PHYSICO-CHEMICAL PROPERTIES OF WATER SOLUBLE FRACTIONS OF CRUDE OIL, DIESEL, KEROSENE AND GASOLINE

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Abstract

Most oil spills occur in aquatic ecosystem and this leads to physical and chemical changes arising from the dissolution of water soluble components of petroleum. This study investigated the physico-chemical properties of water soluble fractions(WSFs) of crude oil, diesel, kerosene and gasoline. The physico-chemical properties, heavy metal content, total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons(PAH) content of the WSFs were determined using standard procedures. The WSF were all acidic with pH less that 6.0, crude oil had pH of 4.8, electrical conductivity (EC) of the WSFs was below 17.00µs/cm while total dissolved solids (TDS) was less than $8.00mgL^{-1}$*. Dissolved oxygen (DO) and biological oxygen demand(BOD) of the WSFs were less than* $5.70mgL^{-1}$ *and* $67.00mgL^{-1}$ *respectively. Crude oil had the least DO* ($0.40mgL^{-1}$ *and the highest BOD)(* $66.0mgL^{-1}$*). WSFs of crude oil, diesel, kerosene and gasoline contain cations and anions such as* Ca^{2+}, Mg^{2+} , K^{+} *, Na,* HCO^{-}_{3}, SO^{2-} *, and* NO^{-}_{3}*. Heavy metals present in the WSFs include Ni, Mn, Fe, Zn, Cu, Pb, Cr, and Cd. Regular monitoring of the physical and chemical* *characteristics of ponds, streams and rivers in oil bearing communities was recommended.*

Keywords: Hydrocarbons, heavy metals, dissolved oxygen, cations, anions.

The water soluble fractions (WSFs) of oil is that fraction that goes into solution during a long period of water-oil contact. When there is a delay in clean up of oil spillage, the water soluble components of crude oil and its refined products go into the solution in aquatic ecosystems (Edema 2009). The WSF is the remaining portion of oil in the water column after weathering and mechanical processes have take place. It is less complex than the oil itself. In terms of ecological effects of oil pollution, the amount of oil components dissolved in water is very important. Edema (2012) noted that it is the dissolved, rather than the emulsified or the adsorbed fraction of the oil that is toxic to aquatic flora and fauna. This is because the dissolved fraction is readily ingested by the organisms at the lower end of the food chain, thereby concentrating and accumulating in organisms at the higher trophic levels. According to Sadani, Faraji, Hajian and Mehrizi (2011) most toxicological studies on crude oil have focused on the water soluble fractions (WSF) because it is the portion that enters an aquatic environment with the greatest ease and has immediate effect on aquatic organisms. The WSF is enriched by the dissolution of the relatively low molecular weight hydrocarbons mainly aromatic hydrocarbons with relatively high water solubility and small amount of high molecular weight compounds with low water solubility (Nwanchukwu and Osuagwu (2014).

According to Nwankwoala and Obirie (2018) total mononuclear aromatics constitute about 89% of the WSF of crude oil and benzene, toluene, ethylbenzene and xylene (BTEX) constituted 87.6% of the WSF. A total of 46 volatile compounds were identified in the WSF of leaded gasoline with aromatic hydrocarbons mainly benzene, 3
toluene, ethylbenzene and xylene (BTEX) being the major component of the total dissolved compounds. Naphthalene and methylated naphthalenes were the major components in the polycyclic aromatic hydrocarbon (PAH) fraction. Diesel oil contains higher level of aromatic hydrocarbons than crude oil and aromatic hydrocarbons are more water soluble than alkanes of similar molecular weight. Diesel also contains BTEX (Liu and Kujawinski, 2015). Approximately 0.7% of kerosene is soluble in water, the aromatic fraction is more water soluble than the aliphatic. WSF of kerosene after 17hours of oil water mixture contains 53.2% by weight of benzenes and substituted benzenes, 44.8% of naphthalene and methylated naphthalenes and 0.5% of alkanes and cycloalkanes. Water soluble fractions of petroleum also contain anions, cations and heavy metals (Edema , 2012).

