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Spatial Variation of Physico-Chemistry and Heavy Metals Profile of Woji Creek, Upper Reaches of Bonny Estuary, Niger-Delta, Nigeria.

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ABSTRACT

Studies on the physico-chemical properties and selected heavy metal profiles namely; Temperature, pH, Dissolved oxygen (DO), Total suspended solids (TSS), Total dissolved solids (TDS), Turbidity, hardness, Nitrate (NO^{-3}), Chloride (Cl^{-}), salinity and Cadmium (Cd), Lead (Pb), Manganese (Mn), Chromium (Cr), Nickel (Ni) and Zinc (Zn) in the water of Woji Creek were investigated. Samples of the water were collected from five established (using GPS) sampling stations along the creek on a monthly basis, for twelve months (October, 2012-September, 2013). Water samples were collected at 4-5cm depth below the water surface using clean, well-labelled 50cl plastic bottles and taken to the laboratory for further analysis. The metals in the water were extracted and their concentrations determined by flame Atomic Absorption Spectrophotometry, (AAS). The mean total values for the physico-chemistry were as follows: Temperature 28.1±0.14^{0}C, pH 6.95±0.01, DO 2.72±0.1, TSS 8.23±0.81,TDS 5432.027±401.23, Turbidity 6.042±0.0.20, hardness 4158.40±342.80, Nitrate 4.268±0.40, Chloride 8790.143±693.38 and Salinity 7.36±0.30. The mean total dissolved solids (TDS), hardness and chloride levels were very high and above the permissible limits recommended by the World Health Organisation (WHO). The mean total values for TDS, hardness and chloride were 5432.027mg/l, 4158.400mg/l and 8790.143mg/l respectively. The mean total Dissolved Oxygen (DO) level (2.720mg/l) was low and well below the permissible limits according to WHO. The mean total concentrations of Cd (0.002mg/l), Mn(0.026mg/l), Ni(0.059mg/l) and Zn(0.009mg/l) in the water were within the permissible limits as recommended by Federal Environmental Protection Agency (FEPA, 1991) and U.S.Environmental Protection Agency, (USEPA, 1986), while those of Cr(0.408mg/l) and Pb (0.163mg/l) were higher than the permissible limits. The presence of these pollutants in the water indicates that the water is polluted and under stress. Fish from this creek are therefore not very safe for human consumption. Bioremediation and regular monitoring of the water body in order to restore and maintain the water quality of the creek and ensure the safety of the organisms for human consumption is recommended.

Introduction

Industrialization and human activities have partially or totally turned our environment into dumping sites for waste materials. As a result, many water resources have been rendered polluted and hazardous to man and other living systems (Bakare et al., 2003). The toxic substances discharged into water bodies bio accumulate through the food chain (Odiete, 1999). A very important pollutant of the environment which has the ability to bio accumulate is heavy metals. Heavy metals are among the most serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Tam and Wong, 2000).

Heavy metals are natural components of the earth's crust. In modern times, anthropogenic sources of heavy metal pollution have been introduced into the aquatic ecosystem. This study focuses on six (6) heavy metals including lead, cadmium, chromium, nickel, manganese and zinc. Sediments play an important role both as sink where heavy metals can be stored and as a source of heavy metal contamination to the overlying water and fish fauna.

Most heavy metals discharged into the river are found to deposit in bottom sediments through complex physical, chemical and biological processes. In mid-ocean, living organisms are primarily responsible for the sediment accumulation, their shells sinking to the ocean floor upon death.

The Woji Creek is a very important water body in the Port Harcourt metropolis since it connects so many communities for various purposes such as fishing, boating, washing and bathing etc. This study is therefore carried out to investigate the profile of physico-chemistry and some heavy metals in the water of the Woji Creek.

Methodology

Study Area

The study was carried out at the Woji Creek which is situated in a strategic location in Port Harcourt, Rivers State, Nigeria. It is a tributary of the upper reaches of Bonny Estuary in the Niger Delta region, and receives domestic and industrial wastes from Trans-Amadi Industrial Layout, main Port Harcourt abattoir and some riverine communities.

