, DO, SO_4, PO^{-3}, and NO^- and also increasing the BOD_5 and TOC (in the sediments).

Conclusions and Recommendations

The outcome of the analysis of the physico- chemistry of the interstitial water and sediments of the Nun River estuary revealed that the estuary is, indeed, “seriously ill”. For the interstial water samples, parameters such as Total Hydrocarbon Content, pH, Dissolved Oxygen, Biological Oxygen Demand, Sulphates, Phosphate, and Nitrates revealed a great deal about the prcarous state of the estuary. The Total Hydrocarbon Content (THC) of the estuary was exceptionally high (ranged from 632.4mg/l - 1996.5mg/l), the pH was acidic (ranged from 5.27 to 6.56), the DO was very low (ranged from 0.59 mg/l to 2.76mg/l), the BOD was high (ranged from 8.66 mg/l to 10.37 mg/l), and the sulphate, possphate, and nitrate concentrations were high- ranging from 214.7mg/l to 935.87mg/l, 0.03mg/l to 1.65mg/l, and 0.12mg/l- 2.08mg/l, respectively. The alteration of these parameters as a result of the illegal oil refinery activities (Kpo fire) is responsible for the massive destruction of the intertidal benthic macro invertebrates and mangroves in the area.

Based on the findings of this research, it is, therefore, recommended that: Proper measures should be put in place to prevent environmental pollution. The government and the multinational oil corporations are advised to carry out proper cleanup of the spilled oil in Nun River estuary.

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