

Assessment of the Impacts of Industrial Effluent Discharges on the Water Quality of Asa River, Ilorin, Nigeria.

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Abstract: *The present study was carried out to investigate the impact of industrial effluent discharges on the water quality of Asa River, Ilorin, Nigeria. Sections of Asa River along its course were studied over the period of twenty four months (between April, 2011 and March, 2013) to determine the effects of effluents discharges on water qualities in term of its physical and chemical parameters, and heavy metal. Water samples were collected and analyzed monthly from three different sites along the river course for physical, chemical and heavy metals using standard laboratory procedures and Atomic Absorption Spectrophotometer (AAS). The results revealed that the level of pollution varied greatly with sampling sites and season, and that the water quality was fairly acceptable at sampling site A and became grossly impaired at the two other sampling sites (B and C), indicating significant pollution from nearby Agricultural, Industrial and domestic premises. Statistically, virtually all the physical, chemical and heavy metal parameters analyzed were found to be significant when compared with the control water sample from sampling site A. Also, there were series of deviations in the obtained values from World Health Organization, National Industrial Standard and National Environmental Standards and Regulations Enforcement Agency's standards. Therefore, the results suggested that the water in the river was polluted and not good for human consumption. It is then, recommended that the careless disposal of such contaminants should be discouraged with strict enforcement of existing legislation and, vigilance.*

Key words: *Industrial Effluent, Human Consumption, Heavy Metals, Water Quality, Water, Physico-chemical, Pollution, Asa River, Anthropogenic, Nigeria.*

I. Introduction

Asa River is a major river that almost divides Ilorin city into two halves. The river has a total surface area of about 303 hectares (Olayemi, 1994; Eleta *et al.*, 2005). This river is highly prone to contamination due to its proximity to industrial congestion which makes the river to be exposed to abuse, such as effluent receptacle leading to contamination. Regularly, it receives wastes from industries located along its course apart from domestic wastes and other activities carried out along it that contributes to its pollution. Despite the fact that the river is not good aesthetically, rapid growth of water hyacinth could be observed downstream of the effluent discharge point. It is also noticed that people living along the course of the river use the water for some domestic chores including drinking, nursing vegetables, washing cars and other home utilities, when portable water is not readily available.

Anthropogenic influences (urban, industrial and agricultural activities, increasing consumption of water resources) as well as natural processes (such as, changes in precipitation inputs, erosion, weathering of crustal materials) degrade surface waters and impair their use for drinking, industrial, agricultural, recreational or other purposes (Carpental *et al.*, 1998). Urban streams are common features of contemporary landscapes, and the effects of urbanization on aquatic/stream ecosystems are complex, with many physical, chemical and biological consequences (Suren, 2000). Increased impervious surfaces due to development of roads and car parks, substantially affects urban stream flow regimes, reducing ground water recharge due to lack of precipitation infiltration, and leads to increasing run off during rainfall (Paul and Meyer, 2001). In addition, urban runoffs can detrimentally alter stream chemistry, bringing with it suspended sediments such as nitrogen and phosphorus as well as heavy metals, polycyclic aromatic hydrocarbons (PAH's), and other pollutants that accumulates during times of low rainfall on roads and car parks (Beasley and Kneale, 2002). These are some of the ubiquitous consequences of urban development all of which can ultimately reduce stream health and biological diversity. Risks of water- borne diseases are therefore a major public health concern in Ilorin city.

The industrial, domestic and agricultural wastes that are discharged into this river contains harmful chemicals such as heavy metals, oil, settle able solids, nutrients and ammonia which may affect the resident species in receiving water body. In addition, plants and animals inhabiting the water body are not spared as their normal functioning and population dynamics is affected by pollution. All these effects will go back to man as its insatiable consumption of fresh water resources remains unending. Thus, man may be facing the physiological threat. Many people in developing countries like Nigeria do not have easy access to safe and clean drinking

water or to adequate amount of water for basic hygiene. In 2004, the World Health Organization reported that about 1.1 billion people representing 17% of the global population were without safe drinking water. Substantial number of these people lives in China, India, Africa and Middle East. The report also had it that 42% of Sub-Saharan Africa lacks drinking water. By the end of 2008, an estimated 884 million people in the world lacked access to improved sources of drinking water and 2.6 billion people lack access to improved sanitation facilities (RADWQ, 2010). Forecast has shown that more than 47% of the global population will face severe water hardship by the year 2030 (Robert, 2008). Despite increasing public sensitization, water pollution continues to generate unpleasant implication for health and community development. The protection of water quality and aquatic ecosystem as a vulnerable resource essential sustainable development is of utmost important to prevent water pollution and degradation of fresh water resources in this region. It is important to continually investigate the quality of surface water to check the influence of the teaming growing population, urbanization and industrialization on it. This study therefore is aimed at investigating water qualities in three different sampling sites along the course of Asa River and its tributaries, using different analytical techniques.

II. Materials And Methods

Description of the Study Area

This study involves three water bodies: Asa River (AS) and two of its tributaries known as Okun Stream (OKS) and Osere Stream (OSS), they are situated in Ilorin, Kwara State, North-Central, Nigeria. These water bodies are the major source of water supply to the general populace of the area. But recently, the water bodies were noted to receive effluents Industries and some other domestic units of operations. The three sampling locations as described in Figure 1 chosen for this work were the same with little modification as those described by Olayemi *et al.*, (2003) on the observed possibility of heavy metals contamination. Asa River has a surface area of 302 hectares with a maximum depth of 14m and is located approximately 4km south of Ilorin Township (Adekeye, 2004). The river lies between latitude $8^{\circ}28'$ and $8^{\circ}52'N$ and longitude $4^{\circ}35'$ and $4^{\circ}45'$ East. The river is very significant to the socio-economic growth of Ilorin and supplies the basic water needs of Ilorin city and its environs after treatment. It also serves as their major source of water for agricultural activities such as irrigation of farmland and most importantly fishing. The river provides fresh fish to the town and serves as water source for both industrial and domestic uses (Adekeye, 2004). Major industries in the town are sited along its bank or its tributaries. The river is also being used for recreational purposes, serving as a tourist attraction center (particularly the Asa dam).

Three sampling sites (A, B & C) were selected in this study in relation to the industrial, agricultural and domestic effluents that enter the stream (Figure 1; Plates 1- 3). **Site A** (SP1) is upstream popularly called Osere stream which is about 1.5km from the effluent discharge point (point B). It receives refuse and sewage from homes, cassava processing units and run-offs from agricultural and poultry farms. **Site B** (SP2) is midstream at which soap and detergent, flour mills and pharmaceutical effluents are discharge along Okun stream. It also receives run-off water from agricultural, poultry farms lands, cassava processing units and refuse dumps from homes including laundering activities. **Site C** (SP3) is the downstream about 1km from the point of discharged (that is sampling Point B). The stream receives effluents from some soft drinks plants (CocaCola and 7^{up}), cassava processing units, agricultural, poultry wastes, and run-offs from diffuse sources. Therefore, the choice of the afore-mentioned sampling points was based on the accessibility, the rate at which they receives effluents from different sources, the extent of their pollution and their distances from the industrial premises.

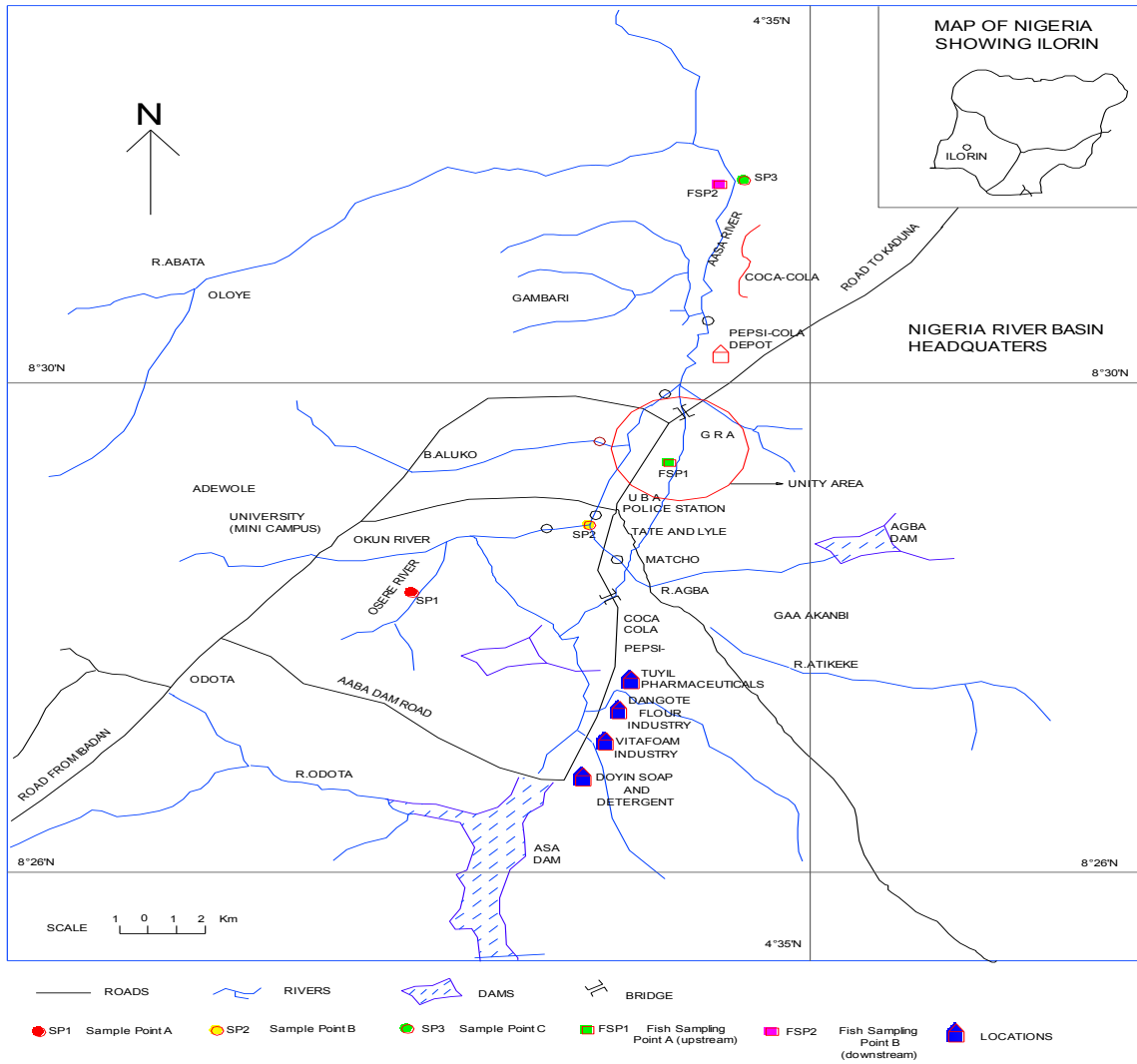


Figure 1: Map Showing Asa River and all the Sampling Sites



Plate 1: The plate showing Water and Sediment Sampling Site A; Plate 2: The plate showing Water and Sediment Sampling Site B; Plate 3: The plate showing Water and Sediment Sampling Site C

Sample Collection and Analyses

Water samples were collected from three sampling sites at various distances from the source of waste discharge over a twenty four month period. The polyethylene bottles used for sample collection were washed, rinsed with dilute nitric acid solution, and rinsed two to three times with some of the water been sampled. Composite samples were prepared and analyzed for some cations and anions. Results obtained were statistically analyzed and compared with recommended standards. Samples were refrigerated prior to analyses; Atomic Absorptive Spectrophotometer (AAS) was used for cations determination, gravimetric method was used to evaluate SO_4^{2+} levels, spectrophotometry method was used to determine PO_4^{3+} and NO_3^- while argentometric titration was used to determine the Cl⁻ in the water samples.

