Assessment of Physicochemical Parameters of Oil and Gas Terminal Effluent of the Bonny Estuary, Rivers State, Nigeria.

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Abstract
A study was conducted to assess resultant impact of industrial activities on the physicochemical parameters of the Bonny estuary. Water sampled at a depth of 100cm from three stations (BE1- E3) were analyzed for 24 parameters. pH, temperature, conductivity, and turbidity were measured in-situ with HORIBA U-10 water quality checker, while TDS was measured with HACH meter. Other 19 parameters were analyzed in the laboratory following APHA (1998) standard method. Students-T test and Snedecor's F-Distribution were adopted to analyze data at 0.05%. Result shows that BOD_5, Cadmium, Chromium, Ammonia, Phosphate, Chloride, Nitrate, Oil and Grease were above Standard recommended by DPR and NESREA for all industries. Temperature, TSS, Lead, Ammonia, Vanadium and Phosphate concentrated highest at the point of wastewater discharged (BE2), signifying obvious effects of the industrial activities on the Bonny estuary, other parameters (pH, Turbidity, Conductivity, BOD_5, Cu, Cr, Cl, Nitrate, Fe, Cd, Oil and Gas) had highest before the point of wastewater discharge is influenced by the flowing water; exposing the estuary resources to potential risk. There is a statistical significant relationship between sample station BE1 and BE2 at 0.05%. It is therefore important to continuously monitor industrial activities in the area to protect end users.

Keywords: *Bonny Estuary, Buck Header, NLNG and BOGT, Water Pollution.*

Introduction

Water is the second most important and abundant of all natural resources on planet Earth after air (Ebuete & Ebuete, 2018), [www.ijert.org]. Water covers about 71% of the earth surface, serving and playing a central role to all known forms of life; yet it is treated with contempt. According to Ebuete and Bariweni (2019); the significance of water to human life is depending on how it occurs and how it is managed. When it is too much or too little, it can bring destruction, misery or death but on the average, irrespective of how it occurs if properly managed it can be an instrument for economic survival and growth.

However, when it is inadequate in either quantity or quality, it can be a limiting factor to poverty alleviation and economic recovery, resulting to poor health, low productivity, food insecurity and constrained economic development (Ebuete *et. al*., 2019), [iosrjournals.org].

Currently, the global human existence is threatened by the inadequacy in quantity and quality of water and according to the United Nations Report (UNEP GEMS, 2006); some 80 nations accounted for about 40% of the world's population are already in the throes of a water stress and only through the improvement in providing, managing and serving water will save man from the perceived monumental crisis in no distance time [iosrjournals.org]. A quick response to save mankind from the crisis of shortage of water and it related diseases, Goal 6 (Clean Water and Sanitation) of the Sustainable Development Goals (SDG) was crafted (encapsulated) to address the need by 2030.

However, with the ever-expanding civilization, urbanization, increasing human population and decaying human consciousness as observed daily on planet earth; achieving goal 6 (Clean Water and Sanitation) remained questionable among developing countries where policy frameworks are without implementations. Regrettably, human are the precipice of environmental collapse and water shortage.

The pathetic story of my beloved country (Nigeria) is that the commonest and free sources of water supply (surface water) available to local communities are fast being severed by a number of anthropogenic factors, of which pollution remains the most dominant factor [www.ijert.org]. A quick perusal of the Nigerian Atlas shows that; most areas of industrial settlements are adjacent to rivers, lake, stream, lagoon, estuaries, sea and oceans which also serve as waste sinks with or without proper treatment; an actions that is obviously a lead cause of human water-borne diseases and tainting in fish among other aquatic lives as observed within the Niger Delta region of Nigeria [www.cas-press.com]. The unmanned and ill operatives of these industries has accorded the Niger Delta region the most oil-impacted and polluted environment globally (Nwankwoala & Omofuophu, 2020), [www.ijiras.com], and as such the Bonny Estuary is among the high risk natural water bodies in the Niger Delta region.

The Bonny Estuary is perceived to receiving effluent from activities of oil and gas within the surrounding environment since late 60s when exploration, exploitation, refining, loading, cleaning of facilities and vessels (scihub.org).

