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Effect of Effluents From Warri Refinery Petrochemical Company WRPC on Water and Soil Qualities of "Contiguous Host" and "Impacted on Communities" of Delta State, Nigeria

John Kanayochukwu Nduka[1] and Orish Ebere Orisakwe[2]*

[1]*Pure & Industrial Chemistry Department, Nnamdi Azikiwe University, P.M.B 5025, Awka, Anambra State, Nigeria.*
[2]*Toxicology Unit, Department of Pharmacology, Nnamdi Azikiwe University, P.M.B. 5001, Nnewi Campus.*

Abstract: This study investigated the effect of refinery effluents on different sources of potable water supply in two areas of Niger Delta contiguous host and impacted on communities of Delta State, Nigeria (surface water, shallow well water and borehole water) in Ekpan, its adjoining communities and creeks. Since open and underground water bodies are regarded as final recipient of most environmental pollutant, we sought through the study to provide data on pollutant load of potable water supply of the study area. Cadmium, chromium, lead and manganese were determined using Atomic Absorption spectrophotometry; physico-chemical parameters such as nitrate,nitrite, pH, Biological oxygen demand BOD, Total hardness TH, salinity and electrical conductivity EC were all determined using their standard methods. Surface water of Aja-Etan and Ijala had highest levels of cadmium (1.45±0.01 and 1.20 ± 0.0(mg/l), that of ifie-kporo and Ekpan had highest lead (1.00 ± 0.01mg/l). Ekpan borehole water is more acidic (4.79± 0.01) than others. Agigba and Ajamimogha surface water had highest level of manganese (2.40 ± 0.03 and 2.20 ± 0.03mg/l). With the exception of Ekpan shallow well, BOD and hardness were in highest concentration in surface water. Some of the parameter were above WHO standards and USEPA maximum contaminant level MCL.

Keywords: Refinery effluents, contiguous host communities and impacted on communities, heavy metal, chemical pollutants, potable water supply, Niger, Nigeria.

INTRODUCTION

There is a strong relationship between human activities and pollution of the environment. The recognition of this connection and the need to protect human health, recreation and fisheries production led to the early development of water quality regulations and monitoring methods [1,2]. Contaminats of aquatic ecosystems can be confirmed by determining levels of contaminants in water, sediment and organisms [3,4]. Industrial effluents, agricultural run-offs, transport, burning of fossil fuels, animal and human excretions, geologic weathering and domestic waste contribute to the metal levels in water bodies [4-8]. Rapid urbanization and industrialization of Warri and its environs between 1968 and 1990 created pollution potentials that are as high as the sources of pollution. The rivers, estuaries, creeks and air have been contaminated for decades [9]. The Warri Refinery and Petrochemical Company at Ekpan is the largest in Nigeria and has a processing capacity of 125,000 barrels per day of crude oil.

Nigeria's crude oil is known to contain heavy metals in varying proportion [10]. The metallic components in crude oil are in the form of metalloporphyrin chelates, transition metal complexes, organometallic compounds, carbonyl acid salts of polar functional groups and colloidal minerals [11]. Other inorganic constituents of crude oil are sulphur, nitrogen and oxygen [12]. It is expected that refinery effluents will contain some of these metals and inorganic substances in reasonable quantity. Discharge of some metals into natural waters at increased concentration in sewage, industrial effluent or from mining and refining operations, can have severe toxicological effects on aquatic environment and humans [13]. These environmental pollutants which are environmentally mobile tend to accumulate in organisms, and become persistent because of their chemical stability or poor biodegradability [14].

Heavy metals gain access into the River system from both natural and anthropogenic sources and these get distributed into the water body and sediments during the course of their transport. A catchment area containing mineralized rocks (River beds containing solid minerals) will usually have elevated metal levels as, the trace metal content of River water is normally controlled by the abundance of metals in the rocks of the River's catchment area and by their mobility [15]. In coastal environments the influence of salt-water intrusion is often significant. The overall implication of this is that the hydrochemical facies of groundwater changes in response to its flow path history, that is, underground water quality is dependent on pollution status of it's environment [16]. The subsurface flow system of the Niger delta is as complex as the braided nature of the streams and rivers therein [17], coupled with the problems of environmental pollution, degradation, river siltation, coastal erosion, as well as extermination of wildlife, fauna and flora that are of the fate of oil bearing communities in Niger-delta region. The Warri Refining and Petrochemical Company (WRPC)

*Address correspondence to this author at the Toxicology Unit, Department of Pharmacology, Nnamdi Azikiwe University, P.M.B. 5001, Nnewi Campus, Nigeria; E-mail: eorish@aol.com

accentuate these problems by discharge of its untreated effluents into adjoining surface waters (natural receptors) hence the essence of this study is to ascertain the pollutant load of potable water in the study area (Ekpan creeks) with a view of comparing the pollution profile of the potable water supply of the coastal or creek areas and Warri mainland data from our previous studies[18], as the data generated will assist policy makers and regulatory agencies on future policy issues.

