POST-IMPACT ASSESSMENT OF OIL SPILLAGE ON WATER CHARACTERISATION

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Abstract. The coastal waters from an oil polluted area in Nigeria were examined for some physico-chemical parameters and heavy metals. The impact of seasonal changes on water qualities was also investigated. The nutrient levels particularly during the dry season are eutrophic. The trends were such that apart from electrical conductivity, total dissolved solids and Zn where averagely <10% , < 17% and none respectively exceeded the WHO guidelines for water at both seasons, other parameters exceeded the guidelines greatly. Additionally, levels obtained rendered the water unsuitable for both recreational and agricultural purposes based on USEPA guidelines. Significant correlations ($p < 0.01$) were observed between the levels obtained between the two seasons. However, only with pH was any significant difference in the mean between the two seasons recorded. The anthropogenic input of oil in the form of spill was observed to influence greatly some water qualities. Thus, not only is the water unfit for drinking but also unsuitable for livestock and agricultural activities which are the mainstay of the inhabitants.
Keywords: *Contamination, oil spill, pollution, toxicity, water quality parameter.*

Introduction

Pollution is an unwanted and detrimental change in a natural system. It is associated with the presence of toxic substances. The introduction of oil into the ocean via oil spill is one major way by which the natural coastal area of Ondo State, Nigeria, is getting polluted. Oil pollution is a serious obstacle to food chain productivity of the sea (Kavitha et al., 1999). Interestingly, a significant quantity of petroleum, estimated at 0.2million tons a years, enters the sea without any help from humans, through natural seeps and continental margin. Thus, oil is a natural constituent of the marine environment (Thomas and William, 2004). Apart from the physico-chemical damage that accompanied oil when released into the ocean, some levels of metals are equally released (Thomas and Kathleen, 1998).

Metals are usually found as ions and complex compounds in the hydrosphere and concentration of metal species in various types of water cover a wide range. The presence of toxic metal such as Pb, Cd, Ni, Cr etc. in the environment, particularly in water has been a source of worry to environmentalist, government agencies and health practitioners (Kakulu and Obibanjo, 1992; Anmar et al., 1993; Fatoki and Awofolu, 2003; Eddy and Ekop, 2007). The heavy metals have been referred to as economic pollutants, which are widely distributed in the environment (O'Neil, 1993).

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The major sources of heavy metals in water especially in the oil producing area (like the study area in this study) has been reported to include crude oil, drilling fluids or mud and production water naturally occurring in the production reservoir. These metals include V, Ni, Co, Cd, Pb, Zn, Mn, Cr and Ti (Thomas and Kathleen, 1998).

The metals in the aquatic environment are of environmental interest and importance because of their interactions with solid phase materials of geological origin and also because of their influence on biological processes. Within the aquatic system, geological weathering and dissolution of aerosol particles from the atmosphere are some of the natural sources of these metals (Gary and Stephen, 2001).

Few people are fully aware of their daily dependence upon crude oil. Awareness is growing as the fragilities of modern civilization, stemming from population growth and economic expansion become recognizable not only as world and natural problem but also a personal problem. However, as human dependence on crude-oil increases especially in a country like Nigeria, the dangers that accompanied it also increase. In spite of the growing concern by private individuals who are environmentally conscious about the associated problems with oil spillage based on global disaster records, the government especially at the state level seems adamant about this silently killing oil-containing pollutant.

The water within the present study area remains the major source of livelihood for the inhabitants. In view of the health concerns alerted by the magnitude of the problems afflicting the inhabitants within most of the communities within the studied area, especially the children, the present work is thus carried out partly to create awareness to the inhabitant and society at large and consequently recommend the urgent need for better understanding of the associated problems that oil spillage and other activities by oil companies within this zone had and still causing especially in organic, ionic and metal enrichments.

Study area

The study area for the work is the oil producing coastal region of Ondo State, Nigeria *(Fig. 1)*. There have been several cases of oil spillage within these coastal communities as a result of the activities of oil companies operating within these zones. The same river leads to the Atlantic Ocean and to some other parts of the country which means that the pollution may have tremendous adverse effect on other parts of the country. The major occupation of the inhabitants are fishing and farming. Most members of these communities are not aware of the environmental impact of oil pollution and most have died due to their ignorance.

Materials and methods

Sampling and sample preservation

Sampling sites *(Table 1)* were chosen with the aim of collecting water samples at a place that truly represent the water body (Wilde et al., 1999).The global positioning system (GPS) was used for site identification to enhance future monitoring. Twenty three (23) representative sites were considered for the physico-chemical parameters so as to comply with the objectives of the study and easy access, out of which nine (9) strategic locations were studied for some heavy metals. The sampling sites were all

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located along the same river course and were averagely at a distance of 2 km from one another. Three reference locations were sampled within the same geographical location with similar ecological conditions. Sampling at each sites were in triplicate in order to ensure better precision. The sampling frequency chosen for this study was based on literature guidance (US EPA, 2004).