These uncontrollable activities may have contaminated the quality of the Bonny Estuary beyond natural Estuary ability to process raw waste; it could be that the physicochemical status of the Estuary may have been compromised from the activities of Nigeria Liquefied Natural Gas (NLNG) facility that is currently processing about 1566MSCF gas per day and the Bonny Light Crude Oil Tank Farm, which treated and untreated waste water are discharged occasionally into the receiving Bonny Estuary. These facilities are all clustered within 200 meters proximity to the Bonny estuary. Regrettably, spite of the fact that the Bonny Estuary is serving as waste sinks within the region, it remained a significant essential heritage and a resource for the Bonny people and host of Huza settlements along it flowing course in terms of fishing and domestic water uses, farming and manufacturing especially during the dry seasons of the year and when the public water supply is irregular.

Therefore, adequate monitoring and sampling of the surface water is of fundamental importance to detect and identify pollutants and their concentrations at the wastewater discharge point and various locations along the Estuary.

The Bonny Estuary has attracted researcher interest due to the activities of oil and gas and other industrial activities along its flowing course (Powell & Chindah, 1990; Erondu & Chindah, 1991; Chindah & Pudo, 1991; Chindah, 1998). Other researcher interest were Chindah and Osuamkpe (1994) on the fish assemblage of the Lower Bonny River, Niger Delta, Nigeria; Izoafuo, Chindah, Braide and Iyalla (2004) on the assessment of sediment quality within the vicinity of marine landing jetties at the Middle Reach of Bonny Estuary, Niger Delta; Chindah, Braide and Nduaguibe (2000) on tolerance of periwinkle (*Tympanotonus Fuscatus*) and shrimp (*Palemonetes Africanus, Bals*) to waste water from Bonny Light Crude Oil Tank Farm and on the contrary, little attentions had been drawn on the impact of the treated waste water discharged into the Bonny Estuary.

Therefore, this work aimed at assessing the impact of waste water discharged in the Bonny Estuary. This will see to the need for routine environmental monitoring for early detection of changes for a more sustainable management of aquatic resources.

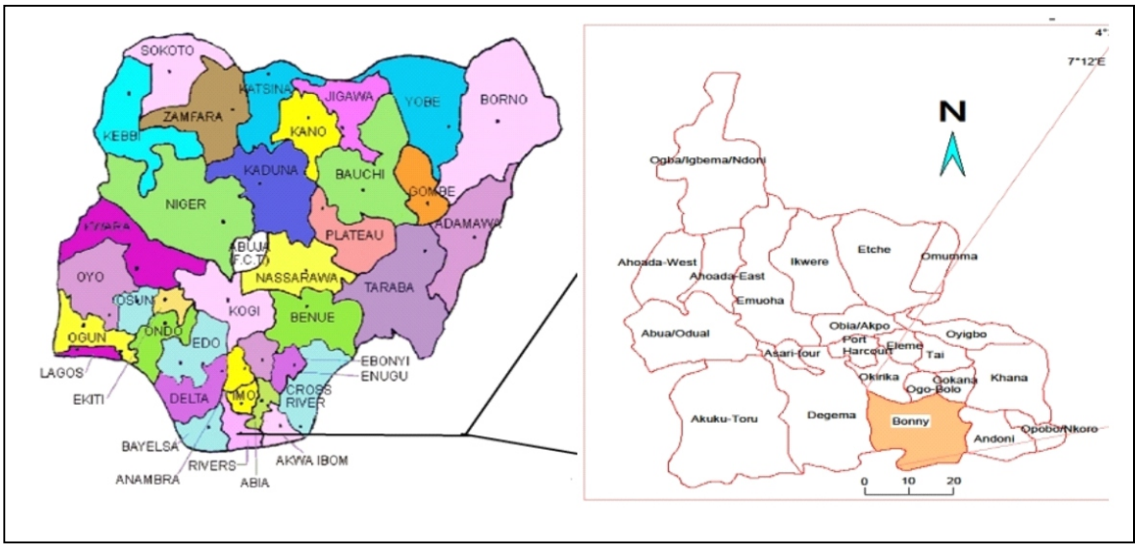
Materials and Methods

Study Area

This study is carried in the Brackish Wetlands of the Bonny Estuary in the South West Port-Harcourt, Eastern Niger Delta. Detailed description of the hydrology, relief, geology and soils of the system is contained in NEDECO (1961); Hart and Chindah (1998); Chindah and Braide (2010) and Ngah, Braide and Dike (2017). The study adopted the experimental study design where sampling points were purposively chosen within and around the Bonny Oil and Gas Terminal (BOGT) discharging waste water into the Bonny estuary at three locations.