Study Areas: Ekpan is located within longitude 5.54^{o}E and 5.7^{o}W and latitude 5.13^{o}N and 5.6^{o}S. It is one of the towns that make up Uwvie local government area of Delta state which has been subsumed by the cosmopolitan city of Warri. It is host to Nigeria's biggest refinery and petrochemical company established in 1978, with a processing capacity of 125,000 barrels per day of crude oil. Ekpan, Ifie-kporo, Aja-Etan and Ijala are refered to as "contiguous host communities". These are the host communities that donated their land jointly for the establishment of the company. The surface water of the host communities receive effluents directly from the company WRPC. The Ekpan River connects these four communities with Warri River which also connects several communities (Creeks)- Agigba, Ugbuwangue, Egboko-Itsekiri, Omadino, Ajamimogha, Ekurede-Itsekiri, Okere, Ikpisan, Ugboko and Inorin referred to as "Impacted on communities''. Impacted on communities are communities whose surface water receive pollutants from surface water of host communities. This is because the surface waters are inter-connected. The River then diversified into numerous creeks and mangrove swamps [19].

Aladja River which receives effluents from Delta Steel Company DSC, Aladja, and is connected with Warri River, is 50km from Ekpan (Fig. **1**). Other activities along the interconnected network of fresh water aquifer include auto-mechanic workshops, fishing, timber logging, River port, loading and offloading of crude oil and refined fractions and rubber processing. The area experiences tropical humidity of the semi-hot equatorial type with a mean annual rainfall of about 3000mm [20]. The wet season period stretches from April to October each year, with occasional precipitation in the dry season November-March. The study areas are located within the mangrove swamp of equatorial rainforest belt of Nigeria, marshy and have shallow water aquifer. The average depth of boreholes in the study area is between 150-200m while that of shallow (hand dug) wells are between 16-45m deep. Though there are seasonal fluctuations with the water column rising during rainy season but it decreases or may dry up in the dry season. Underground water (borehole and shallow well waters) is a well drilled into the sub-surface aquifer for the purpose of exploiting ground water. Aquifer is a porous and permeable rock hosting water or a water saturated geological unit or formation that may be exploited for water for economic use. It is solely to provide water for drinking, domestic and industrial uses. Boreholes are situated in unconfined sedimentary basin that exceeds 2000m.

MATERIALS AND METHOD

The composite water sampling method was employed in collecting the samples. The pH was determined *in situ* using digital pH meter (Consort 121, Belgium). The other samples collected with clean plastic bottles were kept in bucket full of ice blocks, the analysis of other parameters were determined within four hours of sample collection. Nitrate was analyzed using the Bruccine Colorimetric Method [21], while nitrite was spectrophotometrically determined according to the Greiss Method of Montgomery and Dymock [22], spectrophotometric readings were taken at 550nm in a Bauch and Lomb Spectronic 20 photometer and concentrations read off from a standard curve. Complexiometric titration method was employed in the determination of Total Hardness TH while Biochemcal Oxygen Demand (BOD) was determined electrochemically [23]. A digital conductometer (Consort K120, Belgium) was used to determine Electrical conductivity (EC). We used a digital meter (Consort p107) for the determination of the salinity.

Heavy metal determination: Heavy metals (Cd, Cr, Pb and Mn) were determined at their respective wavelength of 227nm, 358nm, 281.5nm and 278nm using the Bulk Scientific Atomic Absorption/Emission Spectrophotometer –200A with detection limit of 0.01mg/l for the four metals. Soil samples were determined after digestion. Two grammes of subsurface soil collected at 100cm depth was digested with 15ml HNO_3: $HClO_4$ (5:3) mixture and heated for 120mins while topping the acid, it was allowed to cool, filtered and made up in a standard volumetric flask with de-ionised water before metal determination.

