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Nitrate and Phosphate Pollution in Surface Water of Nwaja Creek, Port Harcourt, Niger Delta, Nigeria

Adeola Alex ADESUYI[1,3], Valerie Chinedu NNODU[2], Kelechi Longinus NJOKU[3], Anuoluwapo, JOLAOSO[4]

[1]Environmental Impact Assessment, Environment Department,
Shell Petroleum Development Company, Port Harcourt, Nigeria

[2]Department of Environmental Management, Faculty of Environmental Sciences, Nnamdi Azikiwe University,
Awka, Anambra state, Nigeria

[3]Environmental Biology Unit, Cell Biology and Genetics Department, University of Lagos,
Akoka, Lagos, Nigeria

[4]Environmental Biology Unit, Cell Biology and Genetics Department, University of Lagos,
Akoka, Lagos, Nigeria

Abstract: ***Anthropogenic activities are major sources of phosphate and nitrate pollution in aquatic ecosystems. These nonpoint sources of nutrients are difficult to measure and regulate because they are derived from activities dispersed over large expanse of land and are variable in time because of weather and climate changes. In rivers, lakes and streams they cause various problems such as toxic algal blooms, hypoxia, fish deaths, loss of biodiversity and species composition, loss of aquatic plant beds and coral reefs, and other problems. Nutrient enrichment seriously impairs aquatic ecosystems usage, purposes and functions. The impacts of human and industrial activities on the nitrates and phosphate level of Nwaja Creek, Niger Delta, Nigeria were studied in this research work. The surface water samples were collected from seven sampling stations (S1 to S7) along the creek for three months May-July, 2015 (peak period for rainfall) for analyses of their temperature, pH, dissolved oxygen (DO), nitrate and phosphate content using standards methods and procedures. In this present study DO, nitrates and phosphates have high variation across sampling stations and were quite very high when compared to other creeks surface water in Niger Delta. pH ranged between 4.16 – 7.01, temperature ranged between 21.5 – 30.05 ^{o}C, DO ranged between 4.50 – 13.50 mg/L, phosphate ranged between 0.89 – 14.91 mg/L, nitrate ranged between 0.56 – 9.96 mg/L. The statistical analysis of the parameters indicates that Nwaja creek surface water is highly polluted with nitrate and phosphate. Phosphate level is far above FEPA permissible limits (13.50>5.0 mg/L) and nitrate is significantly equal to it (9.96=10.0 mg/L). There is urgent need for constant monitoring and assessment of these creeks (water and sediment) for other pollutants (physicochemical, heavy metals, hydrocarbons etc.).***

Keywords: Anthropogenic, nitrate, phosphate, Nwaja creek, surface water, monitoring.

1. Introduction

Most of the earth is covered by water, about 70% is occupied by freshwater and oceans. The vast majority of that water, however, is in forms unavailable to land-based or freshwater ecosystems. Less than 3 percent is freshwater, most of which are not potable for drinking, or easily available to irrigate crops. And of that 30%, more than two-thirds is locked in glaciers and ice caps. Freshwater lakes and rivers hold 100,000 km^3 globally, less than one ten-thousandth of all water on earth [1]. On earth, water is an essential natural resource for sustaining life and the environment [2].

Worldwide pollution of rivers, streams and lakes has been one of the most crucial environmental problems since the 20th century [3, 4]. The major sources of pollution in streams, rivers, and underground water arises from anthropogenic activities largely caused by the poor and unhygienic living habit of people as well as the unfriendly environmental practices of factories, industries and agricultural practices, resulting in the discharge of effluents and untreated wastes [5, 6]. Studies carried out in most cities in Nigeria had also shown that industrial effluents passed through drainages, sewerages and canal channels till they get into receiving lakes, streams and rivers [5,7-8]. This has led to high load of pollutants such as ammonia, nitrate, phosphorus, sulphates, Pb, Ni, Cr, Ni, Fe, PAHs, TPH etc. in most of water bodies [5, 9].

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, like serving as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fishes [3]. The activities of the oil exploration in the Niger-Delta region of Nigeria have impacted negatively on the surface water quality around the area [3]. Most of the streams, rivers and lakes around the Niger-Delta region of Nigeria are impaired because of pollution by crude oil and other associated pollutants [10-11]. Rivers and groundwater resources are the most important freshwater resource for man. Unfortunately, both resources are being polluted by indiscriminate disposal in sewerage, industrial wastes, acid deposition and plethora of human activities, which affects their physico-chemical characteristics and microbiological quality, and have led to various deleterious effects on aquatic organisms [12].