The sample points lies within the provisional surface coordinate of E:525000m and N:50000m in the Eastern Niger Delta sedimentary basin and it is situated on the East Bank of the Bonny River at 4° 25' N, 7° 20' E and about 27 Nautical Miles (NM) from Port Harcourt (Fig.1). Relatively, the BOGT is adjacent to the Bonny Town at the south-eastern tip of the Niger Delta.

Bonny is the main passage for merchant tankers and shipping route to the inland Port of Onne, Port Harcourt City and the NNPC terminal at Okirika. The terminal is about 2.2km^2 long and it is situated on land reclaimed from the marshes, swamps and creeks. The terminal is accessible through air by helicopter for about 15minutes, while an inland waterway is about one to two hours.



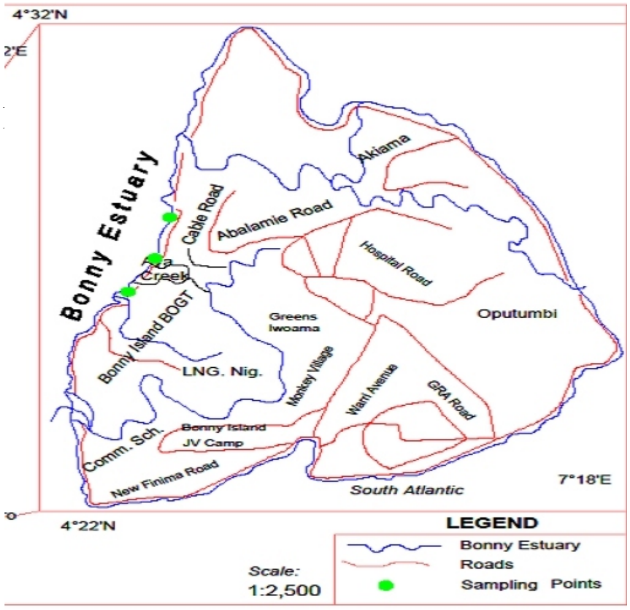


Fig. 2. Map of Bonny Island showing Sampling Points

Sampling Design

Surface water samples were collected from three sample points (100 meters apart), before the discharge points (BE1); which serves as the quality control (QC) to the rest sampling points; at the discharge point (BE2) and after the Bonny oil and gas terminal discharge points (BE3) at a depth of 100cm, twice monthly for four (4) months in a 1Litres plastic containers that were pre-rinsed with trioxonitrate (v) acid for 24 hrs. and rinsed with de-ionized water following standard procedures by the America Public Health Association (APHA, 1998); (Management of Environmental Quality, 2013). *In-situ* measurements was made for pH, water temperature, conductivity and turbidity with HORIBA U-10 water quality checker, while HACH conductivity meter (Model CO 150) was used for Total Dissolved Solids (TDS) and Total Suspended Solute (TSS).

Samples for Laboratory analysis were transported in a box containing ice packs at $4^{O}C$. The Atomic Absorption Spectrophotometer (AAS) analysis was done on all the heavy metals (Cu, Cr, Pb, Ni, Na, Fe, Cd and Zn) following Tiwari, Bajpai, Dewangan and Tamraka (2015); BOD_5, Nitrate, Chloride, Sulphate, Ammonia were analyzed in accordance to Ngah, Braide and Dike (2017) recommendations; An Efficient Napthalene-Based Ratiometric Fluorescent probe was used to determine Cyanide as described by Long *et.al.* (2019) and Tingting *et.al.* (2021); Spectrometric method (GHPSAM) was adopted to analyzed for Phenol following Campins-Falco, Tortajada-genaro, Antequera-baizuli and Bosch-Reig (2006).

Statistical Analysis

The MS Excell 2007 was used to analyze data. Physico-chemical parameters measured were explored using Mean, Range and Standard Error. Variance contributions were used for factor selection. The pair-wise comparison levels of the physico-chemical parameters across sampling period was made with students T-test at P=0.05. The Snedecor's *F*-Distribution of significance at p=0.05 was used to test for parameters relationship between sample stations BE1 and BE2 to determine the influence of wastewater on surface water quality.

