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ASSESSMENT OF THE VARIATIONS IN PHYSICO-CHEMICAL PARAMETERS AND HEAVY METALS POLLUTION POTENTIALS OF EKERIKANA WATERBODY, RIVERS STATE, NIGERIA

Iyama William Azuka*, Eugene-Nwala Obinna and Igoni Israel Kitoye
Rivers State College of Health Science and Technology, Rumueme, Port Harcourt: PMB 5039
Corresponding Author: willy4a@yahoo.com
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ABSTRACT

The Nigerian National Petroleum co-operation generates large proportion of effluents waste water from their process plants. This study was to assess the level of pollution from physicochemical parameters and heavy metals point of view on the adjoining Ekerikana water body. This study established six sampling station such as R, S, T, U, V control sample station X. All samples were collected in accordance with the procedure described in water standard method for water and waste analysis. Physico-chemical parameters were determined using Horiba U-10 model and titrimetry. The analysis conducted indicated that physico-chemical water quality parameters recorded mean concentration values of pH (7.06 - 7.67mg/l), DO (1.02 - 3.25mg/l), BOD (34.2-45.4mg/l), temperature (28.1-29.1^{0}C), electrical conductivity (4090-23,660 µS/Cm), Turbidity (1.4-26.7NTU), TDS (2863-22,820 mg/l) and THC(<0.20-2.42mg/l). The analysis conducted shows that parameters such as electrical conductivity, biochemical oxygen demand, turbidity temperature, and total dissolved solid were all above permissible limit as specified by world health organization and federal ministry of environment though pH was within the permissible limit. The analysis conducted indicated that heavy metal presence was within levels permissible by regulatory bodies It was established from the result of this study that the refinery discharged effluent has impacted negatively on the Ekerikana water quality which has resulted to loss of biodiversity, agricultural activities and hampered environmental sustainability. There is need to also study the trend in both nutrient and microbiological composition of the Ekerikana water body so as to develop a water quality index for it.

Keywords: water quality, assessment, variation, anthropogenic, contaminant, heavy metals, pollution.

INTRODUCTION

Natural water is said to be polluted when it has been changed by human activities so that it is no longer useful for industrial purpose. Any substance that prevents the normal use of water is said to be a water pollutant. Pollutants generally gain access into the water bodies from both natural and anthropogenic inputs. The various sources through which water can be polluted are classified as natural, industrial and domestic. As a result of urbanization and industrialization, the anthropogenic input of certain metal has attracted much attention from researchers. In the past human and other animals enjoyed clean water and air but the industrial revolution in the 19th century and its