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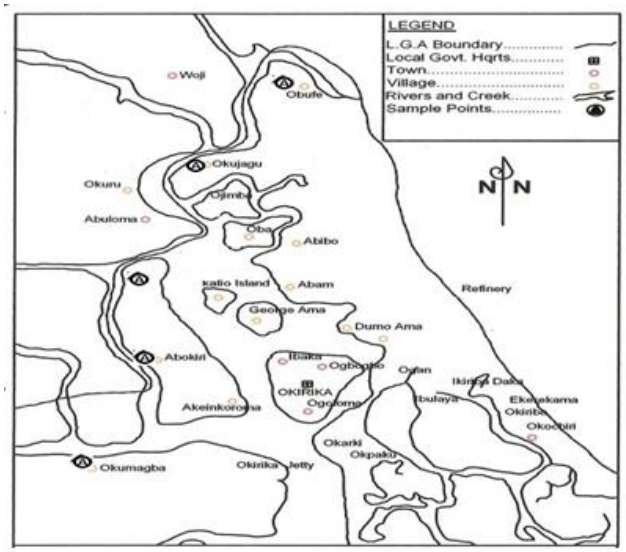

Figure 1. Map of Woji Creek showing the sampling stations.

Woji Creek is located between longititude 6° 55′E and 7° 05′E and latitudes 4° 48′N and 4° 57′N. It passes through many communities including Oginigba, Woji Azubiae, Okujagu, Okuru-Ama, Abuloma, Ojimba, Oba, Kalio-Ama and Okrika.

The occupation of the people around Woji Creek include fishing, farming, boating and dredging. Water from the creek is used for washing, cooking and even drinking.

The vegetation is dominated by Nypa palms (*Nypa fructicans*) and mangrove (*Avicennia nitida* and *Rhizophora racemosa*).

Five (5) sampling stations approximately 500 m apart were established along the length of the creek, from which samples were collected from October 2012 to September 2013

Sample Collection

Water samples were collected in labelled 50 cl plastic bottles at about 4-5 cm depth below the water surface from the 5 sampling stations and stored in a chest of ice before transporting to the laboratory for analysis.

Laboratory Analysis

pH of water samples was taken immediately at the sampling site with the use of a Hach meter. The electrode of the device was immersed into a beaker containing sample and allowed to stand for about 5 min in order to stabilize. The values were then recorded. The salinity of the water was also determined using a Hach meter. A drop of the sample water was placed on the lens of the instrument while the meter was held horizontally.

The sample water was allowed to remain on the lens for about 5 minutes and the salinity read off and recorded in ppt. Other parameters such as dissolved oxygen (DO), total dissolved solids (TDS), chloride (Cl^-), hardness, turbidity, nitrate (NO_3^-) and total suspended solids (TSS) were estimated in the laboratory by using ASTM512-1868 water checker instrument.

In the laboratory, water samples were acidified with HNO_3 and preserved according to standard methods described in APHA 3110 for heavy metal analysis, using the flame Atomic Absorption Spectrophotometer (AAS, Buck Scientific Model-210).

Data Analysis

Data were keyed into Microsoft Excel Spreadsheet and descriptive statistics used to display the means, standard deviations and trends of pysico-chemistry and heavy metal content of surface water of the Woji Creek.

Differences in heavy metal content across sampling stations were investigated by one-way analysis of variance (ANOVA) using the Data Analysis ToolPack of Microsoft Excel, 2013.

Results

Physico-chemistry of Surface water of Woji creek

pH

pH followed a roughly similar trend as DO with mean values ranging from a minimum value (6.78) at STN1 to a maximum value (7.04) at STN4 (Fig 5).

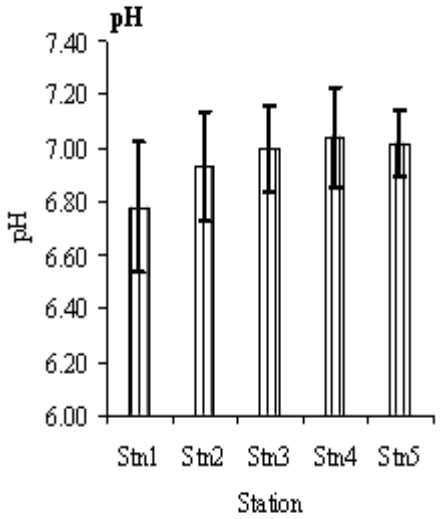

Fig 1. pH of surface water samples from the 5 stations of Woji Creek.

Dissolved Oxygen (DO)

Mean DO of surface water samples were fairly constant and varied minimally across sampling stations, with mean values that fluctuated between a minimum of 2.075 mg/l (STN1) to a maximum of 3.183 mg/l (STN5) (Fig 4). Slightly higher values ranging from 2.933 – 3.108 mg/l were also observed at STN3 and STN4, but never exceeded the peak value recorded at STN5.