The pH was determined using a pH meter (model E512). 50ml of water samples from the three sampling points were transferred into a beaker for pH measurements. The pH meter was standardized by buffer of pH 7 and 9 just before use, each time it was engaged in pH determinations (A.P.H.A, 1985). The Dissolved Oxygen was determined by the method of A.P.H.A (1985). Water samples were collected in 300ml reagent bottles. Two milliliters (2ml) each of manganese sulphate solution and alkali iodide-oxide solution were added to each sample below the surface and the bottles were stoppered carefully to prevent air bubbles. The content of the bottle was mixed by rapidly inverting it twenty times. The bottle was allowed to stand until a precipitate settles to the bottom half of the bottle. This was mixed again by inverting the bottle several times and the precipitate allowed settling. Two milliliters (2ml) of concentrated sulphuric acid was added. The bottle was stoppered and inverted several times to dissolve the precipitate. One hundred milliliters (100ml) of the resulting solution was measured into a 250ml conical flask and titrated with standard sodium thiosulphate solution to a pale straw color. Eight drops of starch indicator solution were added to the solution and titrated until the blue color disappeared. The volume of the thiosulphate used was recorded. The dissolved oxygen content was calculated using the formula of Boyd (1981) i.e.

$$\text{Dissolved Oxygen (mg l}^{-1}\text{)} = \frac{(\text{ml titrant N (8)})(1000)}{100}$$

Electrical Conductivity of the samples was determined by measuring 50ml into a beaker for conductivity measurements. This was achieved with a conductometer (model cm 25) that had been previously standardized by dipping the electrode into distilled water. (WHO, 1988). Biological Oxygen Demand (BOD) was determined in order to measure the dissolved oxygen consumed by microorganisms. Two reagent bottles were used for the BOD analysis. 250cm³ of distilled water was measured and 250cm³ of the water samples were poured into each reagent bottle and titrated with 10ml of 1.4ml tetra oxosulphate (vi) acid and 10ml of 0.1 potassium permanganate was also added. The solutions were incubated for 5 days after which they were titrated with 0.0125M sodium thiosulphate solution with starch as indicator (WHO, 1988). Total Suspended Solids (TSS) was analyzed by placing a Pre weighed filter paper on a holder and washed with distilled water. 100ml of each water sample were filtered and dried through the filter papers. The filter papers were subsequently dried to constant weight for one hour at 105^oC. They were then cooled in a desiccator and weighed (WHO 1988). The TSS values were calculated using the formula:

$$\text{TSS (mg l}^{-1}\text{)} = \frac{\text{Mass of solids on filter paper}}{\text{Volume of sample filtered}}$$

Nitrate (NO_3^-) was determined by measuring ten milliliters (10ml) of water samples from each sampling site into Nessler tubes. 10ml of distilled water was also measured into another Nessler tubes and 0.5ml of brucine and 10ml of concentrated H_2SO_4 were then added to each tube. Drops of potassium nitrate was later added to the Nessler tubes with distilled water until its colour match with the colour of the water samples in the Nessler tube (WHO 1988). The concentration of nitrate was then calculated as:

$$\text{NO}_3^- \text{ (mg l}^{-1}\text{)} = \frac{\text{ml of KNO}_3 \times 0.1 \times 1000}{\text{ml of sample}}$$

Chloride was determined using Argentometric method in which the water sample is titrated against standard AgNO_3 titrant was used for the estimation of chloride. A 25 ml well mixed water sample was diluted to 50ml with distilled water to which was added same volume of 0.02 N H_2SO_4 , followed by 2 to 4 drops of potassium chromate (K_2CrO_4) which changed the color to a pinkish yellow. Amount of chloride present was calculated from the amount of silver nitrate used as a titrant. Sulphate: To 2 ml of sample, the same volume of 0.02 N HCl solution was added that was equal to the volume of 0.02 N H_2SO_4 used, followed by 5ml 0.02M BaCl_2 while boiling. The mixture was cooled to room temperature, to which was then added 1ml 0.02 M Mg Cl_2 +2 to 4ml ammonia-ammonium chloride buffer pH 10(67.5g NH_4Cl in 570ml concentrated NH_4OH and diluted to 1 litre) and a few drops of eriochrome Blank – T (EBT) indicator and titrated against 0.01M EDTA until color changed from red to violet blue. Blank containing only 25ml distilled water instead of sample without adding HCl was also titrated against EDTA. Well-mixed water sample (25ml) was diluted to 50ml with distilled water

to which was added 2-4ml of KOH buffer pH 12.5 [20%(w/u) KOH solution] and 0.2g of murexide indicator (0.2g of murexide per 100g of NaCl). The resultant reddish color solution in the flask was titrated against 0.01M EDTA with continuous stirring until the reddish colour changed to bluish purple (violet). Magnesium Hardness: Well-mixed water sample (25ml) was diluted to 50ml with distilled water in a flask. To this flask, 2 to 4ml buffer pH (1067.5g NH₄Cl in 570ml concentrated NH₄OH and diluted to 1 litre), and 2 to 3 drops of eriochrome black – T 10.5g sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthanol-4-sulfonic acid dye in 100g triethanolamine indicator were added and slowly titrated against 0.01M EDTA with continuous stirring until the last reddish color changed to bluish purple.

Heavy Metal Analysis

Heavy metals like lead, zinc, magnesium, manganese, copper, cadmium and arsenic were determined in both water. 100ml of water sample was measured into a 250 ml volumetric flask was acidified with 5ml of HNO₃ (55%) and evaporated on hot plate to about 20ml. 5ml additional HNO₃ (55%), 10ml perchloric acid (70%) and a few glass heads were added to prevent bumping. The mixture was evaporated until brown fumes change into dense white fumes of perchloric acid (HClO₄). The sample were removed from the hot plate, cooled to room temperature and diluted to 100ml with distilled water in a 100ml volumetric flask. The solution was then aspirated into flame atomic absorption spectrophotometer (AAS) for the determination of heavy metals.

Data collected were collated and analyzed using descriptive statistics (mean standard error and percentage). Level of significance of differences in the values of the parameters was assessed using student's t-test. Variability in the data was evaluated using the co-efficient of variation and the F ratio test. Analysis of variance (ANOVA) and Duncan multiple range test as well as bar charts using SPSS statistical package 17.0, 2007 were used in the comparison of data – where values of P < 0.05 were considered significant and graphs were plotted using Microsoft Excel 2007.

III. Results And Discussion

Water Analyses

Water samples from Oseere Stream (site A), Okun River (site B) and Asa River (site C) were analyzed and compared statistically among the three sampling sites and also with the World Health Organization (WHO), National Environmental Standards and Regulations Enforcement Agency (NESREA) and National Industrial Standards (NIS). Water samples were collected during rainy (April to September) and dry (October to March) season. The samples collected were analyzed for various physical, chemical and heavy metals parameters to determine the extent of pollution in the area. The studied physical and chemical parameters analyzed includes water temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), turbidity, total solids (TS), Biological Oxygen Demand (BOD), total hardness, calcium hardness, magnesium hardness, sodium, chloride, nitrate, sulphate and manganese. Among heavy metals analyzed are Chromium (Cr³⁺), Zinc (Zn²⁺), Nickel (Ni²⁺), Copper (Cu²⁺), Lead (Pb²⁺), Iron (Fe), Cadmium (Cd) and Mercury (Ag).

Water samples from the three sampling sites were analyzed and the results of the mean monthly values of each of the parameters are presented in Table 1 and figures 2 to 25 for physical, chemical and heavy metals: The water samples at site A had temperature range of 20.45⁰C – 28.20⁰C with a mean value of 25.04±0.11⁰C, site B had a range of 24.70⁰C – 31.55⁰C with a mean value of 30.13±0.09⁰C; while site C had a range of 26.20⁰C and 30.00⁰C with a mean value of 28.60±0.08⁰C. The mean temperature for rainy and dry seasons were between 28.22±0.96 – 24.60±0.21 respectively. The Hydrogen ion concentration (pH) of the water samples from all the three sampling sites was in the range of 6.30 – 7.70 with a mean value of 7.13±0.01 for site A, site B recorded a range of 7.20 – 8.51 and mean of 7.92±0.06 and sites C had a range of 7.25 – 7.80 having a mean value of 7.56±0.05. Mean values of 7.30±0.06 and 7.50±0.10 were recorded in the dry and rainy seasons respectively. Color ranged between the value of 1.71 – 2.52pt.co with a mean value of 2.02±2.19 for site A; 1.22 – 2.46pt.co with a mean value of 2.08±2.14 for site B, while site C had between 1.85 – 2.00pt.co with a mean value of 2.03±2.00, having a mean value of 2.50±0.82 for dry season and 1.55±0.02 for rainy season.

Turbidity had between the value of 11.95 – 15.95NTU with a mean value of 14.21±0.40; 18.00 – 22.30NTU with a mean value of 19.95±0.20 for sites B while site C had 15.40 – 18.70NTU with a mean value of 17.15±0.62; dry season recorded 18.96±1.01 and 12.22±0.01 for rainy season. Electrical conductivity had between 1.50 – 1.55µscm⁻¹ with a mean value of 1.52±4.01 for site A; 2.04 – 2.40µscm⁻¹ with a mean value of 2.19±5.51 for site B and 1.45 – 2.15µscm⁻¹ with a mean value of 2.01±3.95 for site C; dry season had 3.51±0.25 and rainy season had 1.35±0.88. Total hardness had between 11.29 – 15.46mgCaCO₃l⁻¹ with a mean value of 14.56±0.98 for sampling site A; site B had 57.40 – 74.35mgCaCO₃l⁻¹ with a mean value of 67.12±0.58 and site C ranged between 58.05 – 73.60mgCaCO₃l⁻¹ with a mean value of 65.71±0.97 while dry season had a mean value of 15.21±0.01 and rainy season with 13.00±0.21.