Causes of water pollution in developing countries are domestic waste based surface water pollution, industrial based surface water pollution, agricultural pollution of surface water and oil spill based surface water pollution [13]. One of the most critical challenges facing developing countries is improper management of vast amount of wastes generated by various anthropogenic activities (domestic and industrial) and Nigeria is not exempted from this crises. In the Niger Delta, the problem of water pollution has been of concern to all stakeholders, following the rate and extent of degeneration of the environment and water bodies by human activities. The oil exploration and exploitation activities in the Niger Delta have increased the surge of human population to major activity areas in the region and one of the major cities is Port Harcourt. The presences of several companies and the high population density in coastal cities have caused adverse effects in the area [14]. Spillage of oil into surface waters is as a result of leakage of hydrocarbon from the pipes either through poor maintenance of oil pipelines, crude theft or sabotage. Waste water from oil and gas production (brines) has also been highlighted to be the main source of introduction of the following pollutants; sodium, calcium, ammonia, boron, trace metals, and high total dissolved solids (TDS) into surface waters in Niger delta [15].

Phosphorus is present in natural waters either as orthophosphate or undifferentiated organic phosphate. In water, the combined form of the element is continually changing due to the process of decomposition and synthesis between organically bound forms and oxidized inorganic forms [16]. Phosphorus gets into the water through various sources including leached or weathered soils from igneous rocks and domestic sewage containing human excrement. Other sources are phosphates from detergents in industrial effluents and run offs from fertilized farm lands. Phosphorus is very important for plant growth including algal growth in water [17]. Phosphates are absorbed by aquatic plants and algae and constitute an integral part of their body component. The total concentration of phosphorus in uncontaminated waters is reported to be about 0.01 mg/L [16]. Elevated level of phosphates in surface water is one of the most serious environmental problems because of its contribution to the eutrophication process and impairment of water quality. Nitrate (NO_3) is the major form of nitrogen found in natural waters and is one of the common pollutants in surface water [18].

Other forms of nitrogen present in natural waters include molecular nitrogen (N_2) in solution; ammonia as NH_3; ammonium and ammonia hydroxides (NH_4 and NH_4OH). Davies *et al*. [19] reported that surface waters rarely contain as much as 5 mg/L and often less than 1 mg/L of nitrate. However where inorganic fertilizers are been used ground waters may contain up to 1000 mg/L. Major sources of nitrate pollution vary from agrochemicals, human and animal wastes, sewage leaks, landfills, application of wastewater for irrigation, industrial wastes, etc. Unpolluted natural waters contain only small amounts of nitrate. In surface water, nitrate is a nutrient which is taken up by plants and assimilated into nucleic acid. Nitrate anion has both beneficial and harmful uses. On the positive side, Nitrates (NO_3^-) are essential plant nutrients that are important ultimately for protein synthesis. They are responsible for the growth of plants and also nitrogen fixation. Nitrates are generally found in nature they are the end product of the aerobic decomposition of organic nitrogenous matter as well as the decomposition of organic micro-organisms. Contamination in drinking water has been implicated to be the causes of major health problems e.g. blue baby syndrome, when present at higher levels; World Health Organisation [20] prescribes a maximum permissible limit of 50 mg/L for nitrate in drinking water.

Environmental monitoring of surface water indicated that streams and rivers in Niger delta Nigeria are showing increasing trend of water pollution due to increased population, industrialization, urbanization and exploration [10, 21]. Many studies on surface water physicochemical parameters and pollution indices have been conducted in various water bodies and their sediments in River states and Niger delta [14], but there is paucity of information with regards to nitrate and phosphate enrichment in the water bodies. This research work is a follow up to Arimieari *et al* [22] research on analysis of surface water in some selected creeks in Port Harcourt, and discovered they are highly polluted with nitrates, chlorides and sulphates. The quality assessment and the physicochemical analysis of Nwaja creek surface water has not been reported, hence, this research was conducted to investigate the pH, temperature, DO, nitrates and phosphates level with a view of providing baseline reference data.