perfection in 20th century, gradually caused air, water and soil to become polluted by the activities of man [1]. The interaction and impact of such waste with the immediate environment (ecosystem) create pollution problems [2]. The level of environmental pollution has risen to a critical level that threatens and endangers the health and survival of humans and other living things. This situation has led to loss of biodiversity of different species [3]. The awareness on this has made some highly industrialized countries to device and adopts certain fundamental measure for the prevention of environmental pollution [4]. Pollution of the aquatic environment stem from different sources/activities. The major activities in this regards include but not limited to oil and gas resource development, citing manufacturing industries/factories along the coast of running waters, movements of vessels and other marine activities [5]. Therefore, the environmental resources around us should be exploited in such a reasonable way to provide our daily needs at the same time not to be exposed to damage, loss of aesthetic. By such a cautious approach our future may be guaranteed. Sustainability development implies the use of finite resources necessary to provide for the needs of the present and future generations but without jeopardizing those of the present and future generation [6]. The world values the ocean so much that 60% of its 5.5 billion people live within 60 kilometers of the coast. In Nigeria, the marine including Lagos estuaries, bays creeks etc, constitute a vast and dynamic store house of energy food and mineral resources that hold lots of promises for rapid socio-economic development. The release of waste into the environment by industries is known as environmental pollution and we have been polluting systematically our water since the beginning of industrial revolution. Industrialization and increased productivity are making an unprecedented demand on natural resources. It has been estimated possibly that as many 1,000 new ones are added each year. All of these production and uses result in wastes that are discharged into the water. Trace metals play an important role in the natural biological life cycles. Their levels help to define the behavior and well being of individual's biological life cycle and the overall character of a water system. Understanding of this role involves appreciation of the mechanisms of transformation of those trace metals in the system. These considerations relate to both the metals that are essential to biological functions and the metals that may be inhibitory to organisms in the aquatic system. The presence of petroleum hydrocarbon in water and sediments has been a major source of concern, especially as it affects the colonies of macro-invertebrate such as fish *etc*. There is information in literature on the ambient levels of hydrocarbons in the surface benthic sediments of marine and aquatic environment subjected to various degrees of pollution [7]. These studies used a synoptic approach to get the hydrocarbon distributions which were achieved in each case by collection of sample, in a given geographical area over a stated period. Earlier, [8] reported the effect of hydrocarbon pollution on the distribution of mullet species along Elechi creek in Port Harcourt, which showed that the total hydrocarbon concentration (THC) in water and sediment, around the industrial jetty was significantly higher than the other sites in Okrika Rivers State of Nigeria throughout the sampling period. Benthic and non-bentic organisms were affected physiologically as well as their attitudes such as their feeding habits and reproductive system [9]. Polycyclic aromatic hydrocarbons are considered to be among the most toxic and carcinogenic components of crude oil and its related compounds; however some microbes are resistant to such prevailing conditions. In the same vein, it was found that many protozoan survived in oil polluted but noted that the more sensitive species has been eliminated and also declining rates in phytoplankton photosynthesis in oil polluted water. Oxygen is also reported excluded from organisms following oil pollution. It had also been observed that oil has toxic effect on zooplanktons, other marine organisms and the sediments [10]. It is relatively easy to monitor the

effects of oil in water for instance, the number of oiled seabirds and mortality of littoral invertebrates. The effects become less easy to distinguish if components of oil passing through the water column become trapped in the sediments.

Pollution of the aquatic environment occurs from many different sources including from oil refineries. Oil refinery effluent, contains many different chemicals at different concentration. The exact composition cannot however be generalized as it depends on the refinery and which units are in operation at any specific time. It is therefore difficult to predict what effects the effluent may have on the environment. In typical crude oil (petroleum) refining system waste water are commonly generated from the following: Production process, Oily sewer water pond, Ballast water release, Sanitary waste water, Chemical waste water, Cooling towers, Demerol effluent from specially designed plants [11]. Each of these sections is essential in the refinery process. All the water generated is channeled into the waste water treatment chamber and thereafter into the close observation pond before being discharged.

MATERIALS AND METHODS

All samples were collected in accordance with the procedure described in water standard method for water and waste water analysis [12]. Physico-chemical parameters were determined using horiba U-10 model and titrimetry.

Okrika is a port town and also headquarter of Okrika Local Government Area of Rivers State. The town is situated on a small Island just south of Port Harcourt, making it a suburb of the much larger city. The average elevation of Okrika is 452meter above sea level. It lies on the north of the Bonny River and on Okrika Island, 35 miles (56km) upstream from the bight of Biafra. According to the 2006 census, Okrika is about 222,026 of native indigenous population [13].

Anthropogenic activities along the creek include sand mining and dredging, fishing navigation, washing, bathing and recreational activities. The vegetation consists of *Rhizophora racemosa* which lined the shores of the station. The creek is tidal in both wet and dry seasons. A major industrial output which is situated in Ekerikana is the Nigerian National Petroleum co-operation (NNPC) refinery. These activities have undoubtedly influenced the natural balance of the aquatic ecosystem and consequently its biota, such as plankton and benthos composition.

Six samples were collected including the control from various points in the study area (Ekerikana) of a distance of 3km apart from each sample station R, S, T, U, V and control, X. The samples were collected at low tide at about 3ft (1metre) deep at different points of the stations around the study area using 1litre of sterilized sample container. Dissolved oxygen (DO) and Biochemical oxygen demand (BOD) were also collected using amber bottles at different points of the stations by lowering the sample container and bottle into the river and allowing water to overflow before it was withdrawn and transferred into an ice box before taking to the laboratory for analysis. All samples were collected in accordance with the procedure described in standard method for water and waste water analysis. Physical parameters were determined using horiba U-10 model. Measurements were done by immersing the probe into the sample and the readings recorded its stability. The pH was determine using horiba U-10 model measurement and determined by immersing the probe into the sample and the readings recorded its stability. The water sample was collected in a 250ml brown bottle, 2.0mls of Winkler 1 solution were added and stoppered carefully to exclude air bubbles and mixed. Then 2.0ml of concentrated H_2SO_4 was added and re-stoppered in the bottle which was then mixed gently by inversion until dissolution was completed. About 0.025N thiosulphate solution was titrated against 100ml sample containing 2ml starch solution until the disappearance of the blue