Soil samples for determination of other parameters were prepared by suspending 100g of the soil sample in 500ml of distilled water. Suspensions were left for 24 hrs for proper sedimentation and filtered through cotton wool in the first instance then Whatman No. 40 filter paper and the filtrates were analyzed as stated above. All samples were analysed in quadriplicates. ***Statistical Analysis***: values were reported as mean $\pm$ SEM. Analysis of variance (ANOVA) was employed for between and within group comparison while student's t-test was used for paired comparison. All differences were considered significant at 5% level, therefore a p-value of $p \leq 0.05$ was considered statistically significant.

RESULTS

Table **1** shows the heavy metal (lead, cadmium, chromium and manganese) levels (mg/kg) of potable water of contiguous host communities (Ekpan, Ifie-Kporo, Aja-Etan, Ijala). Aja-Etan and Ijala had the highest concentration of cadmium (1.45 ± 0.001 and 1.20 ± 0.01mg/l) respectively, that of Ekpan and Ijala had the highest concenration of chromium (0.80 ± 0.02 and 0.89 + 0.02 mg/l) Ekpan and Ifie-Kporo has the highest level of lead (0.090 ± 0.01 and 1.00 ± .0.1 mg/l).

The physico-chemical parameters of potable water supply of contiguous host communities are shown on Table **2**. The pH of Ekpan borehole is more acidic (4.79 ± 0.00), Ifie-Kporo and Ekpan surface water has highest nitrate and nitrite of 8.40 ± 0.01mg/L and 1.50 ± 0.00 mg/L respectively. The electrical conductivity of Aja-Etan, Ijala, Ifie-Kporo and Ekpan rivers were as follows 598.00 ± 0.03, 500.00± 0.03, 372.00 ±0.03 and 320.0 ± 0.02 (μS/cm) respectively. Salinity was highest in Ijala river (100.00 ± 0.02mg/l) and lowest in Ekpan borehole (5.01 ± 0.00mg/l). With the exception of Ekpan shallow well, BOD and Hardness are in highest concentration in surface water.

Table 1. Heavy Metal Levels (mg/L) of Potable Water Supply of Contiguous host Communities

Community	Water Sample	Cd	Cr	Pb	Mn
Ekpan	River	0.76 ± 0.00	0.80± 0.02	0.90±0.01	0.68±0.01
	Shallow Well	0.60 ± 0.01	0.10±0.00	0.22±0.00	0.28±0.01
	Borehole	0.03 ± 0.00	0.05±0.01	0.01 ± 0.00	0.01 ± 0.00
Ifie-Kporo	River	0.56 ± 0.01	0.50 ±0.02	1.00 ± 0.01	0.60±0.02
	Shallow Well	0.20 ± 0.00	0.40 ± 0.01	0.10±0.00	0.03±0.01
	Borehole	0.01 ±0.00	0.02 ± 0.00	0.04 ± 0.00	0.01± 0.00
Aja-Etan	River	1.45± 0.01	0.18 ±0.00	0.52±0.01	0.55±0.01
	Shallow Well	0.50 ± 0.00	0.05 ±0.00	0.22±0.0	0.20±0.00
	Borehole	0.03 ± 0.00	0.01 ± 0.00	0.04 ±0.00	0.02 ± 0.00
Ijala	River	1.20± 0.00	0.89±0.02	0.36±0.01	0.47±0.00
	Shallow Well	0.21 ± 0.00	0.44±0.01	0.10 ±0.00	0.35±0.01
	Borehole	0.04 ± 0.00	0.10 ± 0.00	0.02 ±0.00	0.20 ±0.00
US-EPA Max Cont Levels	Water	0.005	0.100	0.000	0.5- 0.05*

* WHO Guideline
N =4

Table 2. Physico-chemical Parameters of Potable Water Supply of Contiguous Host Communities