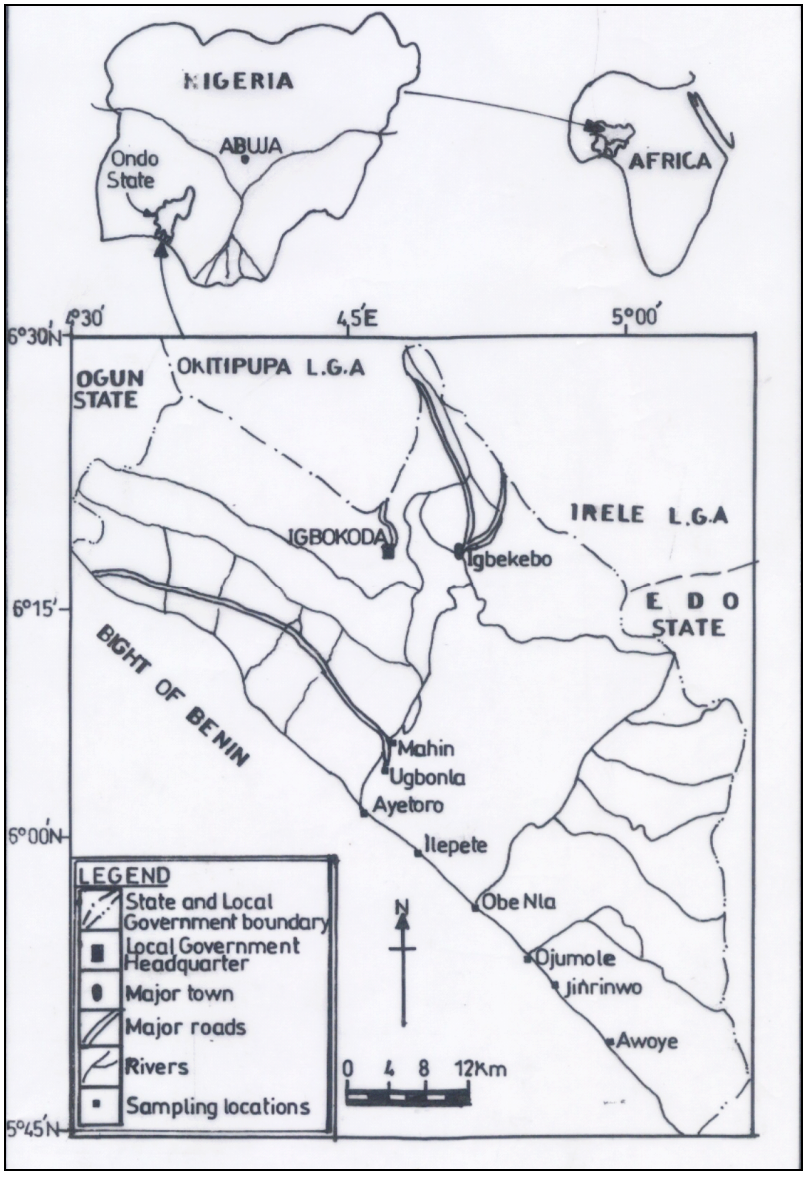

Figure 1. *Map of sampling locations*
(Inserted is the area map of Nigeria and Africa showing the geographical locations)

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Table 1. *Site identification and coordinates. Igbokoda 1, 2 and 3 represent control locations*

	Abbreviation	Names of communities	Latitude (degree)	Longitude (degree)	Altitude (meters)
1	A	Ayetoro (town)	06°06'12.4"	004°46'36.0"	12
2	B	Idi ogba	06°05'56.1"	004°47'13.2"	14
3	C	Alagbin zion	06°04'48.8"	004°47'14.9"	14
4	D	Oroto	06°04'22.3"	004°48'53.7"	14
5	E	Asumaga	06°03'20.9"	004°39'58.9"	12
6	F	Ilowo	06°03'15.6"	004°50'10.1"	11
7	G	Ilepete	06°02'10.0"	004°51'23.3"	14
8	H	Obeadun	06°01'35.5"	004°51'57.5"	16
9	I	Obe Nla	06°00'51.9"	004°52'40.2"	16
10	J	Erebino	05°59'51.3"	004°53'37.1"	15
11	K	Ikorigbo	05°57'15.0"	004°53'59.6"	10
12	L	Obe iji	05°59'16.9"	004°54'09.8"	9
13	M	Obereweje	05°58'55.6"	004°54'27.2"	13
14	N	Obebowoto	05°56'52.4"	004°54'34.4"	13
15	O	Ojumole	05°56'05.4"	004°53'10.2"	15
16	P	Atlantic ocean	05°57'00.4"	004°55'34.7"	16
17	Q	Atlantic (inside)	05°56'59.8"	004°53'52.2"	16
18	R	Otumara	05°56'42.8"	004°55'55.8"	14
19	S	Odonla	05°56'24.5"	004°56'56.7"	13
20	T	Ilu abo	05°55'38.5"	004°56'44.7"	13
21	U	Jinrinwo	05°55'55.1"	004°57'28.7"	10
22	V	Odofado	05°55'18.3"	004°58'03.7"	12
23	W	Awoye	05°54'46.7"	004°57'56.2"	10
24	X	Igbokoda 1[a]	06°09'12.3"	004°44'32.4"	10
25	Z_1	Igbokoda 2[a]	06°09'12.4"	004°43'33.7"	13
26	Z_2	Igbokoda 3[a]	06°09'12.7"	004°44'32.5"	11

On collection, measurements were made of pH, temperature and conductivity using pre-calibrated pH meter (Hanna pH 211 microprocessor), thermometer and conductivity meter respectively. Samples were collected in polyethylene bottles cleansed with 50% HNO_3. Samples for anion analyses were unfiltered and unacidified. However, for cations analyses and metals, the samples were unfiltered but acidified with HNO_3 (Nickson et al., 2005). The essence of not filtering samples was to ensure accurate result. All samples were stored in the refrigerator at a temperature of about 4 °C prior to chemical analysis (Campolo et al., 2002; DWAF, 2002). As part of quality control, field blanks were introduced in the chain of custody.