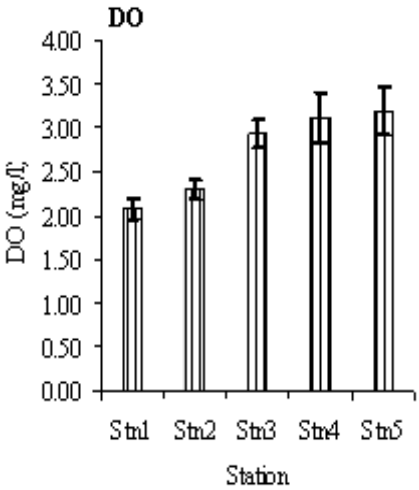

Fig 2. DO (mg/l) of surface water samples from 5 stations of the Woji Creek.

TSS

Results showing the TSS of surface water samples from the study area are as presented in Fig 1 below. TSS showed minimal variability in water samples, with mean values ranging from a minimum value (7.367 mg/l) at STN2 to a maximum value (8.90 mg/l) at STN3

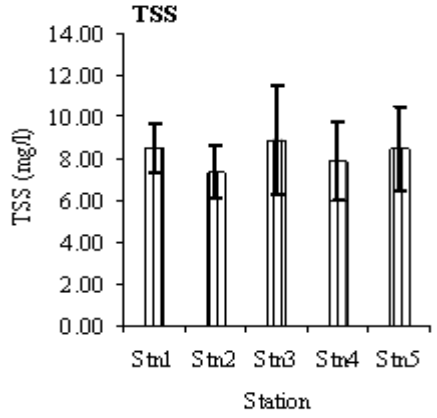

Fig 3 . TSS (mg/l) of surface water samples from the 5 stations of Woji Creek.

TDS

TDS of surface water samples showed slight variation with mean values ranging from a minimum at STN1 (3316.7 mg/l) to a maximum at STN5 (7062.53 mg/l). The minimum recorded at STN1 and the slightly higher value obtained at STN2 (4310.47 mg/l) were comparatively lower than the mean values observed at STN3 (6269.73 mg/l) and STN5 (7062.53 mg/l) (Fig 2).

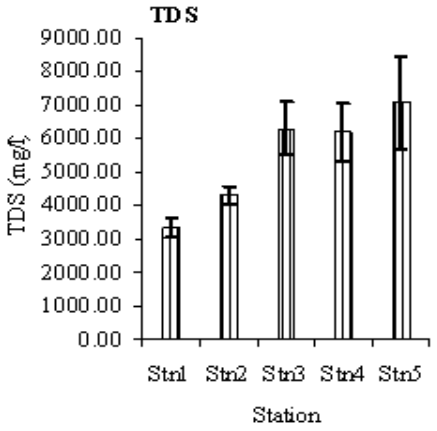

Fig 4. TDS (mg/l) of surface water samples from the 5 stations of Woji Creek.

Turbidity

The highest mean turbidity value was recorded at STN1 (7.372 NTU). A slight drop was detected in turbidity at STN2 (5.818 NTU), thereafter mean values remained fairly stable from STN 2 – STN5 as shown in Fig 7 below.

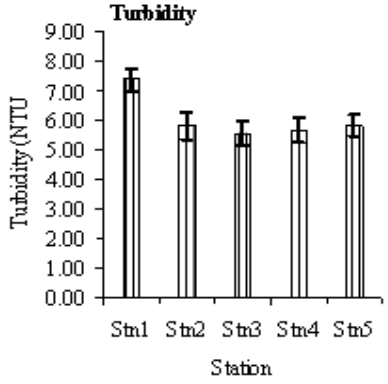

Fig 5 . Turbidity (NTU) of surface water samples from the 5 stations of Woji Creek.

Hardness

From the mean value of 3486.167 mg/l recorded at STN1, water hardness was observed to drop slightly to a minimum at STN2 (2870.000 mg/l) and rose again to a peak value at STN4 (5808.333 mg/l) as shown in Fig 3 below.