Amongst chemical parameters analyzed for the three sampling points are; Total solid which recorded values between the range of $1.30 - 1.60\text{mgO}_2\text{l}^{-1}$ with a mean value of 1.37 ± 5.00 for site A; $1.31 - 1.59\text{mgO}_2\text{l}^{-1}$ with a mean value of 141 ± 4.21 for site B; $1.31 - 2.50\text{mgO}_2\text{l}^{-1}$ with a mean value of 1.44 ± 0.92 for site C; while dry season recorded 1.96 ± 0.00 and rainy season with 1.21 ± 0.01 . Biological Oxygen Demand (BOD) had $2.50 - 3.55\text{mgO}_2\text{l}^{-1}$ with a mean value of 3.03 ± 0.06 for site A; $5.50 - 7.60\text{mgO}_2\text{l}^{-1}$ with mean value of 6.77 ± 0.17 for site B; $4.60 - 7.20\text{mgO}_2\text{l}^{-1}$ with mean value of 5.66 ± 0.68 for site C while the dry season value was 3.91 ± 0.02 and 2.66 ± 0.05 for rainy season. Dissolved Oxygen (DO) had $11.00 - 16.50\text{mgO}_2\text{l}^{-1}$ with a mean value of 13.67 ± 0.50 for site A; $9.00 - 11.50\text{mgO}_2\text{l}^{-1}$ with a mean value of 9.46 ± 0.61 for site B; $8.50 - 10.50\text{mgO}_2\text{l}^{-1}$ with a mean value of 9.54 ± 0.41 for site C while the mean value of obtained for dry season and rainy season were 15.10 ± 0.02 and 10.01 ± 0.02 respectively. Sulphate ranged from $11.15 - 14.40\text{mg l}^{-1}$ with a mean value of 12.95 ± 0.10 for site A; $14.15 - 21.75\text{mg l}^{-1}$ with a mean value of 20.17 ± 0.19 for site B; $17.30 - 18.65\text{mg l}^{-1}$ with mean value of 18.09 ± 0.21 for site C while 15.05 ± 0.26 and 12.02 ± 0.01 were recorded for rainy and dry season respectively. Nitrate values for site A ranged from $1.20 - 1.85\text{mg l}^{-1}$ with a mean value of 1.49 ± 0.21 ; site B had between $2.01 - 3.01\text{mg l}^{-1}$ with a mean value of 2.68 ± 0.28 ; site C had between $2.03 - 2.71\text{mg l}^{-1}$ with a mean value of 2.41 ± 0.11 while mean values of 2.55 ± 1.01 and 1.35 ± 0.00 was obtained for rainy and dry seasons respectively. Chloride value of between $9.56 - 11.71\text{mg l}^{-1}$ with a mean value of 10.83 ± 0.54 for site A; site B had between $12.68 - 15.98\text{mg l}^{-1}$ with a mean value of 14.76 ± 1.17 ; site C had between $10.56 - 14.15\text{mg l}^{-1}$ with a mean value of 12.46 ± 0.96 while both rainy and dry season had 11.58 ± 2.25 and 9.01 ± 0.06 respectively. Sodium ranged between the value of 2.40 and 3.65mg l^{-1} with a mean values of 2.94 ± 0.30 for site A; $13.15 - 15.40\text{mg l}^{-1}$ with a mean value of 14.60 ± 0.25 for site B; $5.45 - 8.20\text{mg l}^{-1}$ with a mean value of 7.13 ± 0.05 for site C; while dry and rainy season had 3.52 ± 0.11 and 2.40 ± 0.96 respectively. Calcium had between the values of $17.11 - 21.10\text{mg l}^{-1}$ with a mean value of 19.51 ± 0.51 for site A; $25.50 - 37.50\text{mg l}^{-1}$ with a mean value of 31.61 ± 0.66 for site B; $21.57 - 26.36\text{mg l}^{-1}$ with a mean value of 22.88 ± 1.11 for site C; while dry and rainy season had between the values of 24.10 ± 0.01 and 21.00 ± 0.21 respectively.

Heavy metals at the three sampling stations showed varied degree of concentrations; Lead had $0.01 - 0.02\text{mg l}^{-1}$ with a mean value of 0.01 ± 0.00 for site A; $0.01 - 0.04\text{mg l}^{-1}$ with a mean value of 0.02 ± 0.01 for site B; $0.01 - 0.02\text{mg l}^{-1}$ with a mean value of 0.01 ± 0.00 for site C while dry and rainy seasons have the mean values of 2.21 ± 1.21 and 1.01 ± 0.20 respectively. Copper had between $0.46 - 0.73\text{mg l}^{-1}$ with a mean value of 0.66 ± 0.01 for site A; $1.02 - 1.58\text{mg l}^{-1}$ with a mean value of 1.36 ± 0.04 for site B; $0.98 - 1.95\text{mg l}^{-1}$ with a mean value of 1.21 ± 0.00 for sampling site C while dry and rainy season had between the mean value of 2.01 ± 0.01 and 0.21 ± 0.00 respectively. Zinc is the next with average values between $0.01 - 0.02\text{mg l}^{-1}$ with a mean value of 0.01 ± 0.00 for site A; $0.01 - 0.03\text{mg l}^{-1}$ with an average mean value of 0.02 ± 0.01 for site B; $0.01 - 0.02\text{mg l}^{-1}$ with a mean value of 0.02 ± 0.01 for site C while both dry and rainy season had the values of 0.05 ± 0.22 and 0.03 ± 0.01 respectively. Iron had between $0.31 - 0.63\text{mg l}^{-1}$ with a mean value of 0.31 ± 0.04 for site A; $0.46 - 0.75\text{mg l}^{-1}$ with a mean value of 0.61 ± 0.02 for site B; $0.40 - 0.74\text{mg l}^{-1}$ with a mean value of 0.63 ± 0.03 for site C while dry season had a mean value of 5.05 ± 0.05 and rainy season had 3.01 ± 2.01 . Cadmium ranged between $0.21 - 0.28\text{mg l}^{-1}$ with a mean value of 0.22 ± 0.01 for site A; $0.15 - 0.59\text{mg l}^{-1}$ with a mean value of 0.45 ± 0.03 for site B; $0.15 - 0.30\text{mg l}^{-1}$ with a mean value of 0.20 ± 0.00 for site C while dry and rainy season had a mean value each of 0.26 ± 1.21 and 0.11 ± 0.10 respectively. Mercury had between the values of $0.01 - 0.02\text{mg l}^{-1}$ with a mean value of 0.01 ± 0.00 for site A; $0.01 - 0.08\text{mg l}^{-1}$ with a mean value of 0.05 ± 0.02 for site B; $0.01 - 0.06\text{mg l}^{-1}$ with a mean value of 0.03 ± 0.01 for site C while 2.11 ± 0.01 and 1.01 ± 0.00 was obtained for dry and rainy season respectively. Chromium had between $0.01 - 0.05\text{mg l}^{-1}$ with a mean value of 0.05 ± 0.02 for site A; $0.03 - 0.09\text{mg l}^{-1}$ with a mean value of 0.08 ± 0.11 for site B; $0.01 - 0.06\text{mg l}^{-1}$ with a mean value of 0.72 ± 0.00 for site C while both dry and rainy season had a mean value each of 5.01 ± 0.55 and 2.11 ± 0.11 . Manganese had between the values of $0.21 - 0.25\text{mg l}^{-1}$ with a mean value of 0.25 ± 0.01 for site A; $0.26 - 0.63\text{mg l}^{-1}$ with a mean value of 0.48 ± 0.00 for site B; $0.34 - 0.54\text{mg l}^{-1}$ for site C with a mean value of 0.34 ± 0.03 while both dry and rainy season had the mean values of 1.66 ± 0.01 and 1.01 ± 0.00 respectively.

Statistically, all the physical, chemical and heavy metal parameters were found significant when compared with the control water sample (sample from sampling sites A). Also, series of deviation in values from World Health Organization (WHO), NIS (National Industrial Standard) and (NESREA) National Environmental Standards and Regulations Enforcement Agency's standard was observed; temperature, pH, turbidity, electrical conductivity, total hardness, BOD, sulphate, nitrate, sodium, calcium, Magnesium, Manganese, Iron and Cadmium were found within the permissible limit for effluent discharge into all categories of water while total solids, Dissolved oxygen, chloride, Lead, Copper, Zinc, Mercury and Chromium were found to exceed FEPA, (1999) standard (Table 1).

Table 1: Mean Values Of Physicochemical Characteristics And Heavy Metal Concentrations Of Water Samples From The Sampling Sites(April, 2011 to March, 2013)