Chemical analyses

Total solids (TS) and total dissolved solids (TDS) were determined using the standard method (APHA, 1989). Walkley and Black method of 1934 was adopted for the determination of total organic carbon (TOC). Chloride and sulphate were determined using the Morhs and turbidimetric standard methods respectively. The Cadmium reduction and ascorbic acid methods were respectively employed for nitrate and phosphate determination. Heavy metals in the water were analyzed after careful digestion with conc. HCl using AAS (Alpha 4AAS, Chemical Tech. Analytical, Euro). Blanks and standards were used as quality control measures. Detection limits

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(µg/l) were; Cd (0.002); Ni (0.05); Pb (0.004) and Zn (0.006). Statistical analysis using the SPSS for windows 13.0 versions was later employed for data presentations.

Results and discussion

Results

Table 2 and 3 present a summary statistics of some water characteristics and heavy metals during the dry and wet seasons. The results did show apparent seasonal

Table 2. *Summary statistics of some water physico-chemical properties*[#]

	pH	**EC (µS/cm)**	**TS (mg/l)**	**TDS (mg/l)**	**SS (mg/l)**
Range (mg/l)	4.1-6.9 (5.8-8.5)	2.2-35.4 (3.0-23.4)	209-3650 (148-2300)	150-2404 (112-1438)	59-1246 (86-612)
Mean (mg/l)	5.43 (6.89)	11.17 (12.05)	1176 (918)	760 (602)	419 (322)
S.D	0.81 (0.77)	7.3 (5.5)	691 (479)	496 (315)	314 (215)
C.V (%)	14.73 (10.00)	65.4 (46.1)	59 (52)	65 (52)	75 (67)
WHO	7.0-8.5	20	500	1000	Na
% Viol.	83(33)	8.3(12.5)	96(79)	16.7(8.3)	-
	Chl (mg/l)	**Sulp (mg/l)**	**Nit (mg/l)**	**Phosp (mg/l)**	**TOC (mg/l)**
Range (mg/l)	266-1012 (352-932)	65-605 (61-416)	40-400 (91-401)	73-703 (69-541)	8.9-41.7 (13.2-32.5)
Mean (mg/l)	664 (606)	235 (206)	164 (198)	302 (222)	20.3 (20)
S.D	216 (170)	169 (110)	101 (79)	190 (125)	9.4 (5.0)
C.V (%)	33 (28)	72 (53)	62 (40)	63 (56)	46.3 (25.0)
WHO	250	250	50	0.5	na
% Viol.	100(100)	46(46)	88(100)	100(100)	-

#: Concentrations are mean of triplicate analysis. Values in parenthesis are results of the wet season
C.V: Coefficient of variation; S.D: Standard deviation; na: Guidelines not available
Chl: Chloride; Sulp:Sulphate; Nit: Nitrate and Phosp: Phosphate;
%Viol: percent of concentration in violation of WHO standard guidelines for drinking water.
Sources: WHO (1993)

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Table 3. *Descriptive basic statistics of the heavy metals contents[#] (mg/l) in the studied water*

Locations	Seasons	Cd	Ni	Pb	Zn
Ayetoro	D	1.01^{a} ±0.37	0.4^{a} ±0.1	14.58^{a} ±5.04	0.04^{a}±0.14
	W	$10.9^{b,c,d}$±0.14	$0.4^{a,b}$ ±0.3	$8.62^{b,c}$ ±2.64	0.04^{a}±0.03
Asumaga	D	0.19^{a}±0.14	<0.1	18.21^{b} ±189	0.09^{a}±0.31
	W	0.17^{a}±0.31	$0.6^{a,b}$ ±0.9	$6.16^{a\rightarrow d}$±1.26	0.05^{a}±0.01
Ilopete	D	$2.27^{a,b}$ ±0.14	0.5^{a} ±0.3	$12.19^{b,c}$ ±2.86	0.11^{a}±0.03
	W	$2.49^{h\rightarrow,j}$±0.23	$0.8^{a,b}$ ±1.2	4.09^{a} ±0.24	0.08^{a}±0.82
Obe nla	D	1.17^{a} ±0.04	2.3^{a} ±0.3	19.89^{a} ±1.64	0.11^{a}±0.12
	W	$1.72^{a\rightarrow d}$±0.72	2.7^{a} ±1.4	$6.19^{a\rightarrow d}$ ±0.59	0.09^{a}±1.12
Ikorigho	D	0.92^{a}±0.14	1.7^{a} ±0.9	19.96^{b} ±1.36	0.11^{a}±0.17
	W	$1.64^{e\rightarrow d}$±1.31	$2.1^{e\rightarrow g}$ ±0.4	$7.19^{c,d,e}$ ±0.94	0.09^{a}±0.63
Ojumole	D	1.30^{a}±0.22	1.9^{a} ±0.9	20.53^{b} ±2.96	0.18^{a}±0.03
	W	$1.65^{d,e,f}$±1.24	$1.9^{e\rightarrow g}$ ±0.1	9.17^{f} ±1.31	0.11^{a}±0.24
Otumara	D	3.49^{a}±0.13	1.9^{a} ±0.7	42.35^{b} ±3.41	0.42^{a}±0.31
	W	3.26^{m}±0.27l	$1.8^{d\rightarrow g}$ ±0.4d	9.92^{f} ±2.13	0.22^{a}±0.14
Odofado	D	$1.96^{a,b}$ ±0.96	0.9^{a} ±0.2	22.39^{b} ±0.12	0.52^{a}±0.37
	W	$2.16^{f\rightarrow j}$ ±1.26	$1.8^{d\rightarrow g}$ ±1.3	$9.14^{e,f}$ ±0.89	0.31^{a}±0.16
Awoye	D	2.28^{a}±0.13a	0.4^{a} ±0.5	21.40^{a} ±1.22	0.57^{a}±0.13
	W	2.39^{g-k} ±0.97	$0.9^{a\rightarrow d}$ ±0.3	$9.40^{e,f}$ ±1.36	0.22^{a}±0.21
Igbokoda*	D	$0.04^{a,b}$±0.14	$1.02^{a,b}$±0.12	$12.21^{c\rightarrow f}$±1.02	0.09^{a}±0.32
	W	$1.10^{a,b}$±0.14	$1.45^{a,b}$±1.05	$9.65^{e,f}$ ±1.12	0.04^{a}±0.53
Mean ± S.D	D	1.52 ± 0.97	1.11± 0.78	20.37 ± 8.57	0.22 ± 0.20
	W	1.76 ± 0.87	1.44 ± 0.74	7.95 ± 1.94	0.13 ± 0.09
Coeff. of Var.	D	64	70	42	91
	W	49	51	24	69
Range		0.17 – 2.49	4.09 – 42.35	< 0.1 – 2.7	0.04 – 0.57
WHO Stand.		0.003	0.02	0.01	3.0
% Viol.		100	100	100	None