Community	Water Sample	pH	NO_3^- (mg/l)	NO_2^- (mg/l)	Conductivity (µS/cm)	Salinity (mg/l)	BOD (mg/l)	Hardness (mg/l)
Ekpan	River	6.4±0.01	4.30±0.01	1.50±0.00	320.0 ± 0.02	85.00 ± 0.01	5.32 ± 0.00	24.00±0.01
	Shallow Well	4.8±0.00	1.20±0.00	0.20 ±0.00	246.00 ± 0.04	15.10 ±0.01	5.60 ± 0.00	12.00 ± 0.00
	Borehole	4.8 ± 0.00	1.00 ± 0.00	0.01± 0.00	61.00 ± 0.02	5.01 ± 0.00	5.31 ± 0.00	2.00 ±0.00
Ifie-Kporo	River	6.8±0.00	8.40±0.01	1.20 ± 0.00	372.00 ±0.03	95.10 ±0.02	7.10 ± 0.03	26.00 ± 0.00
	Shallow Well	5.6±0.00	1.35±0.00	1.14 ± 0.00	250.00 ± 0.02	25.02 ± 0.01	6.32± 0.00	8.00 ±0.00
	Borehole	5.3 ±0.00	0.22 ±0.00	0.10 ± 0.00	56.20 ± 0.01	10.02± 0.00	3.62± 0.02	3.00 ± 0.00
Aja-Etan	River	6.4±0.00	4.70±0.00	0.65 ± 0.01	598.00 ± 0.03	88.00 ± 0.00	6.23±0.01	21.00 ± 0.00
	Shallow Well	5.8±0.00	1.38±0.00	0.05 ± 0.00	158.40 ± 0.03	35.40 ±0.01	5.14±0.01	13.00 ± 0.01
	Borehole	5.4 ± 0.00	1.20 ±0.00	0.01 ± 0.00	101.00 ±0.01	15.02 ± 0.01	4.11±0.00	6.00 ± 0.00
Ijala	River	6.3 ± 0.01	2.63±0.00	1.14 ± 0.00	500.00± 0.03	100.00 ± 0.02	6.32±0.00	23.00 ± 0.00
	Shallow Well	5.9 ± 0.00	1.42±0.00	0.16 ± 0.00	254.00 ± 0.02	20.02 ±0.01	5.42±0.02	19.00 ± 0.00
	Borehole	5.8 ± 0.00	1.10 ± 0.00	0.60± 0.00	138.40± 0.01	5.10 ±0.02	4.36± 0.01	4.00 ±0.00
WHO (1984)	Water	6.5–8.5	10	**0.50***	1,400		10	150-500*

* EU Guideline 1998
N=4

Table **3** shows the heavy metal (lead, cadmium, chromium and manganese) levels (mg/l) of potable water of the impacted on communities namely Agigba, Ugbuwangue, Egboko-Itsekiri, Omadino, Ajamimogha, Ekured-Itsekiri, Okere, Ikpisan, Ugboko and Inorin.Highest level of manganese is from Ajigba surface water (2.40 ± 0.03 mg/L). In all, cadmium, chromium, lead and manganese levels decreased from surface water, shallow well and borehole (surface water > shallow well water>borehole water).

Table **4** shows the heavy metal and physcio-chemical parameters of surface soil of contiguous host communities. There was presence of the four heavy metals in the soil with the highest being chromium (1.78 mg/kg) and lowest lead (0.22 mg/kg) all are in Ifie-Kporo. Soil pH ranged from slightly acidic 6.82 in Ijala to slightly alkaline to 8.43 in Ifie-Kporo. Electrical conductivity was highest in Aja-Etan and least in Ijala respectively while highest level of salinity was

Table 3. Heavy Metal Levels (mg/l) of Potable Water Supply of the Impacted on Communities