Results and Discussion

Physicochemical Parameters of the Receiving Bonny Estuary

The physicochemical parameters of Bonny Estuary receiving treated effluents from the buck header of the BOGT (Bonny Oil and Gas Terminal) and their spatial variations in concentrations are shown in Table 1-2 and Figure 1-3 respectively. According to Adakole, Mbah and Dalla (2003); the quality of any water body is governed by its physicochemical and biological parameters and as such, continues monitoring of these parameters is very important for long and short-term environmental management.

Table 1: Physicochemical parameters of the receiving Bonny Estuary

Parameters	BE 1	BE 2	BE 3	DPR limit.	NESREA
pH	6.8	6.6	6.3	6.5 -8.5	6.9
Temp (^{0}c)	27.0	28.0	27.5	30.0	< 40
Turbidity(NTU)	4.5	3.0	3.0	< 2.5ppm	NA
TDS (mg/L)	5100	5000	5300	5000	2000
Conductivity (µs/cm)	7200	6800	6200	NA	NA
TSS (mg/L)	10.0	12.0	9.0	<750ppm	25
BOD_5 (mg/L)	4.0	3.5	2.4	125	30
COD (mg/L)	7.0	6.5	7.2	125	NA
Copper (mg/L)	0.005	0.004	0.003	NA	0.01
Chromium (mg/L)	0.004	0.003	0.002	0.5	0.5
Lead (mg/L)	0.001	0.002	0.001	NA	0.5
Nickel (mg/L)	0.002	0.002	0.001	NA	1.0
Phosphate(mg/L)	4.20	5.10	4.00	NA	5
Sulphate (mg/L)	5.00	5.00	5.50	NA	500
Chloride (‰)	3200	3000	3100	NA	600
Nitrate (mg/L)	8.50	8.30	8.00	NA	10
Cyanide µm(S/N)	0.001	0.001	0.001	NA	0.1
Phenol (mg/L)	0.001	ND	ND	NA	0.2
Ammonia (mg/L)	0.018	0.025	0022	NA	NA
Vanadium (mg/L)	0.01	0.03	0.01	NA	NA
Iron (mg/L)	0.26	0.18	0.20	NA	20
Cadmium (mg/L)	0.03	0.02	0.01	NA	0.02
Zinc (mg/L)	0.010	0.009	0.025	NA	0.5
Oil and Grease (mg/L)	31 0	25.0	25.0	NA	10

Source: Researcher, 2020.

Spatial Variations in Levels of Physicochemical Parameters of the Bonny Estuary

An organism distribution and productivity level in aquatic ecosystem is largely determined by physicochemical and biological factors to maintain ecological balance. Therefore, increase in contaminant load causes anoxia which acts as stressor that endangers the lives of organisms in that system (Vaidyanath, Pratap & Satyg, 2008). The pH in an aquatic ecosystem is closely linked with the biological productivity as it influences biological and chemical processes within the water body. However, the tolerance of individual species varies with pH level. According to UNEP GEM (2006), a pH value of 6.5 to 8.5 is usually described a good water quality which placed the mean pH value of the current study (6.3-6.8) within a safe limit.

Findings from this study is similar to the report of Iyama and Edori (2014), but slithery lower than the report of Uzukwu, Leton and Jamabo (2013); Onojake, Sikoki, Omokheyeke and Akpiri (2017); Dienye and Woke (2015) in same Bonny Estuary which is been attributed to the increasing volume of water during the wet season.

Temperature of water affects the process of chemical reaction, the rate at which algae and aquatic plants photosynthesize, the metabolic rate of other organisms, as well as how pollutants and parasites interacted within the aquatic biota (Adesalu & Nwankwo, 2008). Temperature of water influences the solubility of dissolved oxygen and other materials in water volume to cause mortality. The temperature values for this study ranges between 27.00 - 28.00°C (27.5 ± 0.3) which fall within the DPR and NESREA limits

Although minimal spatial variations were observed at station BE3 and BE1, due to the discharge of waste water into the estuary (Figure 1). Similarly, Onojake *et.al.* (2017) reported a range of 27-30.20 °C; Meregini-Ikechukwu *et.al.* (2020) reported 27.9-29.0 °C in the Elechi Creek due to seasonal variations during sampling.