colour. The biochemical oxygen demand (BOD) for five days was carried out by incubating the water sample in 250ml bottle for five days at room temperature, on the fifth day the procedure for BOD was carried out for the sample. The Total Hydrocarbon Content (THC) of the water was determined by shaking 10g of a representative water sample with 20ml of toluene. The oil extract was then determined by the absorbance of the extract at 420nm in a spectrum 21-D spectrometer. Oil concentration was then calculated with reference to the standard curve, moisture content and multiplication by the appropriate dilution factor [14].

Heavy metals were determined using Atomic Absorption Spectrophotometer (AAS) as described in APHA 3111B and ASTMD 3651.

RESULTS AND DISCUSSIONS

The results of surface water quality parameters in water obtained from Ekerikana River are shown on Tables 1, 2 and 3 (physicochemical and gross organic pollution and heavy metals). The water quality is then compared to World Health Organization and Federal Ministry of Environment water quality standard.

Table1: Concentration of physical parameters for Ekerikana River Water

Parameters	Sample Stations						WHO/ FMENV
	R	S	T	U	V	X	
Temperature (^{o}C)	29.1	28.3	28.4	29.0	28.1	28.2	24-28
Electrical conductivity µS/cm	4090	31,800	8040	15,300	28,200	32,600	100
Turbidity (NTU)	26.7	4.3	8.8	11.7	1.4	4.6	5
TSS (mg/l)	-	-	-	-	-	-	30
TDS(mg/l)	2863	22,260	5628	10,710	19,740	22,820	500-1000

Table 2: Concentration of Chemical and Gross Organic Pollution Parameters in Ekerikana River

Parameters	Sample station						WHO/ FMENV
	R	S	T	U	V	X	
pH (units)	7.61	7.67	7.06	7.43	7.53	7.49	6.5-8.5
Dissolve oxygen (mg/l)	1.14	3.25	2.31	1.37	1.02	3.25	7.5-10
Biological oxygen demand BODS (mg/l)	45.5	45.5	42.1	43.3	34.2	45.5	10
T.H.C.(mg/l)	2.42	<0.20	0.81	1.61	2.42	1.34	10

Table 3: Heavy Metals Concentration for Ekerikana River

Parameters	Sample Station						WHO/ FMENV
	A	B	C	D	E	X	
Iron (Fe) mg/l	0.003	0.002	<0.001	0.005	0.010	<0.00	0.3-1.0
Manganese (Mn) mg/l	0.022	0.019	0.031	0.038	0.046	0.41	0.4
Lead (Pb) mg/l	<0.00	<0.00	<0.00	<0.00	<0.00	<0.00	0.01-0.05
Copper (Cu) mg/l	<0.001	0.002	0.004	0.002	0.003	<0.001	1.5
Zinc (Zn) mg/l	0.086	0.054	0.076	0.041	0. 034	0.0143	1.0