Community	Water Sample	Cd	Cr	Pb	Mn
Agigba	River	0.30± 0.02	0.12 ± 0.01	0.17 ± 0.01	2.40 ±0.03
	Shallow Well	0.15±0.03	0.04±0.01	0.10 ± 0.00	2.00 ± 0.02
	Borehole	0.08 ±0.01	0.01 ±0.00	0.03 ± 0.01	1.00 ±0.01
Ugbuwangue	River	0.53±0.02	0.15 ± 0.03	0.27 ± 0.03	1.20 ± 0.03
	Shallow Well	0.25±0.01	0.05±0.01	0.13 ± 0.04	1.00 ± 0.01
	Borehole	0.08 ± 0.00	0.01 ± 0.00	0.07 ± 0.01	0.50 ± 0.04
Egbokodo-Isekiri	River	0.70 ±0.01	0.15 ± 0.03	0.40± 0.04	1.00 ±0.01
	Shallow Well	0.30± 0.00	0.07 ± 0.02	0.17 ± 0.03	0.80 ±0.03
	Borehole	0.20 ±0.00	0.02 ± 0.01	0.03 ± 0.01	0.45 ±0.03
Omadino	River	0.30± 0.03	0.08 ± 0.03	0.17 ±0.03	2.00 ±0.03
	Shallow Well	0.80±0.02	0.06 ±0.02	0.03 ±0.01	1.60 ± 0.02
	Borehole	0.03 ± 0.00	0.01 ± 0.00	0.03 ±0.01	1.00± 0.01
Ajamimogha	River	0.35±0.03	0.15 ± 0.04	0.27 ±0.04	2.20 ±0.03
	Shallow Well	0.13±0.02	0.01 ± 0.00	0.13 ±0.05	1.80 ± 0.02
	Borehole	0.09 ±0.00	0.01± 0.00	0.07 ± 0.01	1.20 ± 0.02
Ekurede-Itsekiri	River	0.75±0.05	0.14 ±0.03	0.33 ±0.01	1.50 ±0.03
	Shallow Well	0.45±0.04	0.02 ±0.03	0.27± 0.01	0.80 ± 0.02
	Borehole	0.10 ±0.00	0.01 ±0.00	0.07 ± 0.00	0.20 ±0.00
Okere	River	0.50 ±0.04	0.27 ± 0.02	0.35 ±0.03	1.50 ± 0.04
	Shallow Well	0.30 ± 0.02	0.09 ± 0.03	0.17 ± 0.02	1.20 ± 0.03
	Borehole	0.10 ± 0.01	0.01 ±0.00	0.07 ±0.01	0.80± 0.02
Ikpisan	River	0.25±0.30	0.09 ± 0.02	0.34± 0.03	1.80 ± 0.04
	Shallow Well	0.30±0.02	0.01 ± 0.01	0.13 ± 0.02	1.00 ±0.01
	Borehole	0.10 ±0.01	0.01 ± 0.01	0.03 ±0.01	1.00 ± 0.00
Ugboko	River	0.63±0.04	0.21 ± 0.02	0.34 ± 0.03	1.50 ±0.03
	Shallow Well	0.38 ±0.02	0.06 ± 0.03	0.23 ±0.02	1.00± 0.02
	Borehole	0.11 ± 0.01	0.01±0.02	0.01 ± 0.01	0.45± 0.03
Inorin	River	0.60 ± 0.04	0.23 ± 0.02	0.32± 0.02	1.50 ±0.03
	Shallow well	0.35 ±0.02	0.05 ± 0.01	0.20 ± 0.02	1.00 ± 0.02
	Borehole	0.12 ± 0.01	0.01 ±0.00	0.07 ± 0.01	0.50± 0.03
US-EPA Max Cont Levels	water	0.005	0.100	0.000	0.5- 0.05*

* WHO Guideline
N = 4

seen in Ifie-Kporo. All the soil samples had either very low or non detectable levels of nitrate.

DISCUSSION

Nigeria's vast crude oil and gas deposits and an attempt to explore it has left the country with unique vulnerabilities. A major threat to the future of Nigeria is environmental damage [24]. Delta state forms a large part of the Niger Delta wetland and it is the largest oil producing state in Nigeria. Consequently, the state is exposed to a large proportion of the environmental degradation and health hazards which normally accompany exploration and exploitation of crude oil. The frequency of oil spill in the state is no longer news as its negative impact on the aquatic and terrestrial ecosystem is well known. Surveillance of water quality to ensure safety is a vital public health function especially in developing countries [25].

The levels of both metallic and non-metallic pollutants in this study showed a wide range of variation all through the different communities within the creek or coastal areas of

Table 4. Heavy Metal and Physcio-Chemical Parameters of Surface Soil of Contiguous Host Communities

Community	Heavy Metals (mg/kg)				Physico-Chemical Parameter			
	Cd	Cr	Pb	Mn	pH	NO_3^- (mg/kg)	Conductivity (µS/cm)	Salinity (mg/kg)
Ekpan	0.76 ± 0.02	0.89 ± 0.00	0.36 ± 0.02	0.68 ±0.03	7.2 ± 0.04	ND	206.00 ± 0.04	100.12 ± 0.04
Ifie-Kporo	0.52± 0.01	1.78 ±0.03	0.22 ±0.01	0.60 ± 0.01	8.4 ± 0.03	0.17 ± 0.02	130.60 ± 0.03	150.20 ± 0.03
Aja-Etan	0.58 ±0.03	0.44 ± 0.02	0.32 ±0.01	0.55 ± 0.03	7.9 ± 0.02	ND	224.00± 0.03	100.23± 0.04
Ijala	0.64 ±0.02	1.33 ±0.01	0.90 ±0.03	0.47 ± 0.02	6.8 ± 0.03	0.01 ± 0.01	76.20 ±0.03	84.32 ±0.04

N=4 ND: Not detected

Warri. This may be attributed to the differential derivations of these inorganic pollutants from the source rocks and differential discharge of untreated effluents originating from industries (crude oil production, refineries, oil spillage, gas flare etc), agricultural, aquaculture as well as domestic sewage. Heavy metals are potentially harmful to most organisms at some level of exposure and absorption [26]. Most metals have received attention as both environmental and potential toxicological hazards.