Turbidity refers to water clarity with respect to the concentration of suspended and dissolved solids [mafiadoc.com]. The greater the amount of suspended solids and total dissolved solute in a volume of water, the murkier its appearance which reduces autotrophic production. High turbidity and TSS could reduce primary productivity by autotrophic algae that reduce biotic diversity and abundance.

The mean turbidity (3.50 NTU) and TSS (10.33mg/l) in this study is below DPR/NESREA limits. Minimum turbidity (3.00 NTU) was recorded in BE3 'after wastewater discharged point' while maximum levels (4.50 NTU) were recorded in BE1, due to the flowing effects of the Estuary at the time of sampling (Figure 2). Recorded values were lesser than the previous report of Onojake, Sikoki, Omokheyeke and Akpiri (2017).

Nitrate and phosphate are primary drivers of eutrophication in aquatic ecosystem. Nutrient measures in this study Nitrate (8.28mg/l), Phosphate (4.43mg/l), Ammonia (0.022mg/l) and Sulphate (5.09mg/l) were generally lower than the maximum permissible limits of DPR except Phosphate at BE2 due to the discharge of industrial wastewater at this point (Table 2).

Their ion concentrations varied from 8.00-8.50 (0.50 ± 0.00) mg/l; 4.00-5.10 (1.11) mg/l; 0.018-0.025 (0.007) mg/l and 5.00-5.50 (0.50) mg/l respectively; but maximum levels of Sulphate (5.50mg/l), Phosphate (5.10mg/l) and Ammonia (0.025mg/l) were recorded at the discharge point (BE2), signifying the effects of the industry on the Bonny Estuary and gas flaring within the Environs which is similar to the report of O'Callaghan-Gordon, Orta-Martinez and Kogevinas (2016). However, on the Bonny Estuary, Obinwanne (2015) reported ammonia level of 1.16mg/l which is far lesser than the report from this study.

Heavy metals are toxic elements with an atomic density greater than $6g/cm^3$; a prolonged exposure at higher concentration causes human health problems. The levels of the trace metals (Cu 0.002mg/l, Cr 0.002mg/l, Pb 0.001mg/l, Ni 0.001mg/l, V 0.02mg/l, Fe 0.08mg/l, Cd 0.02mg/l and Zn 0.016mg/l) recorded in this study were below DPR /NESREA limits except for Cd at station BE2 (Table 1). The concentration of these metals also varies as 0.003-0.005 (0.002mg/l); 0.002-0.004 (0.002mg/l), 0.001-0.002 (0.001mg/l), 0.001-0.002 (0.001mg/l), 0.01-0.03 (0.02mg/l), 0.18-0.26 (0.08mg/l), 0.01-0.03 (0.02mg/l), 0.009-0.025 (0.016mg/l) respectively. At 0.05%, there is statistical significance difference (t-0.067 < d.f-1.895) of heavy metals among sample stations.

Furthermore, the high concentration of Cr, Pb, Ni, V and Cd at station BE2 could be linked to the activities of oil and gas process and the direct discharge of wastewater. Babatunde *et.al.* (2017), Ebuete *et al.,* (2019); Onojake, Sikoki, Omokheyeke and Akpiri (2017) has submitted that industrial wastes had the potential for introducing strong acid and trace metals into water bodies which may cause dented effects on both fauna and flora. Results from this study are similar with previous work of Onojake, Sikoki, Omokheyeke and Akpiri (2017).

The exceedance of TDS in Bonny Estuary above NESREA limits during the sampling periods could be attributed to various industrial activities such as shipping, dumping, and discharged of effluents containing dissolved pollutant in solution. High TDS affect the water balance in the cells of aquatic organisms and causes Laxative effects on the aquatic life (more water shrinks off from their cells). It also affects taste and caused water hardness which adversely deteriorate plumbing and appliances.

Conductivity in water refers to the possibility of the water to convey electrical current, which is directly related to the concentrations of ionized substances in that water. The mean Conductivity (6733µs/cm) spatially varies from 6200-7200 (1000µs/cm) is principally influenced by the ionisation processes due to TDS (5133mg/l), cations and anions constituting salinity (3100 o/ooo) which substantiate with the previous studies reported by Onojake, Sikoki, Omokheyeke and Akpiri (2017). On the other hand, the concentration of chloride varies from 3200-3000 o/ooo (20 o/ooo).