This study determined the physical and chemical characteristics of the water soluble fractions of crude oil, diesel, kerosene and gasoline.

Materials and Methods

Crude oil used for this study was obtained from Okporhuru Oil Well, Ethiope West Local Government Area of Delta State owned by Seplat Petroleum Development Company Limited, Sapele. The refined petroleum products were obtained from Total Petrol Station in Sapele, Delta State.

Preparation of Water Soluble Fractions (WSFs) of Crude, Diesel, Gasoline and Kerosene

Water soluble fractions of crude oil, diesel, gasoline and kerosene were prepared using oil to water ratio of 1:3. Five hundred milliliters (500ml) of crude oil was mixed with 1500ml of deionized water and the mixture was stirred using magnetic stirrer for 24 hours at room temperature. After stirring, the mixture was allowed to stand for a minimum of 3 hours to obtain clear interphase between oil and water. The oil was decanted and the mixture was then poured into a glass stopper separating funnel and allowed to stand overnight. Pure and clear WSF obtained at the lower part of the funnel was siphoned into capped bottles to make the stock (100 % WSF). The procedure was repeated using diesel, gasoline and kerosene respectively until sufficient quantities of WSFs of crude oil, diesel, kerosene and gasoline was obtained and were stored in dark brown screw-cap bottles prior to analysis.

Determination of Physical Properties of WSFs

pH was determined using an EIL Model 720pH meter. Electrical Conductivity (EC) was measured using the portable conductivity meter (Hanna) and the value was expressed in 4
µs/cm.

Biochemical oxygen demand and dissolved oxygen were measured using the modified oxygen depletion and Winkler's method (APHA, 2012)

Determination of Chemical Properties

Sulphate

Sulphate was determined by the turbidimetric method. The sample was reacted with barium ion in the presence of sodium chloride and hydrochloric acid solution containing glycerol and ethyl alcohol. The colloidal barium sulfate formed was measured at 420nm using UV/visible spectrophotomer (APHA, 2012).

Nitrate

Two milliliters of brine reagent was added to 10mL of sample in a 25mL volumetric flask and 10mL of concentration of H_2SO_4 was rapidly added. The mixture was allowed to stand for 20 minutes and made up to mark with distilled water before measurement at 470nm with UV/visible spectrophotometer (ASTM, 2010).

Ammonium Nitrogen

To 10mL of the sample in a 25mL volumetric flask was added 6mL of potassium sodium tertrate, 2mL of alkaline sodium phenate solution, and 2mL of sodium hypochlorite solution. The mixture was made up with distilled water and the absorbance value set at 630nm on UV/visible spectrophotometer (ASTM, 2010).

Calcium and Magnesium

Five milliliters of buffer solution and 0.5mL of KCN and hydroxylamine hydrochloride solution were added to 25mL of WSF in 250mL conical flask. Two drops of Erichrome Black T indicator solution was added to the mixture and titrated over a white surface with standard 0.004M EDTA. Sodium and patassium was determined by flame photometry (ASTM D2791-93, 2010).

Heavy metals

Ten milliliters of WSF was transferred to 25mL conical flask. A mixture of perchloric acid, nitric acid and sulpuric acid in the ratio of 1:2:2 was added to the flask. The mixture was heated for 20minutes on the hot plate until white fumes were observed. The heating was stopped and the mixture cooled. After cooling, 20mL of distilled water was added and the solution was analysed with Perkin Elmer atomic absorption spectrophotometer (AAS) (APHA, 2012).