2. Materials and Methodology

2.1 Study Area

Port Harcourt is located within the Niger Delta Basin of Southern Nigeria. Port Harcourt is located within the eastern lower Niger Delta in the south eastern part of Rivers State of Nigeria (Figure 1). It is situated at the right bank of the Bonny River approximately 65km inland from the Bight of Bonny. Geographically, the area lies between latitudes 4030' and 5000'N and longitudes 6045' and 7030'E. It is bounded on the East and West by meandering Creeks, on the South by first the block-yard creeks, then the Bonny River and finally mangrove swamps and on the north by Abia State. The southern part of the town stands largely on raised levees with silts and clay foundation. These afford permanently dry and firm points within the zone of its fresh water swamps of the Niger Delta. It covers an area of 290 km^2 and the mean annual temperature is about 28 ^{0}C.

Nwaja Creek is in the upper Bonny Estuary of the Niger Delta. Seven sampling stations (S1-S7) were located along the Nwaja Creek, to cover all land-based sources of contaminant inputs into the creek as well as presumably uncontaminated locations (Figure 2). The sampling stations and their geographical coordinates were all recorded and documented (Table 1).

Table 1: Nwaja creek sampling stations GPS coordinates

S/n	Sampling station code	Longitude	Latitude
1.	S1	7.015592	4.809313
2.	S2	7.015585	4.809011
3.	S3	7.015562	4.808353
4.	S4	7.015752	4.807685
5	S5	7.015805	4.807083

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6.	S6	7.015737	4.806236
7.	S7	7.015919	4.805435

Figure 1: Showing River state, Niger Delta, Nigeria (Source: google map)

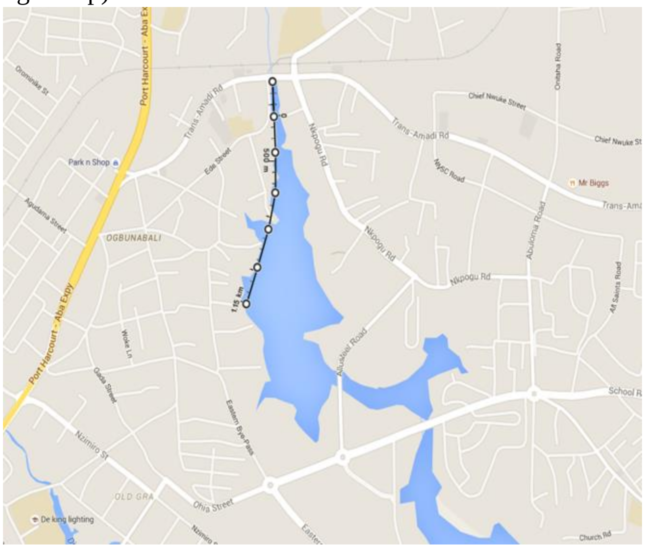

Figure 2: Map showing sampling stations (Source: google earth map)

2.2 Sample Collection and Analyses

The study adopted both field and laboratory based procedures to generate the data required. Surface water samples were obtained at seven sampling stations (S1 to S7) located at equal distances of 100km along the stretch of Nwaja creek (Figure 2). The sampling was monitored for 3 months (May-July, 2015) the peak period for rainfall.

Two 2.5-litre sample bottles that were previously prepared (treated) were used to obtain spot surface water samples using the grab method from the predetermined points on the course of the creek. After collection, the sample bottles were immediately corked under water to prevent oxidation. Of the two samples collected, one was immediately analyzed for the following parameters in the field (In-situ): pH, Temperature and Dissolved Oxygen) using Digital Meters. A second sample was preserved in a cooler of ice (usually, below 5˚C) and taken to the laboratory for nitrate and phosphate analyses. Phosphate and nitrates was determined by standard limnological methods of APHA [23]. Phosphates (PO_4^{2-}) were determined using stannous chloride method adopted for the estimation of phosphate-phosphorus. Nitrate (NO_3) was determined using Brucine method which was based on the reaction of nitrate with Brucine in an acidic medium to produce a yellow colour at moderate temperature. Phosphate and nitrate assessment will help to show if the surface water has marked minor impairment for aquatic wildlife and fishes, major impairment as a source of drinking water) or and major impairment for industrial uses.