PARAMETERS	SITE A		SITE B		
SITE C	WHO	NIS			
Physical Parameter					
Temperature (°C)	25.04 ± 0.11 ^a	30.13 ± 0.09 ^b	28.60 ± 0.08 ^{bc}	-	Ambient
pH	7.13 ± 0.01 ^a	7.92 ± 0.06 ^b	7.56 ± 0.05 ^{ac}	6.5 – 9.5	6.5 – 8.5
Colour	2.02 ± 2.19 ^a	2.08 ± 2.14 ^b	2.03 ± 2.00 ^{ac}	-	-
Turbidity (NTU)	14.21 ± 0.40 ^c	19.95 ± 0.20 ^a	17.15 ± 0.62 ^a	-	-
EC (µscm ⁻¹)	1.52 ± 4.01 ^a	2.19 ± 5.51 ^b	2.01 ± 3.95 ^{ab}	-	-
Total Hardness (mgCaCO ₃ l ⁻¹)	14.56 ± 0.98 ^{bc}	67.12 ± 0.58	65.71 ± 0.97 ^b	<200	-
Total Solids (mgO ₂ l ⁻¹)	137.58 ± 5.00 ^a	141.88 ± 4.21 ^b	144.08 ± 0.92 ^a	<1000	500
BOD (mgO ₂ l ⁻¹)	3.03 ± 0.06 ^{bc}	6.77 ± 0.17 ^a	5.66 ± 0.69 ^{ab}	-	-
DO (mgO ₂ l ⁻¹)	13.67 ± 0.50 ^a	9.46 ± 0.61 ^{bc}	9.54 ± 0.41 ^b	6.0	-
Chemical Parameter					
Sulphate (mg l ⁻¹)	12.95 ± 0.10 ^c	20.17 ± 0.19 ^a	18.09 ± 0.21 ^{ab}	500	100
Nitrate (mg l ⁻¹)	1.49 ± 0.21 ^{bc}	2.68 ± 0.28 ^a	2.41 ± 0.11 ^{ab}	50	50
Chloride (mg l ⁻¹)	10.83 ± 0.54 ^b	14.76 ± 1.17 ^a	12.46 ± 0.96 ^{bc}	-	-
Sodium (mg l ⁻¹)	2.94 ± 0.30 ^a	14.60 ± 0.25 ^b	7.13 ± 0.05 ^{ab}	-	-
Calcium (mg l ⁻¹)	19.51 ± 0.51	31.61 ± 0.66 ^a	22.88 ± 1.11 ^c	<200	-
Heavy Metals					
Lead (mg l ⁻¹)	0.01 ± 0.00 ^a	0.02 ± 0.01 ^b	0.01 ± 0.00 ^a	0.01	0.01
Copper (mg l ⁻¹)	0.06 ± 0.01 ^a	1.36 ± 0.04 ^b	1.21 ± 0.00 ^b	2.0	1.00
Zinc (mg l ⁻¹)	0.01 ± 0.00 ^a	0.02 ± 0.01 ^b	0.02 ± 0.01 ^b	-	-
Iron (mg l ⁻¹)	0.31 ± 0.04 ^a	0.61 ± 0.02 ^b	0.63 ± 0.03 ^b	-	-
Cadmium (mg l ⁻¹)	0.22 ± 0.01 ^a	0.45 ± 0.03 ^{bc}	0.20 ± 0.00 ^a	0.003	0.003
Mercury (mg l ⁻¹)	0.01 ± 0.00 ^a	0.05 ± 0.02 ^{ab}	0.03 ± 0.01 ^b	-	-
Chromium (mg l ⁻¹)	0.01 ± 0.02 ^a	0.03 ± 0.11 ^{ab}	0.02 ± 0.00 ^b	0.05	0.05
Manganese (mg l ⁻¹)	0.25 ± 0.01 ^a	0.48 ± 0.00 ^{ab}	0.34 ± 0.03 ^b	-	-

*Mean of parameter in the same row having different superscripts is significantly different (P ≤ 0.05)

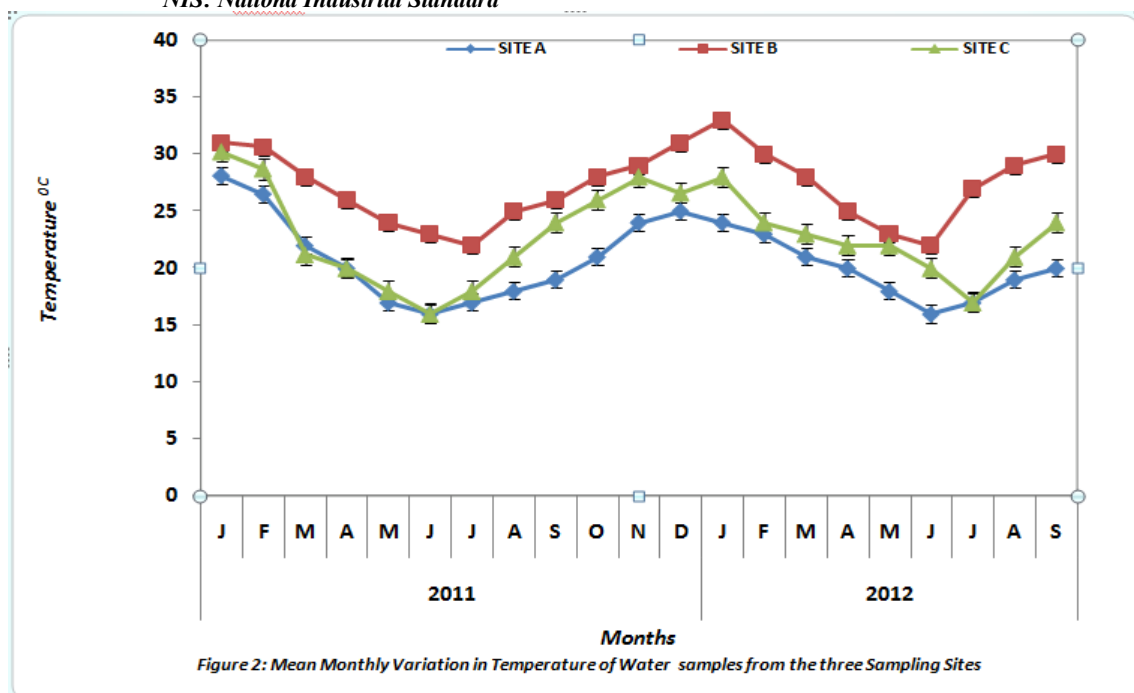
EC: Electrical Conductivity

DO: Dissolved Oxygen

NIS: Nationa Industrial Standard

BOD: Biological Oxygen Demand

WHO: World Health Organisation



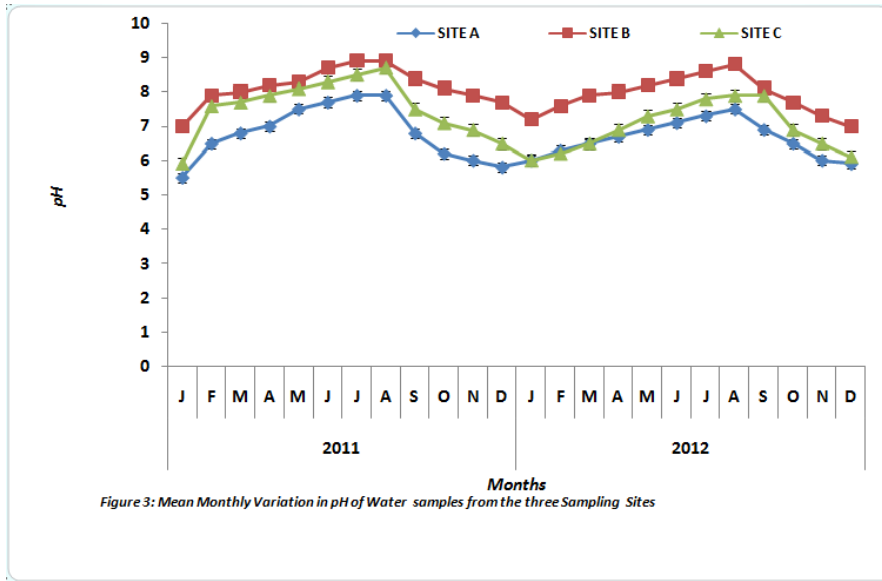


Figure 3: Mean Monthly Variation in pH of Water samples from the three Sampling Sites

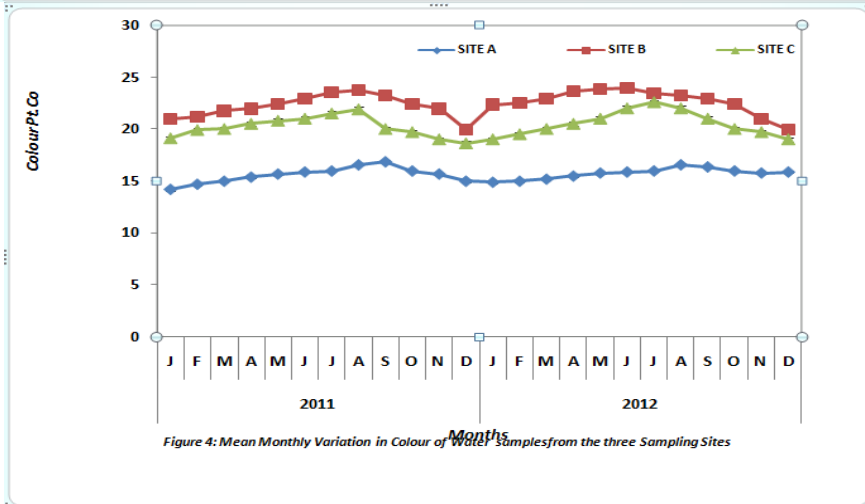


Figure 4: Mean Monthly Variation in Colour of Water Samples from the three Sampling Sites

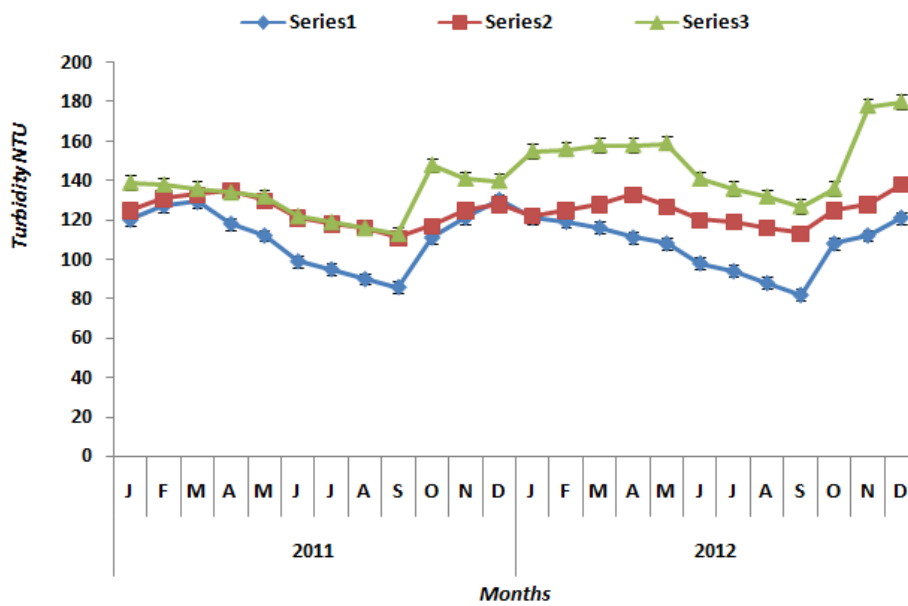


Figure 5: Mean Monthly Variation in Turbidity of Water samples from the three Sampling Sites