Total Petroleum Hydrocarbon (TPH) and Polycyclic Aromatic Hydrocarbon (PAH)

One thousand milliliters of WSF was poured into 2L capacity separating funnel. Thirty milliliters of extracting mixture of 50:50 mix of acetone and methylene chloride was added. The solution was agitated for about 5 minutes and allowed to settle until a distinct layer extract was obtained which was drained into a 20mL beaker. This was repeated twice with 10mL of the extracting solvent. The extract was cleaned by passing it through packed column with silica gel and 10mL of redistilled hexane was allowed to run through the column. The filtrate was concentrated to an injectable volume with evaporator and analysed with Hewlett Packard (HP) 6890 gas chromatograph equipped with HP chemistation software (ASTM, 2010).

Statistical Analysis

Results were expressed as means ± standard error of three replicates. All data were statistically analysed using Statistical Package for Social Sciences (SPSS) version 16.0. Analysis of variance (ANOVA) was performed appropriate to the study. Duncan's Multiple Range Test (DMRT) was used to locate the means were significant differences occurred at $p < 0.05$.

Results and Discussion

The physico-chemical properties of water soluble fractions (WSFs) of crude oil, diesel, kerosene and gasoline used in this study are shown in Table 1.

The data in Table 1 shows that the pH of WSF of crude oil was 4.80. The WSFs of diesel and kerosene had the same pH of 5.30 while the pH of WSF of gasoline was 5.80. The WSF of crude oil had the lowest pH while the WSF of gasoline had the highest pH. The pH of the four WSFs were significantly different from each other ($p < 0.05$). Electrical conductivity (EC) was significantly higher in the WSF of crude oil (17.00 µs/cm) than in the WSFs of its refined products ($p < 0.05$). WSF of gasoline had the lowest EC of 9.00µs/cm while WSFs of diesel and kerosene had EC of 11.00µs/cm and 10.00 µs/cm respectively. Total dissolved so 'DS) was the same in the WSFs of the three refined petroleum products (5.00mg L^{-1}) while WSF of crude oil had a significantly higher TDS (8.00mg L^{-1}) ($p < 0.05$). The WSF of kerosene had a higher turbidity (5.5NTU) compared to WSF of diesel (5.20NTU) and WSF of crude oil (4.50NTU). WSF of gasoline had the least turbidity (4.30NTU). The turbidity of all four WSFs were significantly different from each other ($p < 0.05$).

Dissolved oxygen (DO) was significantly higher in WSFs of the refined petroleum products than in crude oil (0.40mg L^{-1}) ($p < 0.05$). While DO was higher in WSF of gasoline (5.60mg L^{-1}) than in WSF of kerosene (4.00mg L^{-1}) and diesel (2.80mg L^{-1}). All values of DO were significantly different from each other ($p < 0.05$). Biochemical oxygen demand (BOD) on the other hand was significantly higher in WSF of crude oil than in WSFs of the refined petroleum products. The WSF of gasoline had the least BOD (20.00mg L^{-1}) compared to WSFs of diesel (2.80mg L^{-1}) and kerosene (22.00mg L^{-1}). There was no significant difference between BOD of WSFs of gasoline and kerosene ($p > 0.05$)

There were differences in ionic concentration of the different WSFs. The cations present in all four WSFs include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) and potassium (K^+) while the anions include hydrogen carbonate (HCO^-_3), sulphate (SO^{2-}_4) and nitrate (NO^-_3). Ammonium – nitrogen (NH_4^+) was present only in WSF of gasoline (3.15mg L^{-1}). The concentration of Ca^{2+} in the WSFs of the three refined petroleum products was the same (0.64mg L^{-1}) which was significantly lower than the Ca^{2+} concentration in WSF of crude oil (1.28mg L^{-1}). The concentration of Mg^{2+} in WSF of kerosene (1.17mg L^{-1}) was significantly higher than the concentration in WSF of gasoline (0.78mg L^{-1}) which in turn had a significantly higher Mg^{2+} concentration than WSFs of crude oil (0.39mg L^{-1}) and diesel (0.39mg L^{-1}). Mg^{2+} concentration in WSFs of crude oil and diesel were not significantly different from each other ($p > 0.05$). The concentrations of Na^+ in the WSFs in decreasing order were crude oil (1.67mg L^{-1}), diesel (1.08mg L^{-1}), kerosene (0.98mg L^{-1}) and gasoline (0.88mg L^{-1}). They were all significantly different from each other ($p < 0.05$). K^+ concentration in WSF of crude oil (0.83mg L^{-1}) was significantly higher than the concentration of K^+ in the WSFs of the refined petroleum products with gasoline having the least (0.44mg L^{-1})