The results obtained were subjected to statistical analysis using the analysis of variance (ANOVA). Detection of differences among the location means for significance was done by Duncan's New Multiple Range Test (DNMRT) procedures at 5% level of probability.

3. Result and Discussion

Table 2: Result of monthly physicochemical parameters

Parameters	Month	Station 1 Dstream	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7 Upstream	FEPA limit
pH	May	6.91	6.88	4.46	4.99	4.54	4.45	4.89	6.5-9.5
	June	6.85	6.03	5.89	5.08	6.45	5.78	4.16	
	July	7.01	6.23	6.04	6.50	6.23	5.89	6.45	
Temp. (°C)	May	26.9	27.7	23.6	24.8	22.8	27.5	26.2	20-33
	June	26.5	28.9	21.5	28.7	25.5	26.5	25.8	
	July	25.8	30.5	25.9	27.9	24.0	29.7	30.0	
DO (mg/L)	May	5.10	8.20	9.80	9.10	10.90	8.30	8.20	5-7.5
	June	6.45	10.50	13.50	12.80	9.50	11.80	12.40	
	July	4.50	11.80	12.70	15.56	12.58	9.90	11.40	
Phosphate (mg/L)	May	9.98	10.76	12.01	10.15	9.56	12.76	14.91	5
	June	2.55	9.80	7.90	8.60	11.50	7.56	9.44	
	July	0.89	2.56	7.30	5.08	6.65	8.05	8.23	
Nitrate (mg/L)	May	3.59	4.89	5.34	5.78	5.16	9.96	8.98	10
	June	1.45	0.89	0.56	1.05	0.80	0.95	0.97	
	July	2.56	3.56	2.56	4.24	1.56	2.06	1.03	

The water samples from all the points were dark in colour and had foul smell except at sampling station 1 (downstream). The foul smell might be due to presence of human and domestic waste along the creek. According to Fakayode [24], the pH of a water body is very important in determination of water quality since it affects other chemical reactions such as solubility and metal toxicity. The monthly pH values ranged between 4.45 – 6.91 in May, 4.16 – 6.85 in June and 5.89 – 7.01 in July (Table 2). The highest pH value was obtained in station 1 (downstream) while the least was obtained in station 7 (upstream) (Figure 3). There was no monthly significant variation ($P>0.05$). There was also no significant difference ($P>0.05$) across the sampling stations except in station 1 and 2 (downstream). These pH values recorded in this study were relatively higher than 4.00 – 5.61 recorded by Seiyaboh *et al.* [25] in the Nun River but similar to those obtained in Igbedi creek by Seiyaboh *et al*. [26]. The pH values fall within the optimum range of most aquatic organisms and will support rich primary productivity and fish production.

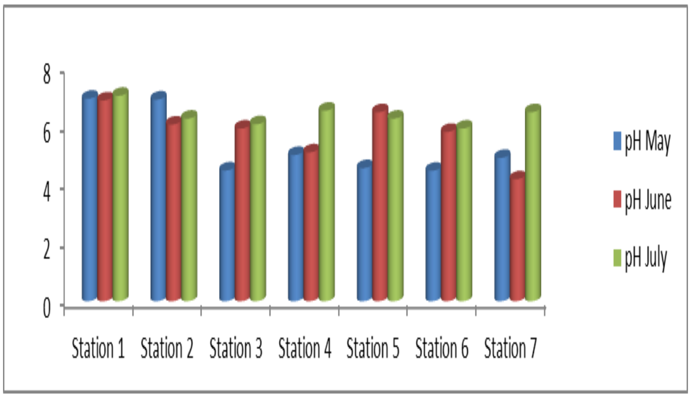

Figure 3: Showing monthly pH data across all the sampling stations

The surface water temperature of the river fell within the acceptable range (20-33^{o}C) as recommended by Nigeria Federal Ministry of Environment for aquatic life in the tropical region. The monthly surface temperature values range between 22.8 - 27.7 ^{o}C in May, 21.5 – 28.9 ^{o}C in June and 24.0 – 30.5 in July (Table 2). The highest temperature was recorded in sampling station 2 (30.5 ^{o}C) while the lowest was recorded in station 3 (21.5) (figure 4). When the results of this study were subjected to statistical analyses, there was no monthly significant difference ($P>0.05$) in temperature but significant variation ($P<0.05$) exists from one sampling station to the other. This is similar to the observation of Chindah and Braide [27] for Elechi creek and Deekae *et al* [28] for Luubara creek. The low monthly temperature in Station 3 could be attributed to the shielding of the sun by woody plants and aquatic vegetation common in this station.