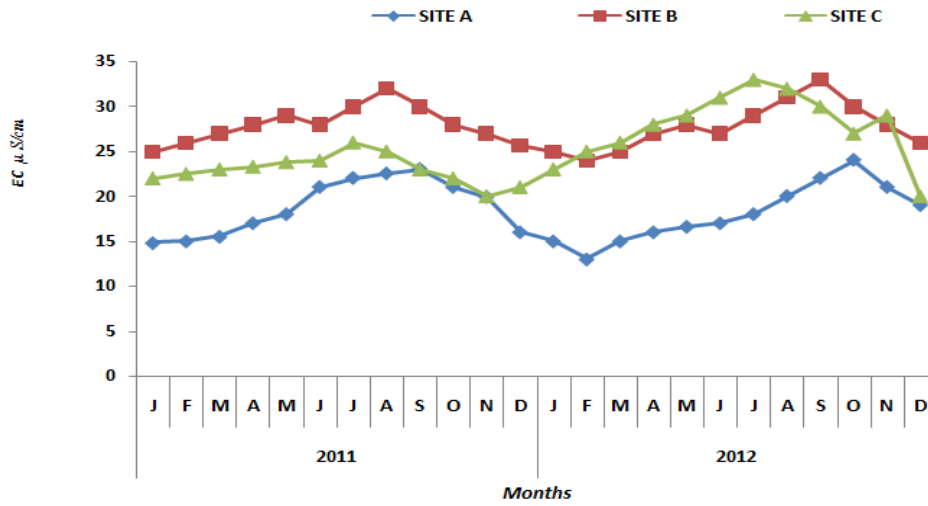


Figure 6: Mean Monthly Variation in Electrical Conductivity of Water samples from the three Sampling Sites

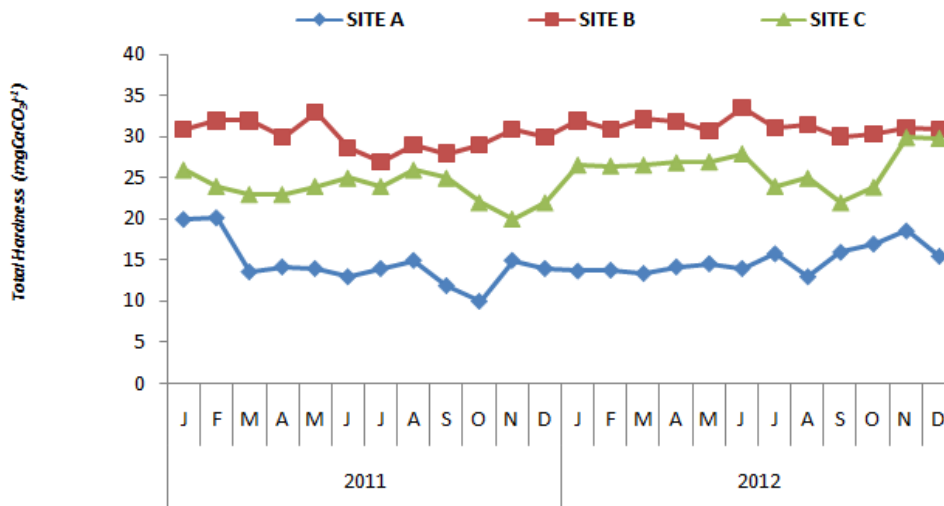


Figure 7: Mean Monthly Variation in Total Hardness in Water samples from the three Sampling Sites

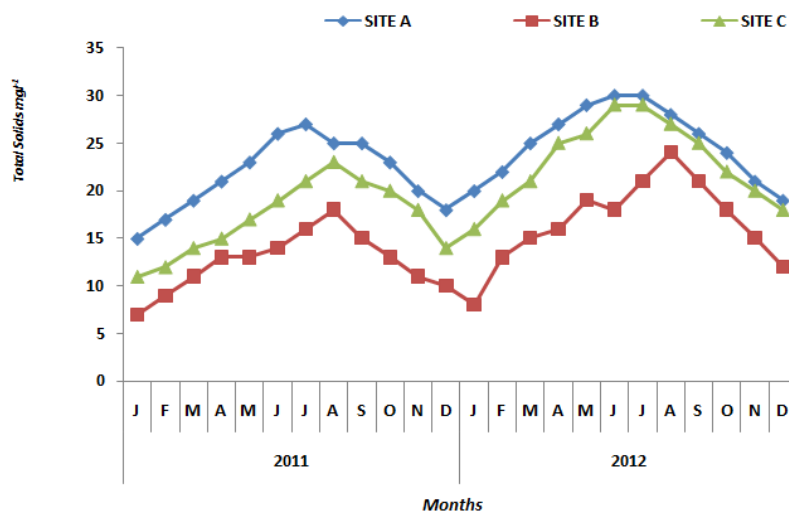


Figure 8: Mean Monthly Variation in Total Solids of Water samples from the three Sampling Sites

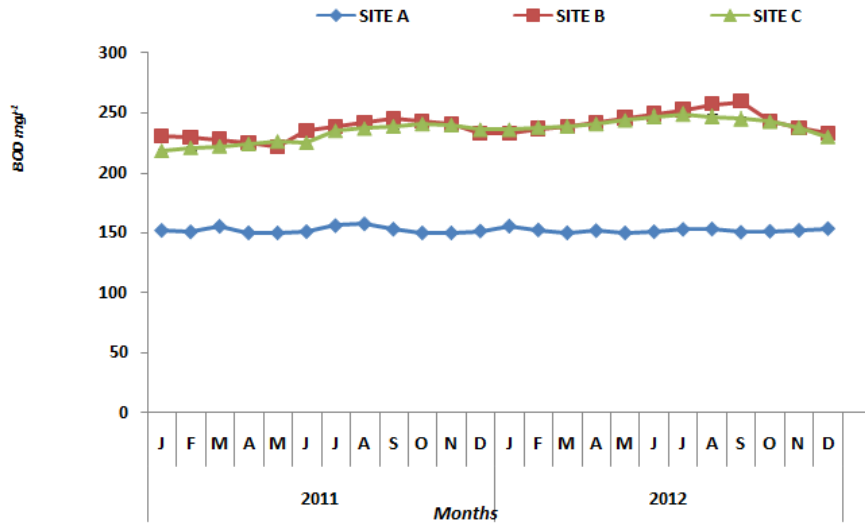


Figure 9: Mean Monthly Variation in BOD of Water samples from the three Sampling Sites

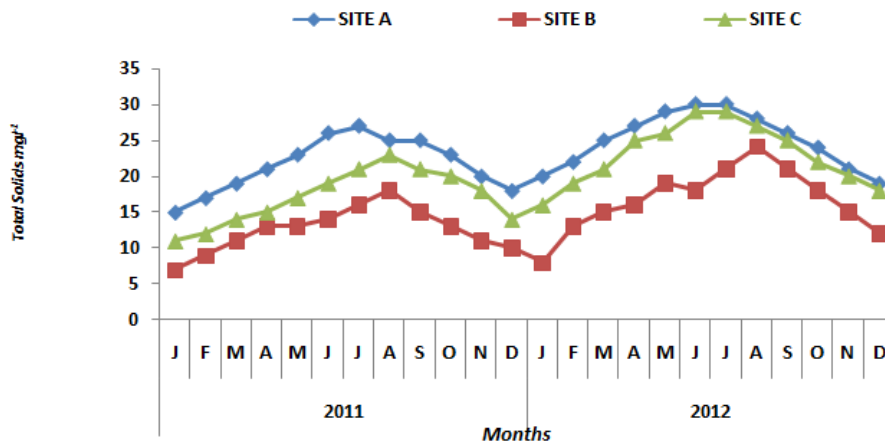


Figure 10: Mean Monthly Variation in Total Solids of Water samples from the three Sampling Sites

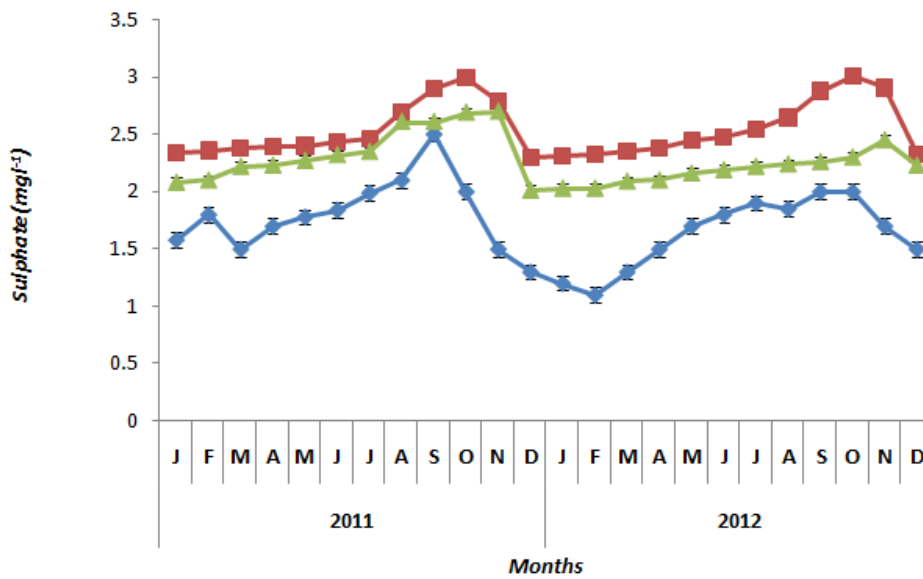


Figure 11: Mean Monthly Variation in Sulphate level in Water samples from the three Sampling Sites

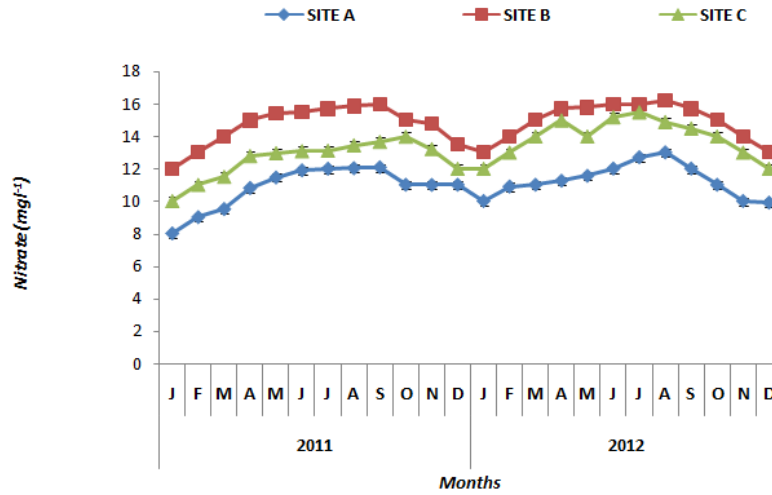


Figure 12: Mean Monthly Variation in Nitrate level in Water samples of the three Sampling Sites