followed by kerosene (0.49mg L^{-1}) and diesel (0.54mg L^{-1}). Among the anions, HCO^-_3 and NO^-_3 were present in higher concentrations than SO^{2-}_4 in all WSFs except in kerosene were SO^{2-}_4 concentration was higher than NO^-_3. The concentration of HCO^-_3 in WSFs of diesel and gasoline was the same (12.20mg L^{-1}), while WSFs of crude oil and kerosene had similar concentration (6.10mg L^{-1}) of HCO^-_3. The concentration of $HC0^-_3$ in crude oil and kerosene were significantly different from HCO^-_3 concentration in diesel and gasoline ($p < 0.05$). In increasing order the concentration of NO^-_3 in the WSFs were kerosene (2.05mg L^{-1}), diesel (3.34mg L^{-1}), crude oil (4.79mg L^{-1}) and gasoline (4.94mg L^{-1}).The NO^-_3 concentration is significantly different in all WSFs ($p <$ 0.05). The WSF of crude oil had a significantly lower concentration of SO_4^{2-} than WSFs of the refined petroleum products all of which had the same SO_4^- concentration of 2.65mg L^{-1}.

Table 1: Physico-chemical Properties of WSFs of Crude Oil, Diesel, Gasoline and Kerosene

Parameter	Crude oil	Diesel	Gasoline	Kerosene
pH	4.80 ± 0.08^a	5.30 ± 0.11^b	5.80 ± 0.09^c	5.30 ± 0.10^b
EC (µS/cm)	17.00 ± 1.12^c	11.00 ± 0.93^b	9.00 ± 0.56^a	10.00 ± 0.82^{ab}
TDS (mgL^{-1})	8.00 ± 0.11^b	5.00 ± 0.06^a	5.00 ± 0.03^a	5.00 ± 0.04^a
Turbidity (NTU)	4.50 ± 0.05^b	5.20 ± 0.10^c	4.30 ± 0.02^a	5.50 ± 0.03^d
DO (mg L^{-1})	0.40 ± 0.00^a	2.80 ± 0.01^b	5.60 ± 0.02^d	4.00 ± 0.01^c
BOD (mg L^{-1})	66.00 ± 1.62^c	28.00 ± 1.11^b	20.00 ± 1.20^a	22.00 ± 1.11^a
Ca (mg L^{-1})	1.28 ± 0.00^b	0.64 ± 0.00^a	0.64 ± 0.00^a	0.64 ± 0.00^a
Mg (mg L^{-1})	0.39 ± 0.00^a	0.39 ± 0.00^a	0.78 ± 0.00^b	1.17 ± 0.01^c
Na (mg L^{-1})	1.67 ± 0.01^d	1.08 ± 0.01^c	0.88 ± 0.02^a	0.98 ± 0.02^b
K (mg L^{-1})	0.83 ± 0.00^a	0.54 ± 0.00^b	0.44 ± 0.00^b	0.49 ± 0.00^b
HCO3 (mg L^{-1})	6.10 ± 0.20^a	12.20 ± 0.10^b	12.20 ± 0.15^b	6.10 ± 0.16^a
SO4 (mg L^{-1})	1.59 ± 0.01^a	2.65 ± 0.02^b	2.65 ± 0.02^b	2.65 ± 0.01^b
NO3 (mg L^{-1})	4.79 ± 0.01^c	3.34 ± 0.00^b	4.94 ± 0.01^d	2.05 ± 0.01^a
NH4-N (mg L^{-1})	nd	nd	3.15±0.01	nd

Key: nd – not detected
*Values with similar alphabets along each row are not significantly different from each other ($p > 0.05$).