#: Concentrations are mean of triplicate analysis. Values in parenthesis are results of the wet season
*C.V: Coefficient of variation; *: Reference location; S.D: Standard deviation*
WHO Stand: World Health Organization Standards for drinking water (1993)
%Viol: percent of concentration in violation of WHO standard guidelines for drinking water.

Means in the same column followed by the same superscript are not significantly different ($\alpha = 0.05$) according to Duncan's New Multiple Range Test differences. The temperature of the water samples ranged from 27.3 °C to 31.8 °C during the dry season. However, the temperature ranged from 25.9 °C to 28.7°C in the wet season. The ranges in pH and conductivity respectively were 4.1- 6.9 and 2.2-35.4µScm^{-1} for the dry season; 5.8-7.9 and 3.0-23.4µScm^{-1} for the wet season. Similarly, ranges (mg/l) during the dry and wet seasons respectively for other parameters are TS (209-3650 and 198-2300), TDS (150-2404 and 112-1438), TSS (51-1100 and 86-1140), Chloride (266-1012 and 401-769), sulphate (65-605 and 61-392), nitrate (40-400 and 91-401) phosphate (73-703 and 69-541) and total organic carbon (8.9-41.7 and 13.2-27.2). The metal displayed similar, increasing mean concentrations in the order Zn < Ni < Cd < Pb at both seasons. The highest and least variation were reported by Zn (CV: 91%) and (CV: 24%) respectively at both seasons.

Water quality dynamics

The dynamics of some of the significant parameters, as obtained in the present study for both dry and wet seasons are shown in *Figures 2a* to *3b*. It is interesting to note the observed differences, in temporal dynamics of water quality between the

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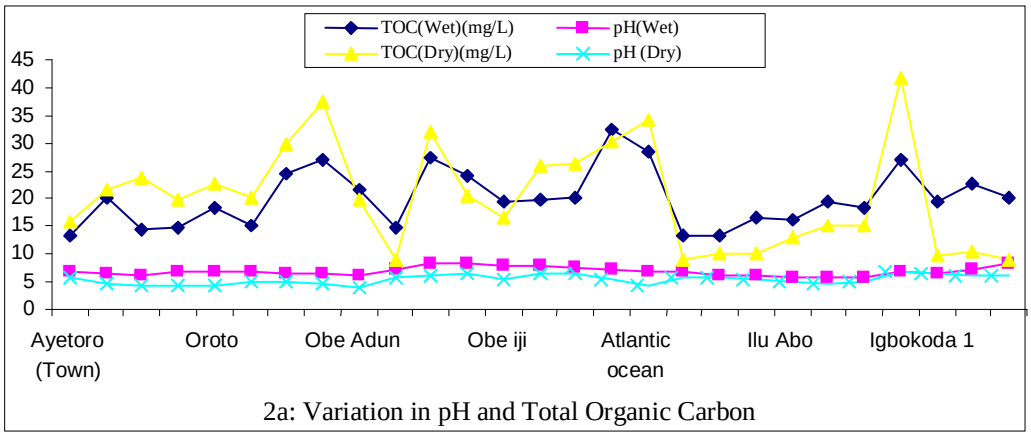
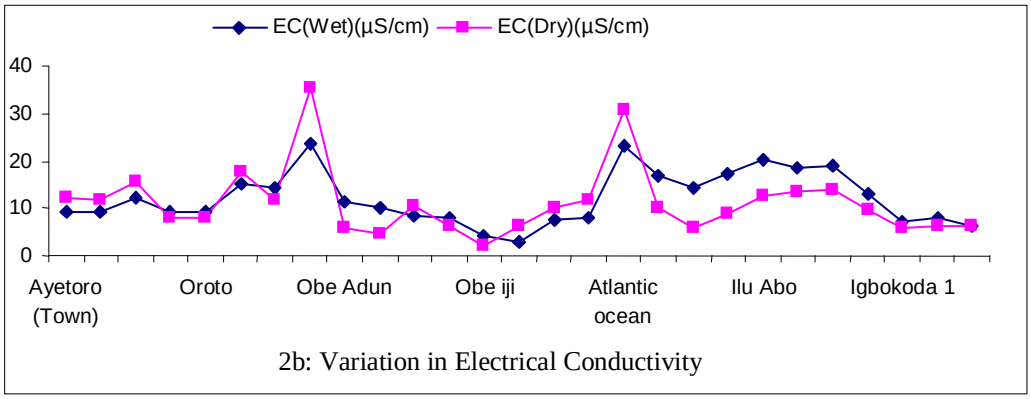
different seasons. The figures indicate that water quality during the two seasons exhibits seasonal changes and distinct dry and wet periods can be identified for most parameters.