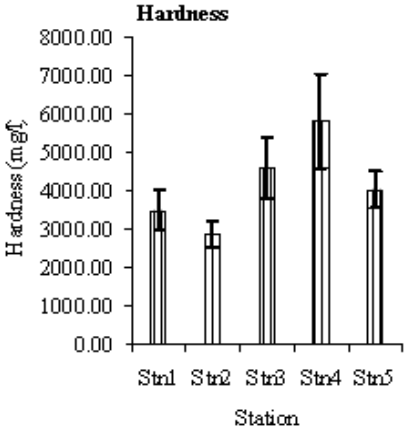

Fig 6. Hardness (mg/l) of surface water samples from the 5 stations of Woji Creek

Nitrate (NO_3^-)

The variability of NO_3^- in water samples was very minimal across stations and mean NO_3^- values were found to lie in the range 3.96 mg/l (STN2) – 4.761 mg/l (STN1) (Fig 6).

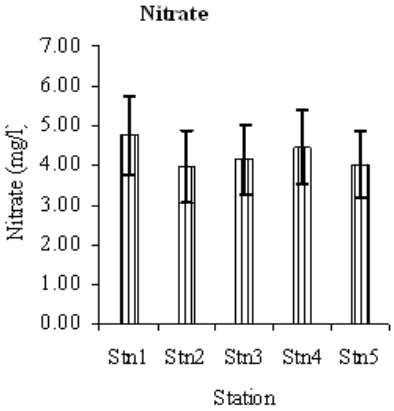

Fig 7. NO_3^- *(mg/l)* of surface water samples from the 5 stations of Woji Creek.

Salinity

Except for the minimum (5.098 ‰) and peak (8.692‰) values recorded at STN1 and STN4 respectively, salinity was relatively stable across sampling stations. Mean salinity values obtained at STN2 and STN3 were somewhat identical and lied in the narrow range of 6.890 – 7.500‰ Fig 8. A similar observation was made in mean values obtained at STN4 and STN5 which also fell in the range 8.617 – 8.692‰.

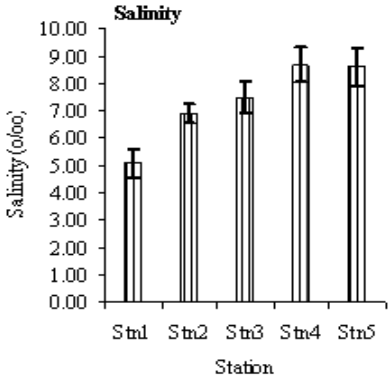

Fig 6. Salinity ($^o/_{oo}$) of surface water samples from the 5 stations of Woji Creek.

Chloride (Cl^-)

Mean Cl^- content of surface water followed roughly similar pattern as salinity with mean values ranging from a minimum of 4577.72 mg/l (STN1) to a maximum of 11756.2 mg/l (STN5) (Fig 9).

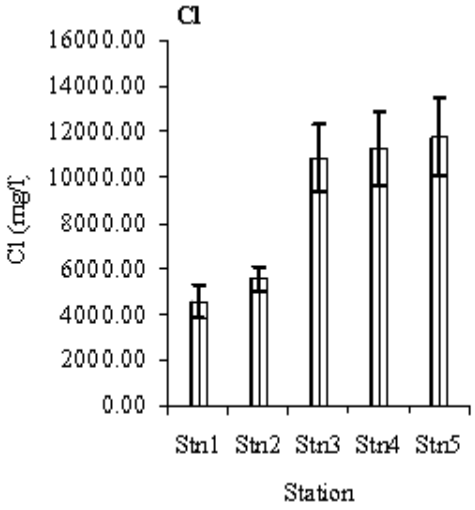

Fig 7. Cl^- concentrations (*mg/l*) of surface water samples from the 5 stations of Woji Creek.

Concentrations of Heavy Metals in Surface Water Samples

Lead (Pb)

Mean Pb values ranged from a minimum of 0.122 *mg/l* (STN1) to a maximum of 0.201 *mg/l* (STN3). Mean Pb values recorded in water samples at STN2 and STN4 were fairly similar and varied from 0.147 – 0.154 *mg/l*. Such consistency was also found in mean values of Pb obtained at STN3 and STN5 (0.191- 0.201 *mg/l*) (Fig 1).