Heavy metals were also detected in all the WSFs (Table 2). While iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), manganese (Mn) and lead (Pb) were present in all the WSFs, chromium (Cr) was present only in WSFs of diesel and gasoline, cadmium (Cd) was detected only in WSF of crude oil and diesel. Manganese (Mn) had the highest concentration in all the WSFs. The concentration of Fe (0.11mgL^{-1}) in WSF of crude oil was significantly higher than Fe concentration (0.08mgL^{-1}) in both diesel and gasoline and kerosene (0.04mgL^{-1}) which had a significantly lower concentration ($p < 0.05$). Zinc (Zn) concentration in crude oil (0.09mgL^{-1}) was significantly higher than in refined petroleum products ($p < 0.05$). The concentration of Zn in WSFs of diesel (0.07mgL^{-1}) gasoline (0.08mgL^{-1}) and kerosene (0.06mgL^{-1}) were not significantly different from each other ($p > 0.05$). Similarly, the concentration of Cu in WSF of crude oil was significantly higher than Cu concentration in WSF of refined petroleum products. The concentration of Mn in WSF of gasoline (0.28mgL^{-1}) was significantly higher than Mn in WSF of crude oil (0.12mgL-1), diesel (0.16mgL^{-1}) and kerosene (0.17mgL^{-1}). Manganese (Mn) concentration in diesel and kerosene were not significantly different from each other ($p > 0.05$). The concentrations of Pb in the WSFs of crude oil, diesel, gasoline and kerosene were not significantly different ($p > 0.05$). The concentrations of the heavy metals in the WSFs were in the following order, crude oil (Mn > Ni > Fe > Zn > Cu > Pb > Cd), diesel (Mn > Ni > Fe > Zn > Cu > Pb > Cr), gasoline (Mn > Ni > Fe = Zn > Cu > Cr = Pb) and kerosene (Mn > Ni > Zn > Fe > Pb).

Table 3 show that the concentration of total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) present in the WSFs differs. The WSF of crude oil had a significantly higher TPH (14.12mg L^{-1}) than the refined petroleum products ($p < 0.05$). Among the refined products, WSF of diesel had a significantly higher TPH (6.34mg L^{-1}) than WSF of gasoline (4.03mgL^{-1}) which in turn was significantly higher than WSF of kerosene (2.31mg L^{-1}). The PAH concentrations in the WSFs were crude oil (0.015mgL^{-1}), diesel (0.09mgL^{-1}), gasoline (0.005mgL^{-1}) and kerosene (<0.001mgL^{-1}). The PAH components in the WSFs include acenaphthalene, acenaphthylene, anthracene, benz (a) anthracene, benzo (a) pyrene and chrysene.

Table 2: Heavy Metal Content (mgL^{-1}) of WSFs of Crude Oil, Diesel, Gasoline and Kerosene

Parameter	Crude oil	Diesel	Gasoline	Kerosene
Fe (mg L^{-1})	0.11 ± 0.00^{a}	0.08 ± 0.00^{b}	0.08 ± 0.00^{b}	0.04 ± 0.00^{c}
Zn (mg L^{-1})	0.09 ± 0.00^{a}	0.07 ± 0.00^{bc}	0.08 ± 0.00^{b}	0.06 ± 0.00^{c}
Cu (mg L^{-1})	0.04 ± 0.00^{a}	0.02 ± 0.00^{b}	0.03 ± 0.00^{b}	0.02 ± 0.00^{b}
Mn (mg L^{-1})	0.12 ± 0.01^{a}	0.16 ± 0.01^{b}	0.28 ± 0.00^{c}	0.17 ± 0.00^{b}
Cr (mg L^{-1})	nd	0.01 ± 0.00^{a}	0.01 ± 0	Nd
Cd (mg L^{-1})	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	nd	Nd
Pb (mg L^{-1})	0.02 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}
Ni (mg L^{-1})	0.11 ± 0.00^{a}	0.10 ± 0.00^{a}	0.10 ± 0.00^{a}	0.11 ± 0.00^{a}
V (mg L^{-1})	nd	nd	nd	nd

Key: nd – not detected.