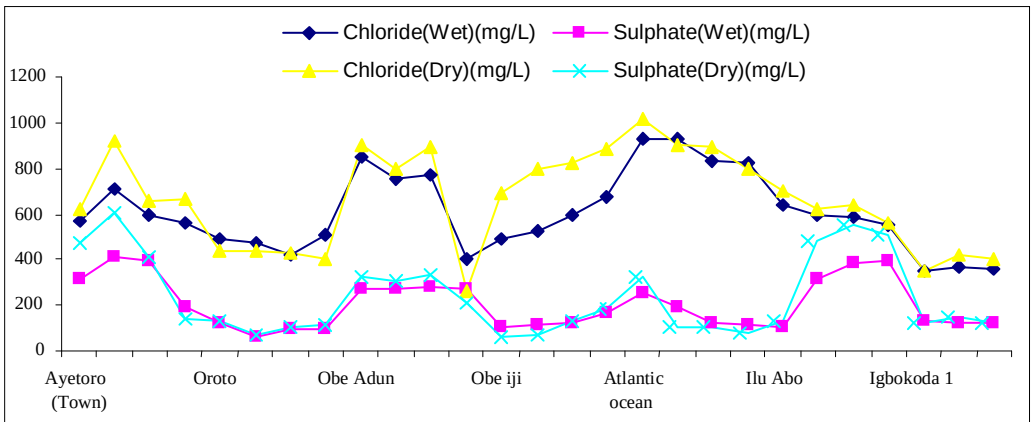
The colour of the water samples varied considerably between the two seasons and even with slight variation within some communities at the same season. In general, the colours varied from brown to light yellow. None was colourless at both seasons, a characteristic that is noted for impure water. The presence of colour at some of the locations, particularly during the dry season is indicative of greater organic and inorganic matter in suspension. This is reflective in the TOC obtained at these locations.



2a: Variation in pH and Total Organic Carbon



2b: Variation in Electrical Conductivity



2c: Variation in chloride and sulphate

Figure 2. *(a-c) Variations of some water physico-chemical parameters*

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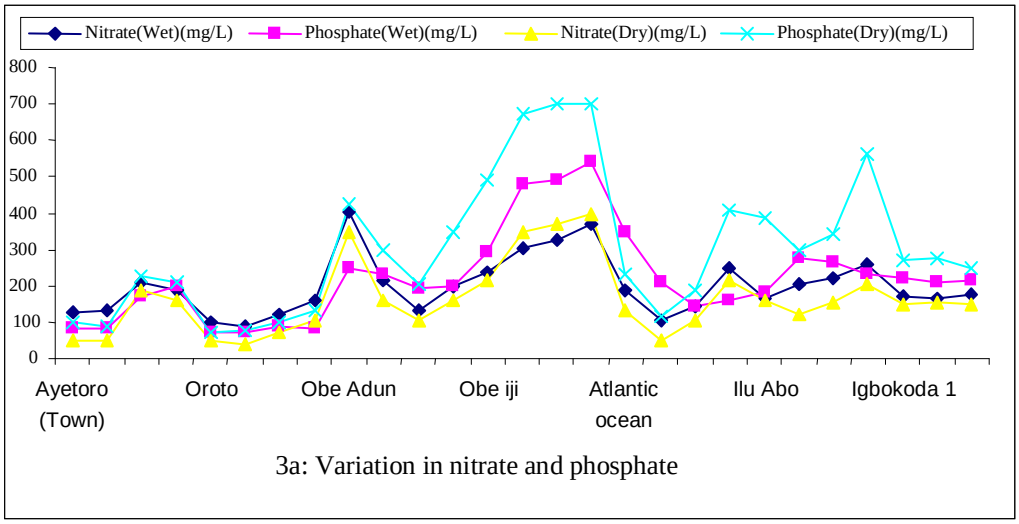
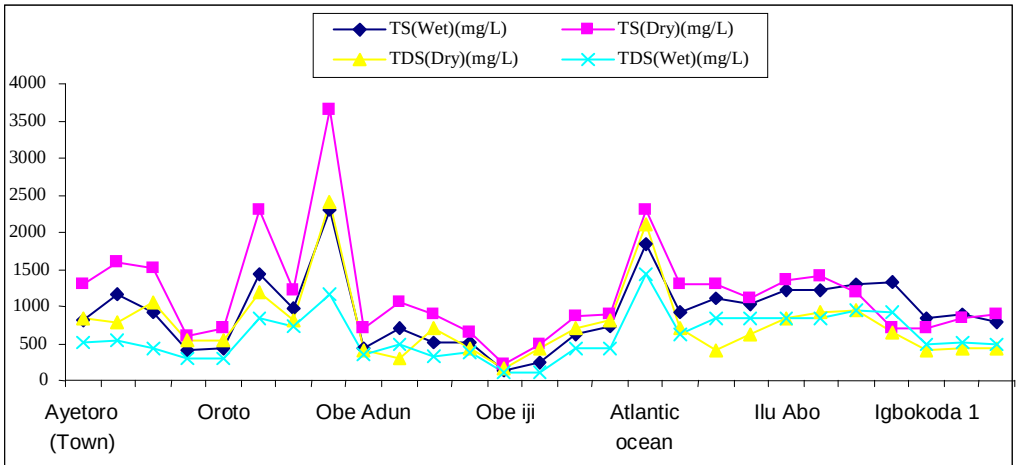