Ekpan River like most open water bodies receives effluents from Warri Refinery and Petrochemical Company WRPC, crude oil and its fraction seepages from numerous loading and off-loading jetties within the river. Some metals and other pollutants may infiltrate from the basement rock and agricultural practices, since rivers are wide open to flooding which carry various contaminants. The combined effect of Delta Steel Company (DSC), which is 50km from Ekpan River and discharges its effluent into Aladja River which is interlinked to Ekpan River by Warri River before emptying into numerous creeks. The recent discovery of three illegal toxic waste dump sites, one measuring 75m x 30m x 6m, the other two sites varying between 15m and 30m belonging to WRPC within the study area could increase the pollutant load of potable water supply of the study area. In this study, we have shown that the surface water within the contiguous host community such as Aja-Etan and Ijala had the highest concentrations of cadmium while Ekpan and Ijala had the highest concentrations of chromium, Ekpan and Ifie-Kporo has the highest level of lead. The levels of lead, cadmium, manganese and chromium exceeded the threshold limits (0.01, 0.003, 0.4 and 0.05 mg/l respectively) set by the WHO health-based guideline for drinking water and this could portend environmental hazards [27]. The lead levels found in this study agree with the data obtained previously also in ground water from Warri, Niger Delta [28].

The manganese levels of potable water supply in the impacted on communities were higher than that of the contiguous host communities. The metal levels of soil from contiguous host communities were low, this is because of the washing of soil into surface water by flood and infiltration into underground water. High level of these metals may also be attributed to other relevant occupational fields (steel making, foundry work, thermal cutting, welding, glass and ceramic production etc) [29]. The health effects of manganese exposure in humans are not well understood. Although dietary manganese is an essential nutrient, high intake of manganese through both inhalational exposure and drinking water have been shown to be toxic [30] Manganese is best characterized as neurotoxin, occupational exposures are associated with a characteristic syndrome called manganism which involves both psychiatric symptoms and Parkinsonism features [31]. Exposure through drinking water has been associated with subclinical neurologic effects in Greek adults [32] and decreased intellectual function in pediatric population in Araihazar, Bangladesh [33]. High manganese concentration in drinking water might have little effect on adult population, but heavily affect embryos and neonates [34]. In addition to Parkinson's disease, exposure to high manganese concentration has effect on the respiratory tracts and the central nervous system [29].

Lead exposure has been associated with microcytic, hypochromic anemia with basophilic stippling of erythrocytes [35], Hyperactivity, anorexia, decreased play activity, low intelligence quotient and poor school performance have been observed in children with high lead levels [36]. The ability of Pb^{2+} to undergo metathesis reactions with Zn^{2+} and Ca^{2+} metalloproteins resulting in loss of metabolic function continues to be a primary hypothesis underlying the detrimental effects of lead exposure [37]. Cadmium is highly toxic, accumulating in the body and eventually causing effects such as tabular dysfunction, disturbances, in calcium homeostatis and metabolism [38]. It is capable of inducing renal, hepatic and testicular injury [39]. Most chromium (VI) compounds are carcinogenic, long exposure may cause kidney, liver and nerve tissue damage [40].

Physicochemical parameters of potable water of the contiguous host communities shows serious pollution burden. The pH of all surface water is within the internationally recommended standard (pH for surface water systems: 6.50-8.50, for underground water systems: 6.00-8.50 [41]. The pH of underground water (shallow well and borehole) in this study is acidic ranging from 4.79-5.91. The low pH of some water sources could have been as a consequence of carbon dioxide saturation in the groundwater [42]. The pH of the aquatic environment can be upset by added acid or alkali from waste water. For a good fish population in a marine environment to be maintained, the pH must be kept in the range of 6.7-8.6 as only few fishes can survive outside this range [43].