Values with similar alphabets along each row are not significantly different from each other ($p > 0.05$).

Table 3: Total Petroleum Hydrocarbon (TPH) and Polycyclic Aromatic Hydrocarbon (PAH) Content (mgL^{-1}) of WSFs of Crude Oil, Diesel, Gasoline and Kerosene

Parameter	Crude oil	Diesel	Gasoline	Kerosene
TPH (mgL^{-1})	**14.12^{d}**	**6.34^{c}**	**4.03^{a}**	**2.31^{b}**
PAH Components				
Acenaphthalene ($mg\ L^{-1}$)	0.003	<0.001	<0.001	<0.001
Benzo(k) fluroranthene ($mg\ L^{-1}$)	<0.001	0.000	<0.001	<0.001
Acenaphthylene ($mg\ L^{-1}$)	0.001	0.000	<0.001	<0.001
Anthracence ($mg\ L^{-1}$)	0.002	0.003	<0.001	<0.001
Benz(a) anthracene ($mg\ L^{-1}$)	0.005	0.003	0.003	<0.001
Benz(b) fluoranthene ($mg\ L^{-1}$)	0.001	0.002	0.002	<0.001
Benzo(ghi) perylene ($mg\ L^{-1}$)	<0.001	<0.001	<0.001	<0.001
Benzo(a) pyrene ($mg\ L^{-1}$)	0.002	0.001	<0.001	<0.001
Chrysene ($mg\ L^{-1}$)	0.001	<0.001	<0.001	<0.001
Dibenz(ah) anthracene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Fluoranthene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Fluorene(mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Indoene (1,2,3, cd) pyrene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Phenthrene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Pyrene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Perylene (mgL^{-1})	<0.001	<0.001	<0.001	<0.001
Total (mgL^{-1})	0.015^{a}	0.009^{b}	0.005^{c}	0.001^{d}

Values with similar alphabets along each row are not significantly different from each other ($p > 0.05$).

The results of this study are consistent with other studies. Edema and Okungbowa (2012) that analysed the WSFs of two crude oil samples and detected the presence of Fe, Cu, Cr, Pb, V, Zn and Mn. Edema, (2009) analysed the WSF of crude oil from Ogini well-head and found it to contain the following ions, Na^{+}, Mg^{2+}, Ca^{2+}, NH_4^{-}, NO_3^{-}, Cl^{-} and SO_4^{2-}. It was found that Fe, Cd, Pb, Mn, Ni and V were present. Similar results were obtained by Edema (2012). When the ionic characteristics of water soluble fractions of Olomoro well-head crude oil was analysed, it was found to contain the cations Ca^{2+}, Mg^{+}, Na^{+} and K^{+} and NH_4^{+} and the anions Cl^{-}, SO_4^{2-} and NO_3^{-}. Heavy metals present include Cr, Pb, Cu, Zn, Mn and V. Analysis of ionic contents of WSF of Amukpe well-head crude oil showed the presence of Cl^{-}, NO_3^{-}, SO_4^{2-}, HCO_3^{-}, Na^{+}, K^{+},

Ca^{2+} and Mg^{2+}. The study also found the heavy metals, iron, copper, manganese, chromium, lead, vanadium and zinc. This is consistent with the result of this study.

The presence of heavy metals in petroleum have been traced to source rocks and depended on the geological age of the rocks (Ahmad, Tsafe, Zuru, Shehu, Atiku and Itodo, 2010 and Oti, 2016). Studies of the ionic characteristics of WSFs of kerosene, diesel and gasoline are scarce but the analysis of the refined products showed the presence of Cd, Cr, Cu, Pb and Zn (Akpoveta and Osakwe, 2014).