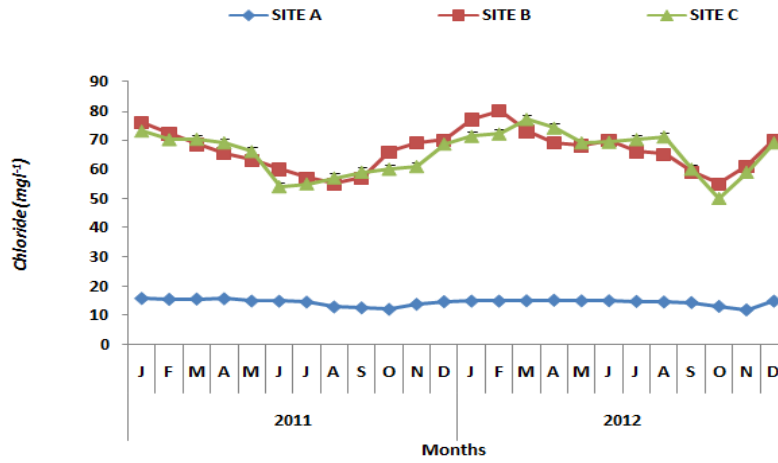


Figure 13: Mean Monthly Variation in Chloride level in Water samples of the three Sampling Sites

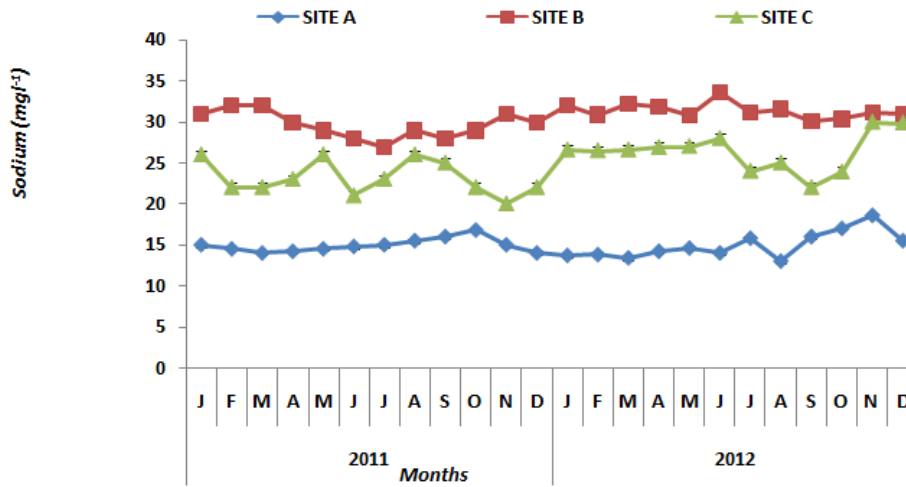


Figure 14: Mean Monthly Variation in Sodium level in Water samples of the three Sampling Sites

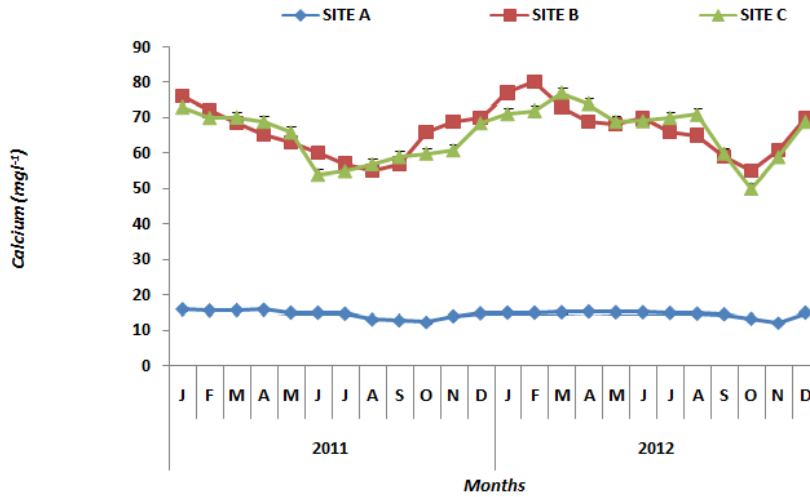


Figure 15: Mean Monthly Variation in Calcium level in Water samples of the three Sampling Sites

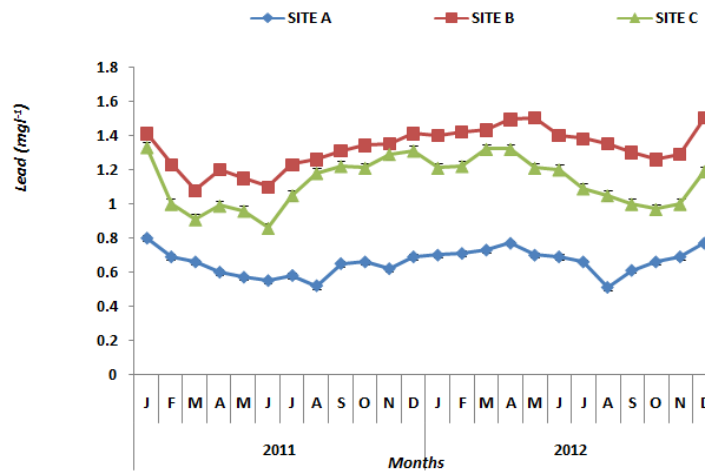


Figure 16: Mean Monthly Variation in Lead level in Water samples of the three Sampling Sites

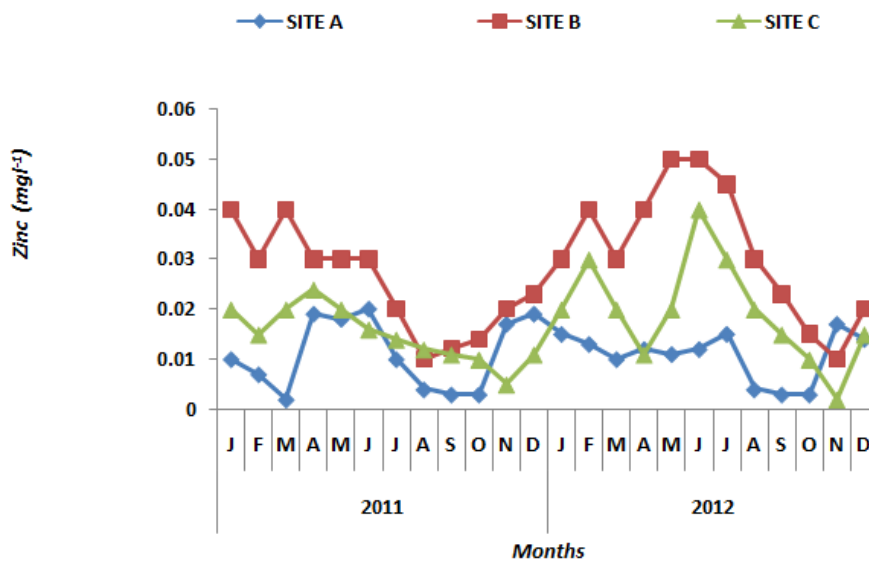


Figure 18: Mean Monthly Variation in Zinc level in Water samples of the three Sampling Sites

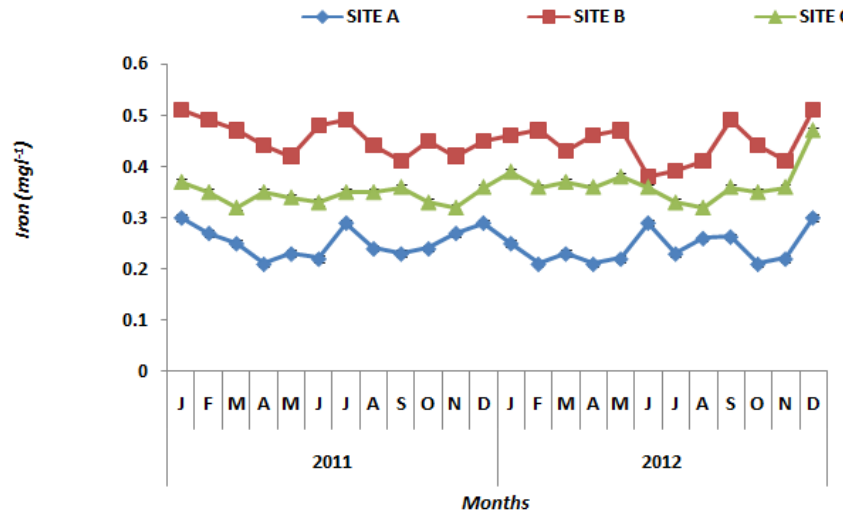


Figure 19: Mean Monthly Variation in iron level in Water samples of the three Sampling Sites

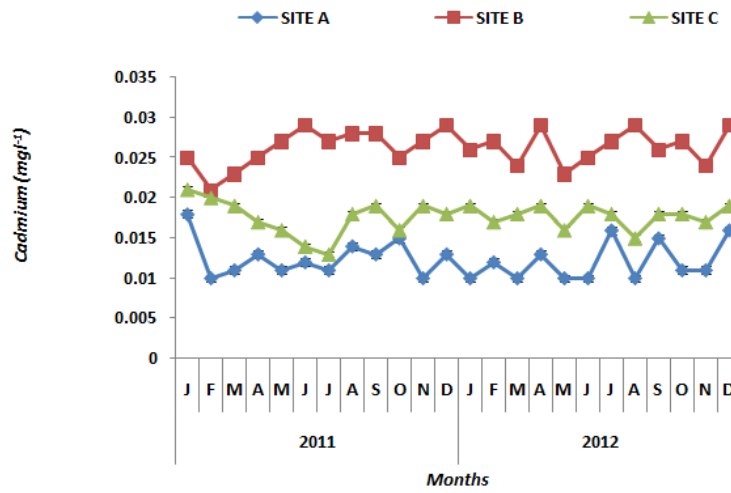


Figure 20: Mean Monthly Variation in Cadmium level in Water samples of the three Sampling Sites

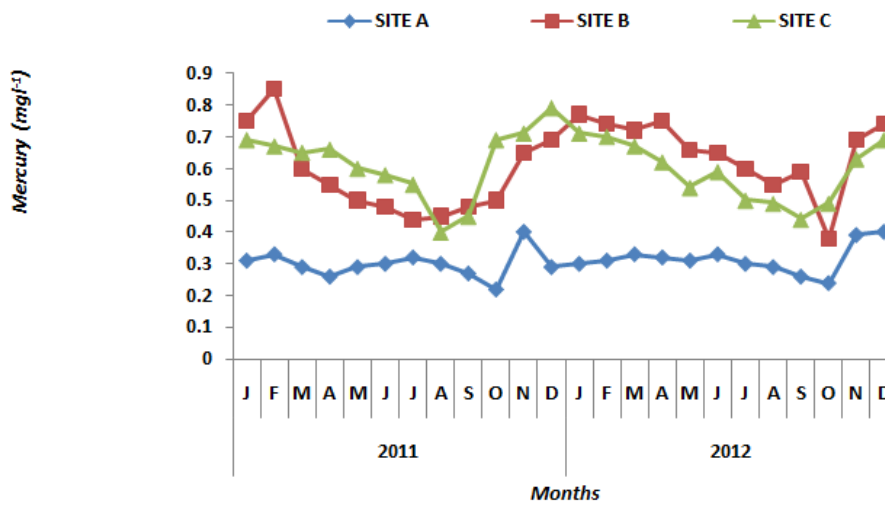


Figure 21: Mean Monthly Variation in Mercury level in Water samples from the three Sampling Sites