3a: Variation in nitrate and phosphate



3b: Variation in total solid and total dissolved solid

Figure 3. *(a-b) Variations of some water physico-chemical parameters*

The pH for most of the water samples (83.3 %) during the dry season fell within 4.13 to 5.97 while those of the wet season were not only fairly increased but fairly constant across most of the sampling locations. However, the comparatively low values of pH (i.e. greater acidity) during the dry season to those of wet season can be attributed to natural sources or some organic matters. Partial decomposition of some organic matters by bacteria and fungi has longed been recognized to produce various organic acids that are capable of lowering the pH of aqueous solution (Bowen, 1986). Most of the pH data in the dry season fall out of the 6.5-8.5 range of WHO standard for drinking water *(Table 2)* and water intended for aquatic life and recreational activities (DWAF, 2002; WHO, 2002; US EPA, 2004).The acidic nature of the water particularly during the dry season is expected to influence the solubility, availability and toxicity of metals in the aquatic ecosystems.

All the water samples did not show any measurable range of phenolphthalein alkalinity. Thus, the entire river shows no excess basic constituent. This has further supported the pH values obtained which fell entirely within the acidic-neutral range. In a similar manner, higher conductivity values in water were obtained during the dry

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season. Highest values were recorded at Ilepete (35.35µS/cm) and Atlantic Ocean (30.88µS/cm) during the dry season. These suggest a large amount of dissolved mineral salts within these communities. At four different locations; L, I, H and R, abnormally low values of 2.21, 4.56, 5.88 and 5.91µS/cm respectively were obtained. These low values were reflective in the amount of dissolved solids (TDS) recorded during the dry season at these locations. Except for one location, each for both season, the ranges for both season fell within the WHO (20µS/cm) for EC in water intended for domestic use (DWAF, 2002; WHO, 2002; NEMA, 2003).

A thorough assessment of the TDS which is slightly above half or almost equivalent of TS at some of the sampling locations indicate a high value for both seasons. The higher values of TDS during the dry season cannot but be associated with the nature of the medium, which is entirely acidic from the pH values recorded. Thus low value of the pH equally depicts water rich in dissolved organic matter and polluted acid drainage. Increased dissolved solid can lead to improved mineralization of receiving water or depletion of oxygen, depending on the nature (either organic or inorganic). Oxygen depletion can result from the oxidation of nitrogen and phosphorous (which are chemically combined in organic compounds) to nitrates and phosphates. The suspended solids were also at a high values even at the control sites (X,Y and Z). The consistent trading activities can be contributing factors to these values.

The organic carbon ranged from 8.9-4.17 mg/l and 13.4-32.5 mg/l during the dry and wet season respectively. The mean are very close and not significantly different ($\alpha = 0.05$, $P = 0.720$).These values are very high and far above the 0-5mg/l guidelines for domestic use (DWAF, 2002). As generally noted, organic matter influences the mobility and flux of the trace metals .The high level obtained in the study is an indication of greater metal input into the aqueous solution in the bioavailable form. This portends danger and serious threat to aquatic life.

It is of interest to note that at both seasons, none of the communities recorded normal phosphate (0.5mg/l), chloride (<250mg/l) and with not less than 88% violating nitrate WHO guideline for drinking water. The level of chloride was very high, much higher than nitrate, sulphate and phosphate especially during the dry season. Of particular interests are communities around the Atlantic ocean and the Atlantic itself (i.e. P and Q) where highest concentrations were recorded, though, this was expected. The high degree of pollution of chloride is indicative of salt-water intrusion. The chloride concentrations were found to generally decrease with distance away for the Atlantic Ocean downstream to site W *(Fig. 2c)*. The normal chloride released into the sea from in-take of petroleum industry in Nigeria is <200mg/l (FEPA, 1992). Chloride values recorded at both seasons are quite higher. About 41% of the total (both seasons) exceeded the maximum allowable concentrations of Cl^- (<700mg/l) in water for agricultural purposes (e.g. irrigation) in Nigeria (FEPA, 1992).

Nitrates and Phosphates are two important nutrients that have been increasing markedly in natural waters since the mid-1960s (Hodgson, 2004). The increase in these nutrients, particularly phosphate, as exemplified in the present report over nitrate is of environmental concern and was not unexpected. This is because, in anaerobic environment, coupled with oil pollution of the sea during the dry season, nitrates are in low concentration and manganese and ferric oxides are abundant. The environmental significance of these metal oxides is that they serve a dual role. Not

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only are they a source of oxidants to micro organism, thus leading to 'algae blooms', they are also important for their capacity to bind toxic metals, deleterious organic compounds, phosphates and gases (Thomas and Williams, 2004). Oil spillage, is a major cause of low biological productivity which can result in appreciable amount of phosphate (Hammerton and Sherah, 1992). Since the equilibrium existing between photosynthesis (Process of cell formation) and respiration (process of cell decay) should be maintained, any disturbance as observed in the present study whereby the rate of cell decay is greater than that of cell formation, especially during the dry season (due to oil spill), will lead to accumulation of excess organic nutrients (see TOC values for dry season) which will in turn stimulate bacteria activity, thus making the water to become eutrophic.