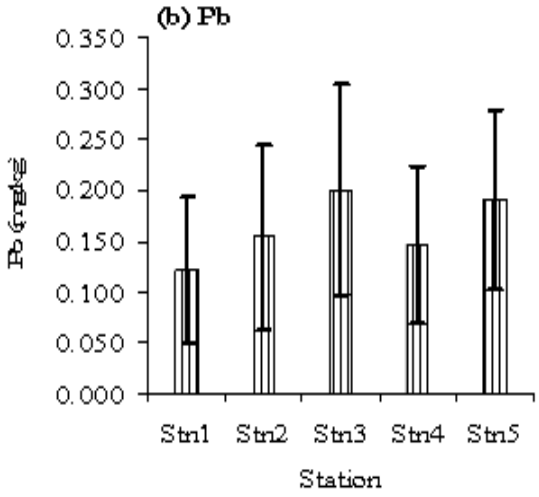

Fig 10. Concentrations of *Pb (mg/l)* in surface water samples from 5 stations of the Woji Creek

Cadmium (Cd)

The highest mean value of Cd was recorded at STN2 (0.004 *mg/l*) than at all other stations. Cd fell to 0.002 mg/l at STN5 but remained fairly constant at STN1, STN3 and STN4 as shown in Fig 2 below.

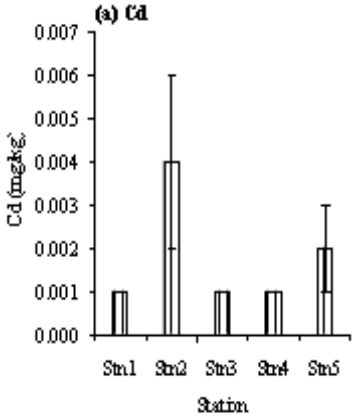

Fig 11. Concentrations of *Cd (mg/l)* in surface water samples from the 5 stations of Woji Creek.

Manganese (Mn)

Mn was detected at low levels in water samples with mean values ranging from a minimum of 0.0020 mg/l (STN4) to a maximum of 0.036 mg/l (STN1). Mn concentrations remained fairly stable in water samples at STN4 and STN5 (0.020 – 0.021 mg/l) as well as STN2 and STN3 (0.025 – 0.026 mg/l) (Fig 3).

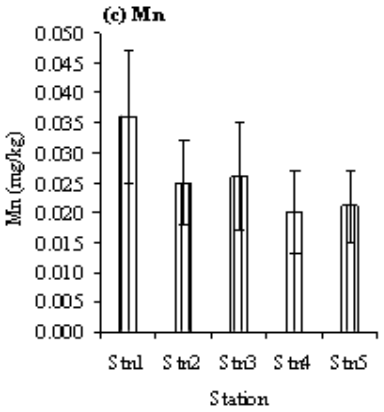

Fig 12. Concentrations of *Mn* (*mg/l*) in surface water samples from 5 stations of the Woji Creek.

Chromium (Cr)

Cr showed minimal variability in surface water samples. Mean *Cr* levels at STN2, STN3 and STN4 ranged from 0.375 – 0.446 *mg/l*. *Cr* values recorded in this study were found to fall in the range 0.375 *mg/l* (STN3) – 0.446 *mg/l* (STN5) (Fig 4).

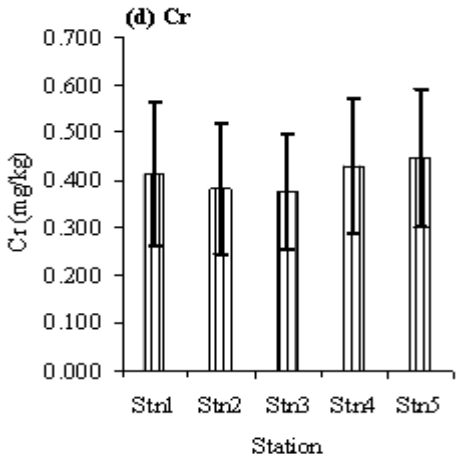

Fig 13. Concentrations of *Cr* (*mg/l*) in surface water samples from 5 stations of the Woji Creek.

Table 1. Comparison of the mean total variation of physico-chemical parameters of water of Woji creek with permissible limits by some regulatory bodies.

Parameters	Total mean levels in Woji creek water	Permissible level by W. H.O.
Temp (°C)	28.143	30-35
pH	6.954	6.5-8.5
TDS (mg/l)	5432.027	500
D O (mg/l)	2.720	5.00-7.00
Chloride (mg/l)	8790.143	250
Hardness (mg/l)	4158.400	300
Nitrate (mg/l)	4.268	45
Turbidity (NTU)	6.042	<5
Salinity (mg/l)	7.359	200
TSS (mg/l)	8.225	500

Table 2. Comparison of the mean total concentrations of heavy metals in the water of Woji creek with permissible limits of some regulatory bodies.