In addition, drinking water may be contaminated with nitrates. The health effects of presence of nitrates in water are linked to methemohemoglobinemia. Children between the ages of 12 to 14 years drinking water containing greater than 105mg/l of nitrate have been reported to exhibit delayed reactions to light and sound stimuli [44]. An increase of these parameters in drinking water indicates contamination with wastewater. The high levels of nitrate observed in this study could probably be attributed to poor sanitation, probably leaching of nitrates from the nearby pit latrines. In Nigeria, for example, nitrate levels in **s**hallow wells were demonstrated to correlate with high human population density [45]. Residence time in the shallow groundwater systems is likely to be short, and groundwater nitrate will be controlled by the degree of faecal loading and on mineralisation and nitrification of faecal nitrogen. Nitrate, the most highly oxidized form of nitrogen compounds is commonly present in surface and groundwater because it is the end product of the aerobic decomposition of organic nitrogenous matter. Unpolluted natural waters usually contain only minute amounts of nitrate. It has been suggest that long term exposure to drinking water nitrate at levels below the maximum contaminant level (10mg/l) is not associated with pancreatic cancer [46-47], but high levels of nitrate and nitrosamines in drinking water have been associated with increased mortality [48], and incidence of some cancers and lesions [49].

The BOD test is useful for determining the relative waste loading to treatment plants and the degree of oxygen demand removal provided by primary treatment, a high BOD therefore indicates the presence of large amount of organic pollution caused by microbial organisms in water [29]. We have previously shown that surface and shallow well waters with more coliform count had high BOD [18]. Regarding water hardness, there are no distinctly defined levels of what constitutes a hard or soft water supply. The values from our study were below the generally accepted classification of less than 75mg/l of $CaCO_3$ as soft, 75-150mg/l moderately hard and above 150mg/l for hard water. Electrical conductivities were higher in surface water than in others (boreholes and shallow (hand dug) well). This is an indication of high dissolved solids. Higher salinity level was seen in the soil than in water samples. In Nigeria, borehole water supply is regarded as safe as most middle class of socio-economic strata rely on this source of water supply. Our study has shown that it may not be safe as it was thought to be.

This is compounded by the fact that adequate public and safe drinking water supply is almost non-existent in Nigeria. A worst scenario seen in the study area where the only source of water supply to the poor rural dwellers who have borne the scourge of several years of oil pollution and gas flaring is surface and shallow well waters. There is no significant difference in pollution profile of these two sources, since most shallow well waters are recharged by surface water and rainfall. Comparatively potable water supply in Warri mainland [18] with data from the creeks presented in this study, show that drinking water in the creeks are more polluted than the mainland. The reason may be because the creeks (coastal area) are the interface between mainland and the Atlantic Ocean and therefore the final recipients of pollutant before discharge into the ocean.

Our study showed higher lead levels and electrical conductivity data but lower levels of nitrate and BOD when compared to the data presented previously [50] on the physico-chemical characteristics of some river and hand-dug well waters used for drinking and domestic purposes in the oil rich Niger Delta area of Nigeria.

In a study of the physical and sanitary quality of hand-dug well waters from oil-producing area of Nigeria [51], it was found that the water was slightly acidic at 6.04 ± 0.66 and may be attributed to emissions from gas flaring and petroleum refining activities, which is common in the area. In the present study we found pH values as low as 4.79 ± 0.00 and 4.81 ± 0.00 for borehole and shallow wells in Ekpan respectively. The water quality of Nigeria's surface water bodies is believed to be gradually deteriorating particularly in the industrialized axes [52, 53]. The results suggest that the use of such waters for drinking and domestic purposes may pose a threat to the health of the users and calls for the intervention of government agencies. The objective of wastewater treatment is to reduce the concentration of specific pollutants to a level where discharge of the effluent will not adversely affect the environment. To solve the problem of water pollution emanating from waste water, the degree and type of treatment of any waste water therefore depends on variables which requires engineering decision. In context above, adsorption process is the most widely used and known mechanism in physicochemical treatment process. We have established that biological wastes such as rice husks and groundnut husks serve as effective means of treating waste water and that activation (carbonization) and particle size (large surface area) enhances the efficiency [54]. Industries could utilize this cheap materials by passing their waste water through a pipe packed with pre-treated (activated) biological wastes before discharge into open water bodies (natural receptors).

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Received: August 25, 2008 Revised: October 20, 2008 Accepted: December 19, 2008