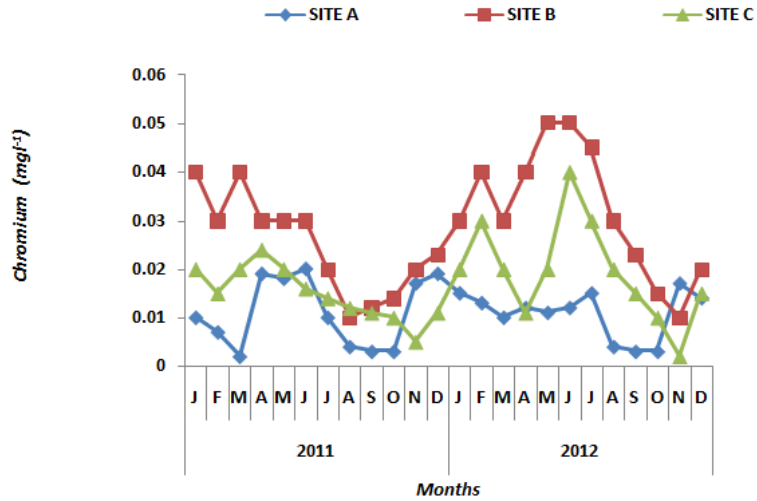


Figure 22: Mean Monthly Variation in Chromium level in Water samples of the three Sampling Sites

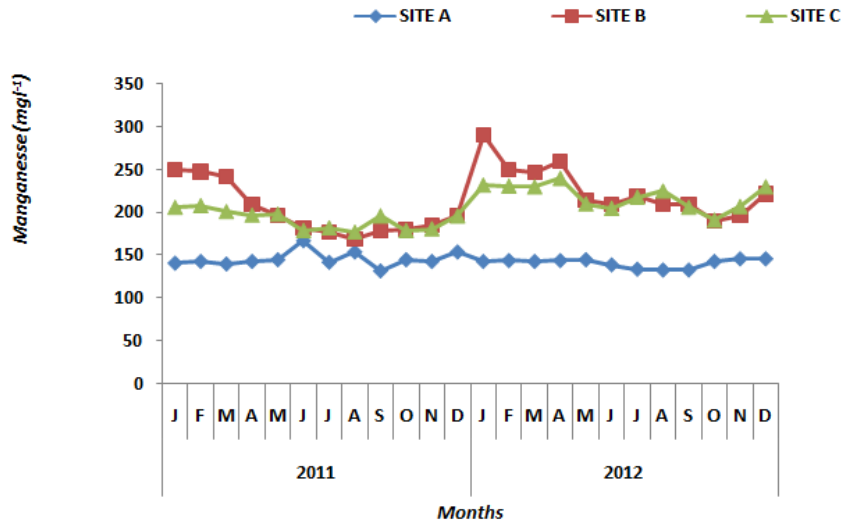


Figure 23: Mean Monthly Variation in Manganese level in Water samples from the three Sampling Sites

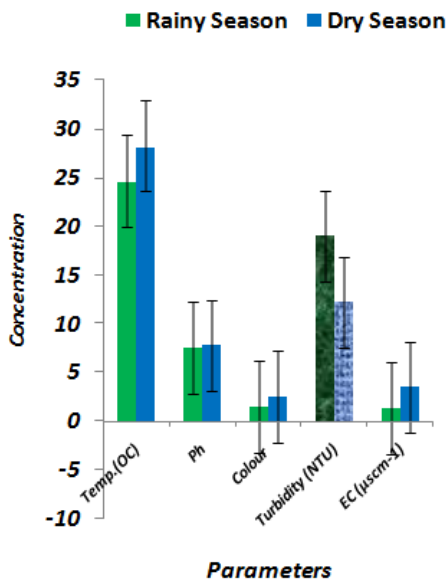


Fig. 24: Seasonal Variations in some Physical Parameters in the Water sample from the three sampling Points

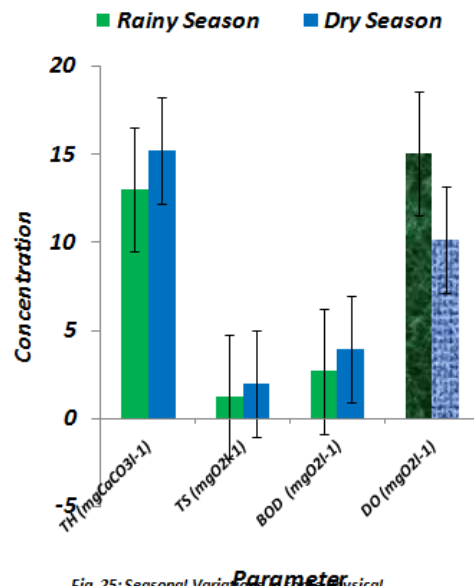


Fig. 25: Seasonal Variations in some Physical Parameters in the Water sample from the three sampling Points

IV. Discussion

Physical and Chemical Parameter in Water

The physical and chemical parameters investigated in this work have been widely used to assess the water quality of African lakes, ponds, reservoir, freshwater and marine waters (Nhiwatiwa and Marshall, 2007). These parameters along the stretch of Asa River revealed different level of variations across the three sampling sites and as well as within the two seasons of the sampling years. Higher values were mostly encountered at sites B and during the dry season of the sampling periods. The temperature recorded in sampling sites A, B & C was in the order of 25.04 °C, 30.13°C and 28.60°C respectively, with an average value of 28.22°C and 24.60°C for dry and rainy seasons respectively. The temperature values varied significantly in the two seasons and between the three sampling sites. High temperature was recorded in the months of November, December, January and February which coincided with the period of dry season. Significantly high ($P < 0.05$) temperature recorded at sampling sites B and C were found to be seasonal dependent. The low values obtained in the months of June, July, August and September (which is the months that corresponded with late rainy season) could be attributed to the cooling and diluting effects of the rain water. The average temperature values for all the three sampling sites were $< 40^{\circ}\text{C}$ depicting temperature range that is supportive of good surface water quality (NIS, 2007; WHO, 2011).

Generally, the variation in water temperature obtained in this work is a direct reflection of low depth of the water bodies and the irregular slow movement which does not ensured a complete mixing of the entire water phase. This observation agreed with the submission of Ajao, (1990) and on the temperature profile of Lagos Lagoon. This is also in line with the temperature range of 24.5°C to 31.5°C reported by Eleta *et al.*, (2005) from Asa River. There were significant differences between the three values obtained for the three sampling sites and between the two seasons of the year.

The pH values are expressed as the negative logarithm of hydrogen ion concentration. For acidic water, pH varies from 0 to 7 and for alkaline water pH varies from 7 to 14. It determines the solubility of chemical nature of most of substances. Medium values are favorable for biological production. The pH values recorded in this work are indicative of good water quality which was within the acceptable limits (NIS, 2007; WHO, 2011). The high values of pH (7.92±0.06 and 7.56±0.05) recorded at sampling sites B and C respectively could have been due to the influx of industrial effluent and the synergistic effects of these effluents on the water bodies. A slight alkaline pH value recorded may be due to the alkaline treatment given to the effluents before discharging into the river (Amao, 1998). Eleta *et al.*, (2005), that influx of effluent in alkaline form into water could affect the pH. The fluctuations observed in the surface pH indicated the buffering capacity of total alkalinity, high water volume, greater water retentions and good buffering capacity of total alkalinity may have been the reason why pH was in neutral or moderate alkaline medium during the rainy season and for most part of this study. Using the pH as a water quality index, Asa River and its tributaries has good water quality with the mean pH of 7.13, 7.92 and 7.56 for point A, B & C respectively; since most natural waters have pH between 6.5 and 8.5 (Tepe *et al.*, 2005) and such pH values will also allow the survival of aquatic organisms and its use as drinking water. In this present situation, the maximum pH of 7.80 ± 0.06 was recorded in the dry season and this may be linked to the decreased volume of water by evaporation; the minimum value of 7.50 ± 0.10 obtained during the rainy season may be attributed to shorter day length and decrease in photosynthetic activity (Salve and Hiwara, 2006).

The water samples from the three sampling sites were more turbid by physical examination with 14.21 TNU, 19.95 TNU and 17.15TNU recorded for sites A, B & C respectively. Sampling site B has the highest value followed by site C while site A has the minimum value. The highest value recorded by sampling site B may be linked with the land use within these steep areas dominated by intensive small scale farming activities where majorly food crops and vegetables are grown. The same area occur in the flood plains with very high human and livestock population density coupled will heavy industrial effluent discharges at sampling site B which flows down to Site C. Conductivity is a numerical expression of the ability of water to carry on electric current, which in ionic strength as conductivity is a measure of total ions. The ionic strength of a sample depends on the ionization of solutes and other substances dissolved in it. The electrical conductivity of the three sampling sites in this work was found to be statistically high at the point of discharge (Site B) of industrial effluents to downstream (Site C) compared to upstream (Site A). Sampling site A which is less impacted sub-catchments had lower concentrations as compared to stations located in areas with high human activities like agricultural practices and industrial activities (Sites B and C). Low electrical conductivity experienced at site A might be responsible for soft nature of the water; while high conductivities may be due to high aggregation of total solids recorded in Sites B and C and this observation conformed with the report of Mustapha (2008) and Adewoye, (2007) on Oyun River and Asa River respectively. Asa River and its tributaries can be classified to be soft waters based on the range of mean total hardness (11.29 – 15.46mgCaCO₃⁻¹) recorded which fell within the NESREA, (2007) hardness scale classification for soft waters. This range will support aquatic fauna and is ideal for drinking water supply (APHA, 1995). This result is in contrary to the findings of Adewoye, (2007) who

recorded 87.61 and 130.94. The influx of industrial, domestic and agricultural discharges into sites B and C may be traced to high total hardness recorded in these two sites. Seasonal variation in the conductivity may be due to the increased concentration of salts because of discharge of domestic effluents and organic matter from the nearby residential areas into the water bodies. High level of conductivity reflects the pollution status as well as tropic levels of the aquatic body (Anitha, 2002). In this present work, high value of conductivity was recorded in the dry season and low during the rainy season; Chandrashekhar and Kodarkar, (1996) also reported similar observations in Saroonagar Lake, Hygerabad.