The fairly clear appearance with low light penetration, foul smelling odour coupled with scarce varieties of fish especially during the dry season; at the time of sampling for the present study are essential features of eutrophic waters (Samir, 2003). Moreover, since primary producers in water such as cyanobacteria, phytoplankton and algae depend so much on sunlight and as such limited to the region near the surface of the ocean, where sunlight can penetrate i.e. the euphotic zone (Thomas and Williams, 2004), the presence of oil on the ocean has limited all possible microbial activities. Thus, oxygen supply of the ocean gets exhausted making the existing bacteria to shift from predominantly aerobic to anaerobic microorganisms that generate noxious products (NH_3,CH_4 and H_2S) of anaerobic metabolism. In general nitrate levels are observed to be less during the dry season while those of phosphates were observed to be higher *(Fig. 3a)*. The levels of NO_3^- and PO_4^{3-} obtained in this report are exceedingly too high for both aquatic life and irrigation purposes with guideline values of <0.5mg/l for NO_3^- and <0.05mg/l for PO_4^{3-} respectively (FEPA, 1992; Campolo et al., 2002). The water is not equally suitable for livestock watering and recreational activities with guideline of <10mg/l for NO_3^- and <0.05mg/l for PO_4^{3-} respectively (FEPA, 1992; WHO,2002). The results of the sulphate obtained at both seasons are relatively comparable with almost half violating the WHO guideline values. The results of the TOC for both seasons were not with exceptions as virtually all the sampled water violated the <5mg/l quality guidelines values for domestic uses (Campolo, 2002).

In an attempt to further ascertain the pattern and trend of the water physico-chemical characteristics, a comparison was made with previous studies within the ecological zone (*Table 4)*. Most of the parameters apart from EC were observed to be recorded at higher concentrations than the previously obtained data. This can be said to be an enrichment of the aquatic ecosystem with pollutional nutrients.

Heavy metals enrichment

The range of results obtained from the river water displayed slight variation at both seasons. Cadmium and Ni were observed to be lower while Pb and Zn were at higher concentrations in the dry season. Significant mean differences occurred in Pb (P = 0.000) and Zn (P = 0.030). Based on Pearson correlation, *(Table 4)*, there are 1).Significant ($\alpha \leq 0.01$) positive correlation between Cd and Zn. 2) Significant ($\alpha \leq 0.05$) positive correlations between Cd and Pb; Cd and Ni:Zn and Pb during either the wet and/or dry season(s). From the correlation result, it can be said that the heavy metals are directly and significantly related. With the limited available data, all the

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metals except Zn exceeded standard guideline values (WHO, 2002; NEMA, 2003) *(Table 3)*.

In addition, levels of Cd and Pb are higher than the maximum contaminant level (MCL) for livestock drinking (0.02 and 0.01mg/l); agricultural purposes such as aqua culture (0.01 and 0.2mg/l) and irrigation (0.2-1.8µg/l and 1.7µg/l) respectively (US EPA, 2004).This showed that water from the river is generally unsuitable for these activities with regards to the values obtained in this study, which could have chronic health effects on various users. Cadmium remains a metal without any known biological significance.

Toxicity in water is expected based on the levels obtained in this study. Chronic exposure to Pb has been linked to growth retardation in children (Schwartz et al., 1986). Lead toxicity studies conducted on female animals revealed mostly miscarriages, premature delivery and potent mortality (Tapieau et al., 2000). A concentration of Pb ≈ 0.1mg/l is detrimental to foetuses and children with possible development of neurological problem (Fatoki et al., 2002).

Apart from very few locations, levels of Ni obtained are higher than the guideline values. More importantly, attention has to be focused on the toxicity of Ni in low concentrations due to the fact that Ni can cause allergic reactions and that certain Ni compounds may be carcinogenic (Mokenzie and Smythe, 1998). All Ni compounds except for metallic Ni have been classified as carcinogenic to humans. Some of the health related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation (Awofolu and Fatoki, 2005).

Levels of Zn in the river water are quite less than the 3.0mg/l WHO guideline value. Hence, no detrimental effects from domestic water usage are expected. However, the USEPA levels for Zn in water for safe aquatic ecosystem, irrigation and livestock watering are 0.003mg/l, 0-0.1mg/l and 0-0.1mg/l respectively (US EPA, 2004). Consequently, the water is unfit for the sustenance of the aquatic ecosystem but could still be utilized for irrigation and livestock watering at some of the studied locations where concentration fell below the USEPA levels.

Generally, the elevated level of metals and physico-chemical properties examined in this study and possibly some other factors which we hope to look into in future studies complicated the economic sustenance of the inhabitants within the studied area. It equally represents what can be obtainable anywhere where oil operation (on-shore and off-shore) are being carried out It must however be emphasized that the source of these metals concentration cannot totally be associated with petroleum if one considers the percentage of metals in petroleum. Consequently, they must have been sourced, in addition, through anthropogenic and in particular natural seepage. Increased in metals could also have resulted from annual drilling and disposal, a regular operation being carried out within these communities by oil companies.