The mean BOD_5 (3.3mg/l) and COD (6.9mg/l) were below DPR, NESREA limits, depicting a low level of organic pollutants and chemical oxidizable substance in the estuary. Biological Oxygen Demand (BOD_5) varies between 2.40-4.00 (3.30) mg/l, while the Chemical Oxygen Demand (COD) varies from 6.50-7.20 (6.90) mg/l. The minimum COD (6.5mg/l) and BOD_5 (2.4 mg/l) concentration were recorded in BE2 & BE3 while their maximum mean concentration (7.2 & 4.0) were at station BE3 and BE1 respectively due to the flowing effects of the Estuary at the time sampling.

Oil and grease are significant pollutant in the oil industry. Hydrocarbons are by far the most abundant class of compounds present in oils and are capable to impede the exchange of gases in the water and coat bodies of birds and fishes. The mean concentration of Oil and grease (27mg/l) is far above the recommended allowable values of 10mg/l by NESREA for all industries (Table 1). The concentration varies from 25-31(6mg/l); indicating the presence of small quantities of oil and grease in the wastewater routinely discharged into the environment (Fig.1).

The presence of this material can cause fish stock depletion and could buildup in the tissue of aquatic organisms to prompt natural process of bio-concentration and bio-magnification; a great threat to human health. Similarly, Emuedo, Anoliefo and Emuedo (2014) reported a mean concentration of 1823.25±73.47 for Nembe, Okirika and Okpare Rivers and submitted that oil activities is responsible for the poor surface water quality in the Niger Delta region; Nwankwoala and Omofuophu (2020) also reported concentration range of 29-45mg/l in Bonny Island.

The concentration level of phenol (0.001mg/l) and cyanide (0.001mg/l) were both below the DPR/NESREA limits. Aquatic lives get affected by phenol through direct toxic action or by impairing taste to inflict both sever and long lasting effect of human health. Cyanide compound are grouped into free, simple and complex as hydrocyanic acid (HCN) plus cyanide ions CN-. Cyanide is dangerous to both aquatic and human life due to their carcinogenic property. The toxicity level of cyanide may be aggravated by the presences of zinc or cadmium according to Khopkar (2007) and Prasad (2008).

There is a significant correlation in levels of the physicochemical parameters during the study period which indicates relatedness of some parameters in the water while at Station BE2, there was statistical significance difference (t:10.81 > d.f:2.015) among parameters. The concern is the contamination of water resources by potentially toxic metals from Buck header of the LNG waste water discharge point into the Bonny Estuary. The spatial temporal variations of Temperature, Oil and Grease were shown in fig.1; pH, Turbidity, TSS, BOD_5, COD, Phosphate, Sulphate and Nitrate were shown in fig.2, spatial temporal variations in heavy metals (Cu, Cr, Pb, Ni, V, Cu and Zn) is shown in fig.3.

Fig. 1: Spatial variations in Temperature and Oil and Grease on the receiving Bonny Estuary

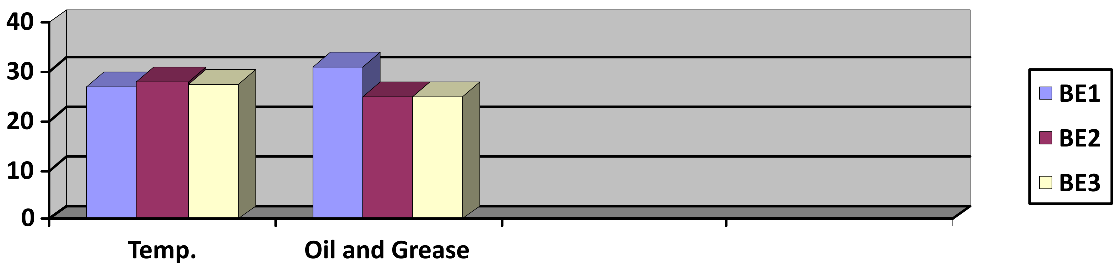


Fig. 2: Spatial variations in some Physico-Chemical parameters of the receiving Bonny Estuary