Total suspended solids are the cause of suspended particles into the water body, it influences turbidity and transparency. The high value of total solids recorded in sampling sites B and C in the dry season compared to that of rainy season may be attributed to low volume of water experienced during the dry season while the dilutions of ionic substances as a result of large volume of water in the area could be the main reasons for lower level of total solids encountered in the rainy season. Also, high value of total solids observed in sites B and C during the dry season, could also be as a result of influx of effluents from industrial premises, thereby bringing about increase in the level of conducting ions, electrical conductivities and turbidity of the affected water bodies. It could also be due to siltation, deterioration and heavy precipitation. These observations' agreed with the findings of Fagade *et al.*, (1993) on River Ogunpa and Ona; Rabaru and Okeyo –Owuor, (2002) on River Nyando, Lake Victoria Basin in Kenya, and Ayoola and Kuton, (2009) on Lagos Lagoon in Nigeria. The level of total solids were higher at sites B down to C during dry season compared to low value for rainy season, this is in agreement with the observation of Ajao (1990) that effluents can introduce some reaction which precipitate more solid in the solution, leading to high total solids which can decrease downstream due to natural filtration. This situation observed in this work also conformed to the submission of Khabade *et al.*, (2002) which submitted maximum suspended solids in monsoon, moderate in summer and minimum in winter.

The high BOD recorded in sites B and C in the dry season could be as a results of accumulation patterns of organic materials due to continuous influx of industrial effluents into the water bodies which may eventually results in reduction of oxygen content; this observation conformed with the reports of Manson, (1991), Rabaru and Okeyo –Owuor, (2002), Ayoola and Kuton, (2009), and that when organic matter is abnormally high in an aquatic phase, the biological oxygen demand level reduces and this may eventually disrupt the behavioural responses of the organisms and reduces the fitness of a natural population of fish. The BOD pattern observed in this work indicate considerable level of nutrients and this conforms with the report of Van Note *et al.*, (1980) that rivers with high BOD have high nutrient levels in the water where organisms consumes most of the oxygen. Naturally, unpolluted waters will have BOD of small or less and this negates what was obtained in this work where sites B and C had $6.77 \pm 0.17\text{mg l}^{-1}$ and $5.66 \pm 0.69\text{mg l}^{-1}$ respectively. High amount of BOD recorded during the rainy season can be attributed to increased effect of surface run-off, soil erosion and effluents discharges into these receiving water bodies and this conforms, considerably to the submission of Oyewo, *et al.*, (1999).

The dissolved oxygen observed in this study was higher than the 6.0 recommended level by NESREA, 2007; NIS, 2007. Oyewo, *et al.*, (1999) also reported that the desired range for the culture of warm water fish is 5mg l^{-1} and above but not more than 12mg l^{-1} . Lower value of DO was also obtained for dry season in this work, and this may be due to low level of dilution rate and water volume during dry season with little self-purification process of the pollutants. The DO level obtained for sites B and C fell below the $10\text{mg O}_2\text{l}^{-1}$ recommended for unpolluted waters (WHO, 1988), but far greater than 6.0 recommended value documented by NIS, 2007 and WHO, 2011. The continuous influx of industrial discharge into the water might likely support the growth of aquatic weeds and formation of flocks on the surface of the water, hence a reduction in the dissolution of oxygen into water. Morrison *et al.*, (2001) however stressed that the depletion of dissolved oxygen in a water body could be due to common practice of dumping of wastes into such water body. Sulphate is the most abundant form of sulphur, which exist as anion sulphate. Sulphate is ecologically important for growth of plants and its short supply may inhibit the development of plankton. Sulphur is also very important in protein metabolism. Nitrogen is less soluble in water than oxygen. But as it constitutes 78% of the atmosphere, it still account for 65% of the dissolved gases at equilibrium. Nitrogen is important as it is a necessary element in the structure of protein, chlorophyll, RNA and DNA and so on. It is essentially required by all living organisms, being a necessary element of biochemical substances.

There was a marked seasonal variation on the nutrients level of the sampling sites with the lowest value at sampling site A while sites B and C had higher values while dry and rainy seasons recorded lower and higher values respectively. The high concentrations of sulphate nitrate and chloride could have resulted from leaching and run-off of sulphate fertilizers from nearby farm lands and sulphate rich effluents from nearby industrial premises. The concentrations of these ions were higher during the rainy season, because the period is usually the peak of agricultural activities around the river area. Probably, this could also have resulted from washing of Pens, cow dung, bathing and washing of cars and home appliances with phosphate based detergents and soaps into the water, which could have also caused the high level concentrations of these ions. These events can lead

to eutrophication of the water bodies with subsequent bloom in algae and changes to water quality. Carpenter *et al.*, (1998) and Carignan *et al.*, (2000) reported that non-point source of nutrient inputs from watershed are leading cause of eutrophication and water quality problems while Armengol *et al.*, (1999) implicated sulphate in the eutrophication of water bodies. Eutrophication was more pronounced in both sites B and C probably due to its shallowness Ekholm *et al.*, (1997) and this could affect water quality by giving rise to unpleasant taste, odor and color, and affects the dissolution of other gases, most especially dissolved oxygen as a result of algae bloom. It could also pose a threat to fish population in rivers, because it may destroy food web, decrease biodiversity at higher trophic level (Hanson and Butler, 1994) leads to disappearance of population and induces changes in yield and species composition (Miranda, 2008). In any Fresh water where calcium is the dominating cation (Golterman and Koowe, 1980), the ionic composition of the such water usually exhibit variations in the values obtained for sodium and calcium hardness, and this may be attributed to chemical denudation due to dilution from heavy rain coupled with the rivers circulation and weathering from rock, and run-offs from surrounding water shed. An irregular pattern of sodium and calcium hardness recorded in this work might be traced to heavy down pour of rain resulting in flood, which might have contained a high concentration of magnesium and this could be the reason for the significant difference in the concentration of ion between the two seasons. Then, the presence of this ion in moderate levels classified the sampling sites B and C as eutrophic which will support diverse plant and animal life including fish; except for the additive effects of such ions, physical parameters and heavy metals that may limit their population. According to Adeniyi and Yusuf (2007) waters with calcium levels of $< 10 \text{ mg}^{-1}$ are usually oligotrophic, while those above 20 mg^{-1} are said to be eutrophic and this is a reflection of what was observed in this work, that both sampling sites B and C could be said to be Eutrophic while site A could be regarded as oligotrophic. A trend that could be traced to the rate of influx of effluents into each segment of the river.

Heavy Metal Concentrations in the Water Samples

Asa River and its tributaries were exposed to heavy metals containing contaminating materials, capable of initiating the impairment of the water quality. This present investigations has revealed the concentrations of certain heavy metals such as Pb, Cu, Zn, Fe, Cd, Hg, Cr and Mn which were generally high in sampling site B followed by site C and A ($B > C > A$). The values obtained in Table 1 for surface water heavy metal concentrations could be adduced to anthropogenic activities going on around the sampling sites and because of its exposure to domestic, agricultural and industrial influences. This is similar to the report of Adeniyi *et al.*, (2007) based on their research at Agboyi crack segment near the Lagoon with high surrounding human population density recorded higher levels of metals in sediment and water samples. Of all the three sampling sites; sampling site B were noticed to produced high concentration of heavy metal and this may not been unconnected to continuous discharged of industrial effluents at this point and dense agricultural activities centered on this portion of the river; Site C is next to B in terms of heavy metals concentration while A had the lowest. All the heavy metals concentrations obtained in this work were found to be higher than those reported previously by Eleta *et al.*, (2003); Eleta and Adekola, (2005); Adewoye, (2008).

The concentration of Pb in Site B was significantly higher than that of Sites C and A. value obtained from the sampling site B was also found to be higher than maximum permissible limits of 0.01 mg/L set by WHO, (2011) and NIS, (2007). This is an indication that lead is ubiquitous in our environment with diverse pollution source. The same trend was observed in the case of all other heavy metals measured; and, this is in consonance with the work of Mohd *et al.*, (2007) in their work on heavy metals in meretrixroding, water and sediments from Estuaries in Sabah, North Borneo. Nevertheless, low level of metals concentrations in surface water might not necessarily reflect that such areas were pollution free. The additive effects of these heavy metals among each other and with physical and chemical parameters is capable of forming toxic compounds that create large surface area for decomposition of such compounds; this process tends to lower the oxygen content of the water which is enough to lower the population of valuable aquatic faunas and floras. Also, the biotas living in such areas might have accumulated the metals from water continuously and this situation stand the chance of disrupting a functioning food chain or web. Of all the metals measured, Pb, Cu, Zn and Hg were found to exceed the permissible limits for any categories of water bodies. Seasonal variations were also observed in the collated data in this work. Higher values were obtained in the dry season than in the rainy season. This situation is expected in view of the reduction in the pollution load in the rainy season arising from increase in dilution and water flow. It is to be noted that the river is at its highest volume and flow in the rainy season. Generally, water samples from sampling site B and C recorded higher metal values than that of site A and the cumulative metal contamination is in the order of site $B > \text{site C} > \text{site A}$ with the metal pollution index of $\text{Cu} > \text{Fe} > \text{Mn} > \text{Hg} > \text{Cr} > \text{Zn} > \text{Pb}$ with respect to sampling site B.

V. Conclusions

This study complements previous studies on the impact of industrial, agricultural and domestic discharges on the limnological parameters of aquatic environment. The study however revealed the following:

The industries, agricultural fields and domestic usages in the vicinity of Asa River discharges their wastes containing high physical, chemical and heavy metal components into the river, thus raising the level of these parameters beyond the recommended levels of World Health Organization and National Industrial Standard's guidelines. Virtually all the measured parameters still remained higher even in the downstream part of the river water showing sub-lethal concentrations of contaminants in the water. The volume of these discharges into Asa River was already overtaking their capacity for self-purification and the prevailing practice of unregulated and uncontrolled discharge of such wastes into water bodies constitutes serious abuse and portends serious danger to the resident species and beneficial use to the municipality. It could be seen in this study that Asa River water was grossly polluted and the level of pollution decreased downstream and it was much higher during the dry season and relatively lower during the peak of rainy season. These wastes, apart from making the river water unsightly, it also render the water dangerous to the consumers and caused undesirable effects on the biotic community, especially the fishes. Therefore, proper treatment is imperative for the river to be appropriate for portable, domestic and industrial purposes.

Acknowledgement

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