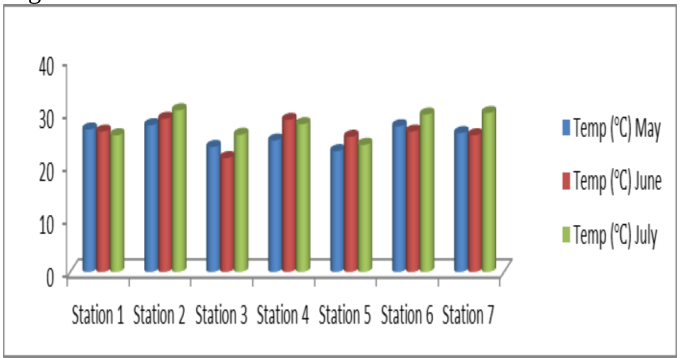

Figure 4: Showing Surface temperature across all the sampling stations

Dissolved oxygen (DO) is very crucial for survival of aquatic organisms and it is also used to evaluate the degree of freshness of a river [24]. The DO variations (Table 2) between months and stations were significant ($P<0.05$), it ranged between 4.50 – 6.45 mg/L in station 1, 8.20 – 11.80 mg/L in station 2, 9.80 – 13.50 in station 3, 9.10 – 13.56 mg/L in sampling station 4, 9.50 – 12.58 mg/L in station 5, 8.30 – 11.80 mg/L in station 6 and 3.70 to 12.40 mg/L in station 7 (Figure 5). The DO level of this water has high variation and it is relatively high as compared with other result by Onwugbuta-Enyi *et al*. [29] in Bodo creek but similar to DO values recorded by Atobatele and Olutona [30]. A lot of factors could be responsible for this finding; the perpetual dumping of waste especially domestic wastes have been implicated to increase the levels of nitrate and phosphate in the stream water leading to increase in plant and algae growth in the water which subsequently deplete the oxygen levels and long days of intensive heat as a result of sunlight which seem to have increase photosynthesis by phytoplankton, utilizing carbon dioxide and giving off oxygen. The standard for sustaining aquatic biological life is stipulated at 5 mg/L; a concentration below this value adversely affect biological life, while concentration below 2 mg/L may lead to death for most fishes [31].

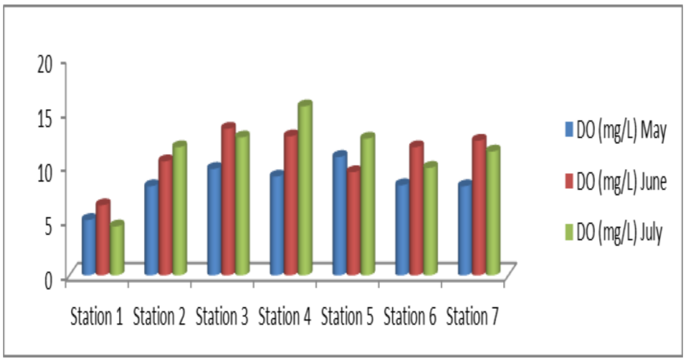

Figure 5: Showing dissolved oxygen (DO) across all the sampling stations

Phosphate (PO_4^{3-}) can be found as a free ion in water systems and as a salt in terrestrial environments used in detergents as water softeners. Phosphates can be in organic form (organically-bound phosphates) or inorganic form (including orthophosphates and polyphosphates) [30]. The concentration of phosphate varied from 0.89 – 8.23 mg/L in the month of May, 2.55 – 11.50 mg/L in June and 9.56 – 14.91 mg/L in July (Figure 6). The highest concentration of phosphate was obtained in station 7 (14.91 mg/L) and the least in station 1 (0.89 mg/L). The elevated phosphate concentration in water have been linked to increasing rates of plant growth, changes in species composition and proliferation of planktonic and epiphytic and epibenthic algae, resulting in shading of higher plants [31]. In this study, phosphate was more concentrated than nitrate. A plausible reason underlying the concentration differential is the unique behavior of phosphorus in shallow waters. Phosphorus in its soluble state (phosphate) quickly adsorbs at the surface of mud and re-enters the water column [29].