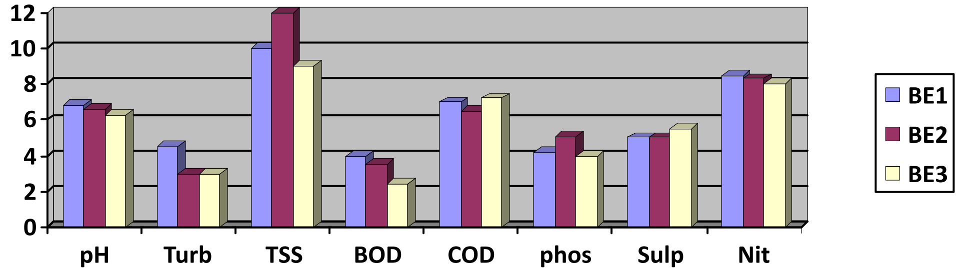
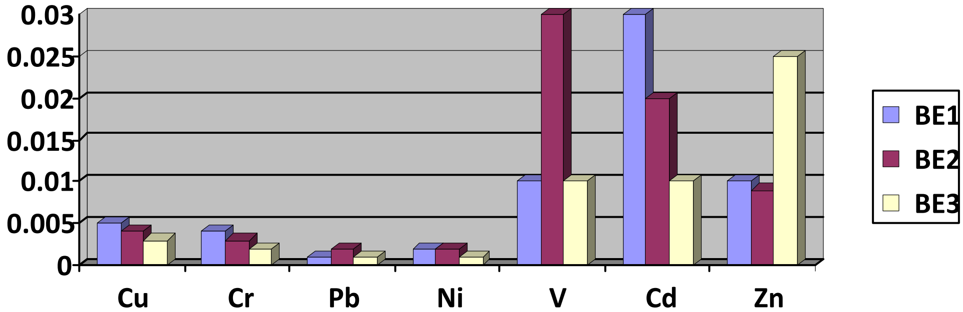


Fig. 3: Spatial variations in Heavy Metals concentrations of the receiving Bonny Estuary



Summary and Conclusion

Assessment of water is unlimited to suitability for human consumption but also in relation to agricultural, industrial, recreational and commercial uses as well as the ability to sustain aquatic life. The study revealed that water from the Bonny Estuary is polluted with toxic substances from related oil and gas activities as well as other allied industrial activities. The values of BOD_5, cadmium, chromium and Ammonia, Phosphate, Chloride, Nitrate, Oil and Grease were above recommended limits by DPR and NESREA for all industries; thereby polluting the water from the Bonny Estuary; making it unsafe for consumption. Statistically, there is a statistical significance difference among heavy metals sampled. More so, it was also discovered that out of the 24 parameters considered from the Bonny Estuary, a total of seven (7) parameters (T°c, TSS, Pb, Ammonia, Vanadium, Sulphate and Phosphate) had their highest concentration at the point of waste water discharged (BE2), signifying obvious effects of the industrial activities in the cause of Waste water discharged on the Bonny Estuary. At Station BE2, there was a statistical significance difference (t:10.81 > d.f÷2.015) among parameters. However, among the eleven (11) parameters (pH, Turbidity, Conductivity, BOD_5, Cu, Cr, Cl, Nitrate, Fe, Cd, Oil and Gas) with highest concentration recorded before the point of waste water discharge was influence by the water flow, moving concentration ions from the point of discharge along its course of flow. There was statistical relationship (F=198.57 > d.f=4.74) between sample station BE1 and BE2 at P=0.05% applying Snedecor's F-Distribution. This further explained that, waste water discharged at point BE2 has the capabilities of influencing the concentrations of ions at another points in a flowing water system. Hence, the discharged wastewater by the industries is negatively impacting on the surface water quality and the aquatic organisms longitudinally. Portends risk of accumulation in resident organisms of the Estuary may lead to bioaccumulation and biomagnifications in other aquatic organisms, tainting in fish and death of organisms and extinction of others that may not tolerate elevated levels. Thus, water pollution is a challenge impeding domestic water used and development of tourism in the Bonny Estuary.

Recommendations

The study therefore recommends for:

1. DPR should develop more standard limits for all parameters, especially on parameters yet to be specified.
2. A test of Bioassays should be carried out to investigate the quality of aquatic organism (fish) for their wholesomeness.

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