According to Tijjani, Ike, Usman, Malami and Matholo (2012), diesel showed higher concentration of the heavy metals Cu, Zn, Mn, Si, Na and Fe than kerosene and alcohol. The study reported a higher constitute of TPH in WSF of gasoline than in kerosene and diesel. This study showed higher TPH concentration in WSF of diesel than in gasoline. High levels of metals such as Zn, Cr, Fe, Hg, Mn and Pb are associated with petroleum polluted waters (Achudume, 2009). Refinery effluents contain NH_4^+, NO_3^- and SO_4^{2-} including the heavy metals Ni, Pb, Zn, Fe, Cu and Cr. Ground water contaminated with petroleum showed high level of chemical pollutants (Nwachukwu and Osuagwu, 2014).

In addition to changes in chemical characteristics, there were variations in physical characteristics of the WSFs such as pH, EC, TDS, Turbidity, DO and BOD. Several studies show that petroleum pollution cause changes in physical characteristics of water (Achudume, 2009; Aghoghovwia, 2011; [illegible]ekwe and Achudume, 2011). The total petroleum hydrocarbon (TPH) content in W[illegible]f crude oil was higher than TPH content in the WSFs of the refined petroleum products in this study. The WSF of diesel had the highest TPH content followed by WSF of gasoline and WSF of kerosene. This finding is consistent with that of Pinedo, Ibanez, Lijzen and Irabien (2013), which observed higher TPH concentration in crude oil, than refined petroleum products with gasoline, however having the least TPH concentration.

Although some heavy metals are considered toxic, others play important roles in metabolic processes in living organism. Trace elements such copper, cobalt, nickel, zinc, chromium and manganese are essential for growth and normal development of plants and are involved in many enzymatic metabolic reactions (Rusin, Gospodarek, and Nadgorska, 2015). Others such as cadmium, lead and mercury are toxic to plants even in low concentrations (Nagajyoti, Lee and Sreekanth, 2010). Some heavy metals have carcinogenic and mutagenic effect and can cause degradation of DNA and RNA, they are also capable of being bioaccumulated thereby increasing their toxicity (Ali, Khan and Sajad, 2013). The heavy metal content of the WSFs in this study are within the maximum permissible limits set by WHO (2011). Similar results were also obtained by Edema (2012).

High levels of physical characteristics such as pH, EC, TDS, Turbidity, BOD, are indication of pollution (Aghoghovwia, 2011). The values in this study range from pH (4.80 – 5.80), EC (9.00-17µS/Cm); TDS (5–8 mgL^{-1}), Turbidity (4.30 – 5.50NTU), DO (0.4-5.60mgL^{-1}) and BOD (20.00 – 66mgL^{-1}). While EC, Turbidity and TDS are within the maximum limit set by WHO (2011), others such as pH and DO are below the limit while BOD is above the limit. There is no generally set maximum limit to cover all TPH constituents. Limits are set for each hydrocarbon component based on several factors. Examples include benzene 10µgL^{-1}, toluene 700µgL^{-1} ethylbenzene 300µgL^{-1} and xylene 500µgL^{-1}. For aromatic with carbons atoms between 12 – 35 acceptable maximum limit is 0.09mgL^{-1} (UNEP, 2011).

Conclusion

Oil pollution altered the physical and chemical properties of water. This has significant implication for aquatic ecosystems especially for aquatic flora and fauna. Oil spillages which are frequent in the Niger-Delta region of Nigeria lead to pollution of streams, rivers and ponds which the communities hosting oil facilities depend on. Regular monitoring of such water bodies was therefore recommended.

Oil companies must ensure that they maintain high standard of cooperation to reduce accident that leads to oil spills. The Federal Government must ensure that oil producing communities benefits from the revenue generated from crude oil sales. This will be in form of provision of education, health and social infrastructure.

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