Water quality parameter of Ekerikana river showed that pH recorded the highest value in station S with a value of 7.67(units) and recorded the minimum in sampling station T with a pH value of 7.06 (units). The pH value of most natural water is between 6.0 and 8.5, although lower values can occur in dilute waters high in organic content and higher value in eutrophic waters. The mean pH value for Ekerikana water was found to be 7.5 (units). However, the mean values of pH were in the permissible limits as specified by WHO and FMENV. DO concentration value of water varies with temperature, salinity, turbulence, the photosynthetic activity of algae and plants and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase [15]. The concentration of DO was highest in sampling station S and X with DO values of 3.25mg/l each and recorded the minimum value at sampling station V with a value of 1.02mg/l. The mean value for all sampling stations was 2.05mg/l which is below the permissible limit as specified by WHO and FMENV recorded the higher levels of dissolved oxygen during his research which could be as s result of decrease in the presence of organic matter and nutrient during the sampling. BOD recorded the highest value at sampling station X, R and S with BOD value of 45.4mg/l each with its minimum value being recorded at sampling station V with a value of 34.2mgl. The mean value of BOD in all sampling stations was 43.68mg/l. However the values of BOD were above the permissible limit as specified by WHO and FMENV in all sampling stations. The temperature of surface water is influenced by latitude, altitudes and seasons, time of day, air circulation, cloud cover, the flow and the depth of the water body [15]. Temperature recorded the highest and minimum value at sampling station R and V with a temperature value of 29.1^0C and 28.1^oC respectively. The mean temperature was recorded as 28.5^oC which is above the permissible limit as specified by WHO and FMENV recorded a lower temperature which is within the permissible limit which probably may be as a result of low altitude or flow and depth of the water body. The electrical conductivity of Ekerikana river water recorded had the highest value at sampling station X of 32,600 (µS/cm) and minimum value at sampling station of 4090 (µS/cm) with a mean value of 20,005 µS/cm which is above the permissible limit as specified by WHO and FMENV. Turbidity of Ekerikana river water recorded the highest value at sampling station R and minimum value at sampling V with a value of 26.7 (NTU) and 1.4 NTU respectively. All other sampling stations were below the permissible limit as specified by WHO and FMENU except for sample station R, T and U that were above the permissible standard recorded higher levels of turbidity in all sampling stations which ranged from 19.83 NTU to 62.50NTU in Ekerikana River. Total suspended solid (TSS mg/l) value was insignificant as TSS was not recorded in all sampling stations. The value of total dissolved solid ranged from 2863mg/l to 22,820mg/l. Sampling station X recorded highest value of TDS with 22,829mg/l and minimum value of 2863 was recorded in sampling station R with a mean value of 14003.5 which is above the permissible limit as specified by WHO and FMENV. Total

hydrocarbon content recorded the highest value in sampling station R and V with a value of 2.42 mg/l each and minimum value at less than 0.20 which was insignificant and below permissible limit as specified by WHO and FMENV.

Iron (Fe) exhibited the lowest concentration in all sampling station compared to the high concentration recorded by Manganese (Mn) exhibited a concentration below the permissible limited as specified by W.H.O. and FMENV. Lead (Pb) mg/l the concentration of lead recorded in all sampling station compared was statistically insignificant. Zinc (Zn) mg/l exhibited a low concentration when compared with the high values reported by other researchers in the preliminary assessment of heavy metals level in surface water.

Iron (Fe) exhibited its highest concentration at sampling station A with a value of 0.086mg/l and the lowest value at sample station X with 0.0143mg/l. The mean value of Fe, Mn, Pb, Cu, Zn are 0.005mg/l, 0.094mg/l, <0.001mg/l, 0.00275mg/l, 0.05mg/l respectively. These values are less significant when compared to the value determined by on similar water bodies.

It was seen from the result that the discharge of refinery effluent into Ekerikana River has been the major cause of pollution in the creek; though the treatment plant was not efficient to remove pollutant to appreciable levels, it has affected the colonies of macro-invertebrate (fishes, mosses *etc*). An earlier literature by has also observed the toxic effect of oil on zooplanktons and other marine organism though the sediment environments are not left out of the effect of the pollution.

CONCLUSION

No matter how little the contaminant may be in the discharged waste water, the interaction of such residual chemical/biological with the existing physical environment may subject the ecosystem therein to partial or outright pollution and loss of environmental aesthetic. The analyzed result indicated that the surface water from Ekerikana River had a high concentration of physico-chemical parameters discovered to be above the permissible limit as specified by WHO and FMENV except for pH and dissolved oxygen that were within and below the permissible limit respectively. The result obtained from the present study area has shown that Ekerikana River is highly polluted. However, all the metals examined were all within the acceptable limits by WHO and FMENV. An effective approach towards controlling effluents discharged via catchment needs should be considered so as to minimize or reduce pollution of Ekerikana River; however, there is need for continuous monitoring of pollution levels in the River.

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