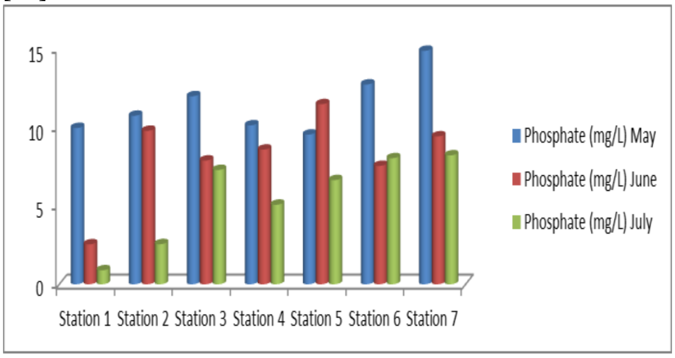

Figure 6: Showing phosphate level across all the sampling stations

The monthly nitrate values ranged between 3.59 – 9.96 mg/L in

May, 0.56 – 1.45 mg/L in June and 1.03 – 4.24 mg/L in July (Figure 7). The highest value of nitrate (9.96 mg/L) was recorded at sampling station 6 (upstream) in the month of May while the lowest (0.56 mg/L) was recorded at sampling station 3 (midstream) in the month of June. There was no significant (P>0.05) variations in the nitrate values across the sampling station except at station 6 and station 7. There was monthly significant difference (P<0.05) across all the stations. These values are similar to those observed previously by Seiyaboh et al. [25] in surface water in the Niger Delta. However, these values are quite high but it is still below the FEPA limit of 10 mg/L. High nitrate level in Nwaja creek surface water could be caused by the release of human waste and sewages. Runoff and organic matter decomposition in surface water also produced inorganic nutrients such as ammonia, nitrate and phosphates with resultant effects of eutrophication and other serious ecological impairments of such water body [8].

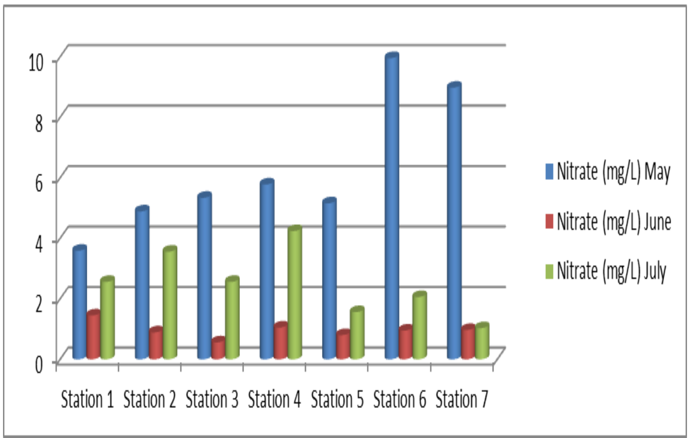

Figure 7: Showing nitrates level across all the sampling stations

High nitrate levels in water have serious health implications and can result in a number of diseases. This is why the World Health Organization (WHO) originally sets the drinking water standard of 45 mg/L. Generally, nitrate is a cause for concern in drinking water at levels greater than 10 mg/L. At concentration levels greater than this there is an increased risk of babies developing infant methaemoglobinaemia, a disease commonly known as 'blue baby' syndrome [32]. Clinical effects become obvious when drinking water contains nitrate in the neighbourhood of 50 mg/L. It has also been suggested that chronic exposure to high levels of nitrate in drinking water may have adverse effects on the cardiovascular system. The WHO [20], however, reported that an inverse relationship between cardiovascular mortality and nitrate concentration in water supplies had been demonstrated. Bowman [33] also reported that increased concentrations of nitrate often caused blood disorders.