Metals	Mean total concentrations in water (mg/l)	Permissible limits(mg/l) according to FEPA (1991)	Permissible limit(mg/l) according to USEPA (1986)	Permissible limit(mg/l) according to FAO/WHO (2003)
Cd	0.002	0.003	0.01	0.003
Pb	0.163	0.1	0.05	0.05
Mn	0.026	0.05	0.15-0.05	0.04
Cr	0.408	0.05	0.05	0.05
Ni	0.059	0.05	0.02	0.02
Zn	0.009	1.0	1.0	-

Discussion

The physico-chemical parameters of any water body are important and influenced by natural and man-made activities. The mean water temperatures were similar across the stations. This is typical for tropical estuarine waters (Obire *et al*, 2003; Hart and Zabbey, 2005; Davies *et al*, 2008). The highest mean temperature recorded at station 4 could be due to lack of marginal vegetation at that station. Higher mean temperature during the dry season can be due to longer photoperiod and higher sunlight intensity. Similar results were also reported by Davies *et al*, (2008). The mean water temperature of Woji creek was below the permissible limits recommended by WHO. pH is the scale of intensity of acidity and alkalinity of water and the measure of the concentration of hydrogen ions (Neha, 2003). The pH range was within the permissible limits by WHO standard. The pH of Woji Creek range from slight acidity to slight alkalinity (from 6.780 to 7.040). This is an indication that the various anthropogenic inputs did not alter the ambient pH of the water (IJC, 1977; Davies *et al*, 2006). The higher mean pH in the dry season pH and lower in the wet season can be attributed to increased photosynthetic rates of aquatic plants (Eyesink and Solomon, 1981). Water turbidity is caused mainly by sand, silt, clay, phytoplankton, microorganism or organic materials suspended or dissolved in the water. The mean total turbidity of the water was within the permissible limit according to WHO. The highest chloride concentration in water indicates the presence of organic wastes, particularly of animal origin (Saksena *et al*, 2008). The chloride level in the Creek water was very high and above the permissible limit according to WHO. Davies *et al*, (2008) also reported very high chloride level when working on the physicochemical parameters of Trans- Amadi creek.

The chloride level increased downstream from station 1 to station 5. This suggest the influence of seawater on the chloride level. The lower mean chloride concentration in the wet season and higher mean chloride concentration in the dry season may be due to the dilution effect and increased municipal runoffs during the rains (Chindah and Braide, 2004; Davies *et al*, 2008). Salinity is the concentration of dissolved salts in water. Salinity was within permissible limits recommended by WHO and it increases downstream from station 1 to station 4. This can be attributed to the proximity of the creek to the sea. Salinity is the concentration of dissolved salts in water. The mean total dissolved solids (TDS) was much higher than the recommended limits by WHO. This is an indication of very high organic pollution from anthropogenic sources (Saad *et al*, 1994) the higher mean TDS level in the wet season than during the dry season might be due to high surface runoff, overland flow and higher discharge of organic wastes into the water body (Dejoux *et al*, 1981). TDS indicate the general nature of salinity of water. Hardness of water is caused by excessive presence of bicarbonate, chloride and dissolved sulphate in water (Kamal *et al*, 2007). Hardness level of the water of Woji Creek was very high and above the permissible limit recommended by WHO. This high level of hardness is characteristic of brackish water environment (Edet, 1987). Dissolved Oxygen (DO) is the amount of gaseous oxygen dissolved in the water. The mean DO of Woji Creek as at the time of the study was low and below the WHO permissible limits. The higher level of mean DO in the wet season and lower level in the dry season may be due to the fact that oxygen dissolves easily in cooler water than in warmer water. The mean nitrate level was very low and below the WHO permissible limit. The low nitrate level of the creek could possibly be due to high photosynthetic activities by aquatic plants. The mean total suspended solid (TSS) in the water was low and below the WHO permissible limits.

The mean total concentrations of Cd, Mn, Ni and Zn in the water of Woji creek were within the permissible limits as recommended by Federal Environmental Protection Agency (FEPA), 1991 and USEPA, 1986., but the mean total concentration of Pb, and Cr exceeded the permissible limits. The high concentrations of Pb and Cr in the water may be attributed to the discharge of untreated wastes from the engineering and chemical industries around the study area directly into the water body. The mean total concentration of Cd was however much higher than the permissible limits set down by FEPA (1991) and UNEP (1985). The high concentration of Pb and Cr in the water of Woji creek can be attributed to the direct discharge of untreated wastes from the engineering and chemical industries around the creek into the water body. It can also be as a result of all the washing, bathing and boating activities carried out in the creek.

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