Using the available data from studies carried out within the same ecological zone and other parts of the country *(Table 5)*, the range of most of the metals are lower than most reported concentrations. The mean cadmium, Ni, and Zn levels in this study are lower than the range reported by some authors (Kakulu, 1985; Okoye, 1989; Asaolu, 1998). Lead is unique in the sense that the range reported in this study is higher than those reported by other workers identified above. This again signaled that probably, leaded gasoline has not yet been phased out of our oil operation.

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Table 4. *Correlation Matrix of Physico-Chemical Properties for Dry and Wet Seasons*

	EC-1	EC-2	TS-1	TS-2	TDS-1	TDS-2	Cl'1	Cl'2	$SO_4^{2-}1$	$SO_4^{2-}2$	NO_3^--1	NO_3^--2	PO_4^{3-}-1	PO_4^{3-}-2	TOC-1	TOC-2	pH-1
EC-1	1																
EC-2	.734**	1															
TS-1	.840**	.841**	1														
TS-2	.741**	.908**	.866**	1													
TDS-1	.895**	.743**	.930**	.736**	1												
TDS-2	.734**	1.000**	.841**	.908**	.743**	1											
Cl'1	.403*	.170	.144	.169	.280	.170	1										
Cl'2	.099	.021	-.071	-.034	.033	.021	.888**	1									
$SO_4^{2-}1$	.077	.051	.086	-.032	.075	.051	.269	.249	1								
$SO_4^{2-}2$	.147	.140	.210	.072	.188	.140	.207	.212	.948**	1							
NO_3^--1	-.240	-.193	-.291	-.353	-.240	-.193	.162	.345	.092	.052	1						
NO_3^--2	-.351	-.236	-.383	-.407*	-.333	-.236	.070	.311	-.091	-.143	.956**	1					
PO_4^{3-}-1	-.283	-.127	-.291	-.364	-.209	-.127	.131	.405*	-.047	-.085	.763**	.841**	1				
PO_4^{3-}-2	-.322	-.283	-.332	-.462*	-.257	-.283	.003	.253	-.059	-.096	.866**	.925**	.841**	1			
TOC-1	.018	.333	.199	.102	.182	.333	-.082	.001	.041	.083	.332	.324	.368	.337	1		
TOC-2	.133	.532**	.280	.289	.213	.532**	.007	.058	.186	.195	.189	.186	.173	.190	.710**	1	
pH-1	-.648**	-.321	-.504**	-.402*	-.504**	-.321	-.261	-.101	-.186	-.299	.127	.257	.373	.328	.306	.122	1
pH-2	-.483*	-.449*	-.277	-.440*	-.248	-.449*	-.293	-.169	-.110	-.173	.114	.235	.337	.448*	.122	-.066	.632**

Significant / r / * ($P < 0.05$) 1 = Wet season
** ($P < 0.01$) 2 = Dry season

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Table 5. *Comparison of Water Quality Characteristics of Rivers in the Present Study with Previous Studies within the Ecological Zone and FME Limits* [#]

Parameter	Present Study	Okitipupa SE Belt[a]	Ondo Coastal Water[b]	River Oluwa[c]	Niger Delta[d]
pH	4.13-8.46	5.37-7.70	6.00-7.43	6.90-7.50	
EC(µS/cm)	2.21-35.35	10.00-125.00	10.00-3658.00	-	
TSS(mg/l)	51-1246	2.15-29.40	0.20-3.75	< 20	
TDS(mg/l)	112-2404	5.19-75.45	0.0005-19.99	200	
TS (mg/l)	148-3650	10.55-85.18	0.26-21.67	-	
Cl^- (mg/l)	266-1012	6.97-29.60	10.24-1627.50	-	
NO_3^-(mg/l)	40-401	nd-42.00	nd-0.04	-	
PO_4^{3-}(mg/l)	73-703	nd-88.00	21.70-297.25	-	
SO_4^{2-}(mg/l)	61-605	2.36-11.08	nd-475	-	
Cd (mg/l)	0.17-2.49	-	0.1-9.6	-	0.67-5.07
Pb (mg/l)	4.09-42.35	-	0.2-36.0	-	0.67-5.07
Ni (mg/l)	< 0.1-2.7	-	2.0-9.3	-	nd-22.45
Zn (mg/l)	0.04-0.57	-	0.6-17.6	-	nd-42.86

Sources: [a]Ayesanmi [b]Asaolu (1998); [c]Ajayi and Osibanjo (1981); [d]Kukulu (1985)
[#] Water quality standard for aquatic life
- = Not determined
NS = Not Specified

Conclusion

Oil pollution (i.e. water pollution due to oil spills) is one problem for which no effective and final solution has been found anywhere in the World and in spite of every concerted effort to abate it, it has remained an inseparable part of the oil based operation. Some of the parameters determined were recorded at levels above the WHO standards for drinking water. It was equally observed that the levels of some of these parameters rendered the water unsuitable for recreational and agricultural purposes. The higher levels of most of the parameters over previous reports from the same ecological zone are indicative of anthropogenic enhancement and poor monitoring system. The persistent incidence of oil spillage into these coastal environments can be said to be contributory to the unusually high concentrations of some of the parameters determined in this study. The observed seasonal differences with higher concentrations of some parameters in the wet season than in the dry season may be attributed to increased land based run-off to the water body. Other possible reason may be due to increased water current and wave action, which may largely disturb the sediment, with the concomitant resurfacing of the previously leached materials into the sediment. It is therefore recommended that proper assessment and monitoring system be set up by the government so that aquatic and human lives would not be endangered.

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