4. Conclusion

According to Mitsch and Gosselink [34] mangrove wetlands are rated high nutrient environments, input of nitrate and phosphate into Nwaja creek through runoffs from adjoining agrarian lands and wastes (human and domestic) cannot be overemphasized. This exogenous claim for the elevated nitrate-phosphate status is further strengthened by the fact that the lithology of the Niger delta is essentially poor in these nutrients [35]. As reported by Arimieari *et al.* [22] about high pollution of nitrates, chlorides and sulphates in some selected surface waters of Port Harcourt creeks, Nwaja creek surface water is also becoming highly polluted with nitrates and phosphates and there is urgent need for environmental intervention of pollution in Nwaja creek and other Port Harcourt creeks to protect the water bodies, maintain their water quality and enhance their usage for domestic purposes. Commissioning of monitoring and assessment team for aquatic environment to document (where data is available) and provide evaluation studies (where there is paucity of data) for environment planning and management of the vast endowed water bodies. The team will compare data with guidelines and prescribes environmental protection measures and control.

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Authors Profile

Adesuyi, Adeola Alex is a PhD Research Intern in the Environment Department at Shell Petroleum Development Company in Port Harcourt Nigeria, where he is part of the Impact Assessment Team. He holds a B.Tech. (Hons) and MSc. Degree in Environmental Biology from Ladoke Akintola University of Technology, Ogbomoso, Oyo state, Nigeria in 2008, and University of Lagos, Akoka in 2012 respectively. He is presently a PhD student in Environmental Biology, Cell Biology and Genetics Department, University of Lagos, Akoka. His interests are but not limited to; Environmental monitoring, Impact assessment and evaluation studies, waste management and control, water and effluent treatment, ecotoxicology, remediation.
Email: biologistalex@gmail.com.

Nnodu, Chinedu Valerie is a Professor of Environmental Management of Nnamdi Azikiwe University, Awka Anambra State, Nigeria. She holds a B.Sc. Degree with Honours in Geography from the University of Sierra Leone (Fourah Bay College) in 1983. M.Sc. in Geography specializing in Hydrology and Water Resources, from University of Nigeria, Nsukka, Enugu State in 1986. Another M.Sc. Degree in Environmental Management in 1998 and a Ph.D. Degree also in Environmental Management in 2009, both of which are obtained from Enugu State University of Science and Technology, Enugu.
Her area of specialization is Hydrology and Water Resources. Areas of research interest are: Urban Water Supply and Sustainability Indicators, Water, Land and Air Pollution, Environmental Impact Assessment, Climate Change Issues and Mitigation Measures and Environmental Geomorphology and Soil Erosion Studies. She has published extensively in scholarly journals, both nationally and internationally. Some major publications include development of Sustainable Indicators for Sustainable Water Supply for Developing Countries, Development of an Integrated Plan for Flood Early Warning System (FEWS), developing a Community Livelihood Action Plan (CLAP) for Assessment of Erosion Ravaged Communities in Anambra State. Prof. Nnodu, First Vice President of Environmental Management Association of Nigeria (EMAN); Member –Third World Organization of Women in Science (TWOWS), Environmental and Behaviour Association of Nigeria (EBAN)
E-mail address: valeriennodu62@gmail.com

Njoku L Kelechi is Senior Lecturer in the Department of Cell Biology and Genetics, University of Lagos, Akoka, Nigeria. He holds a Bachelor Degree in Biology (1997) from the University of Calabar, Calabar, Nigeria, and then completed a Masters and PhD degree in Environmental Biology from the University of Lagos, Akoka, Nigeria in 2002 and 2008 respectively. His research focuses on environmental monitoring and impact assessment studies, remediation, biotoxicity etc. Dr. Njoku is currently working on the assessment of the environmental status of Lagos Lagoon wetlands, vermiremediation of polluted soils etc. He has extensive publications in both national and international scholarly Journals. He is a member of Nigerian Environmental Society (NES); Nigerian Society for Experimental Biology (NISEB); and Society for Environmental Toxicology and Pollution Mitigation (SEPTOM).
E-mail address: kecynjoku@gmail.com.

Jolaoso Anuoluwapo is a PhD student in the department of Cell Biology and Genetics (Environmental Biology option), University of Lagos, Akoka, Lagos, Nigeria. She holds a BSc. Edu. in Biology from University of Ilorin, Nigeria, in 2005 and an MSc in Environmental Biology from the Department of Cell Biology and Genetics, University of Lagos, Lagos, Nigeria in 2012. Her research interest has been on environmental audit and impact assessment, ecotoxicology, and remediation. She is presently working on a number of environmental monitoring projects.
E-mail: anujolaoso@gmail.com.