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Atomic Absorption Spectrophotometric Determination of Elements in Water, Fish and Sediment of Atabong River, Nigeria

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Abstract: Water pollution is a serious environmental problem. It comprises of the damages done to the physical, chemical and biological properties of water due to anthropogenic activities. Such damages could have serious detrimental effects on the quality and suitability of the water and even the aquatic organisms in the water, for any use. In view of this, levels of Pb, Ni, Mn, Cr and Cd were evaluated in water, fish (*Brycinus nurse*) and sediment from Atabong River in Okobo, Nigeria, during the dry and wet seasons in order to ascertain the suitability of the water and fish for human use. Samples were digested according to standard methods and analysed using Unicam 939/935 atomic absorption spectrophotometer. Physicochemical parameters were also quantified in the water samples using standard procedures. The results revealed variable levels of the investigated physicochemical parameters in the water samples from each of the sampling stations. For instance, dissolved oxygen (DO) ranged from 4.2 to 5.25 mg/L in the two seasons. Trace metals levels in water followed the trend: Cr > Ni > Mn = Cd > Pb, and Cr > Ni > Cd > Mn >Pb for dry and wet seasons, respectively. In sediment, the trend was: Mn > Cd > Cr > Ni > Pb, and Cr > Cd > Ni > Mn > Pb for dry and wet seasons, respectively. In fish, it was: Cr > Mn = Cd > Ni > Pb and Mn > Ni > Cr = Cd > Pb. The trace metals levels in water, fish and sediment were below the permissible limits stipulated by WHO and USEPA. Bioaccumulation factor analysis revealed the trend: Pb > Mn > Ni > Cr > Cd for dry season and Mn > Pb > Ni > Cd > Cr for wet season with regards to fish pollution status. Health risk assessment due to consumption of fish, water and dermal contact with the water, showed low risk as the hazard quotient and hazard index were less than unity in each case. In conclusion, the analysed fish, water and sediment contained variable levels of the investigated trace metals and the levels were below the limits that could cause toxicity in humans consuming the water and fish at the time of the study. For the purpose of monitoring and documentation, periodic investigation of the investigated trace metals in the river system is highly recommended.

Keywords: Elemental Analyses, AAS, Water, Fish, Sediment, Pollution, Atabong River

1. Introduction

Obviously, one of the most serious environmental problems in the world today is water pollution [1]. Water pollution comprises of the damages done to the physical, chemical and biological properties of water due to anthropogenic activities. Such damages could have serious detrimental effects on the quality and suitability of the water and even the aquatic organisms in the water, for any use [2, 3]. Sincerely speaking, in any industrial community, the effluents are often discharged into a nearby body of water

which ultimately degrades the quality of such water. Water is a universal solvent which is important and essential to humans and other living things. Water dissolves soluble pollutants present in an aquatic environment which therefore alters the physicochemical parameters of the water in the area where these pollutants are present [4]. Many insoluble solid pollutants are water-borne which are either floating in water or adsorbed on the sediment [5]. According to Udosen, the extent of pollution of any water body depends on the quality and quantity of wastes and effluents discharged into the water as well as other factors prevalent in the water [1].

It had been established that, hazardous chemicals do not only have adverse effects on human health, but can also disrupt ecological systems that exist in rivers, lakes, oceans, seas, estuaries, wetlands, forests and soils [6]. According to IPCS, the contaminants in the aquatic environment that pose the greatest threat include hydrocarbons, sewage, pesticides, and trace metals [6]. Trace metals and pesticides that originated from land based sources, are of particular concern to the marine environment because they exhibit both toxicity and persistence and are known to bioaccumulate in the food chain [6].

Protection of water sources against all forms of contaminations which continually threatened the terrestrial and aquatic ecosystems due to increasing inputs of untreated wastes and chemical agents that are capable of causing damages to the environment are of great concern [7, 3]. River waters are quite vulnerable to pollution because they are naturally open, easily accessible, and substantially used in agricultural, industrial, and municipal processes [8, 3]. Indeed, the most often polluted environmental phases are the aquatic systems. This is obvious because contaminants in the air, soil or on land ultimately end up in the aquatic systems via local precipitation, water runoff and leaching of rocks and solid wastes [3]. It has been established that toxic trace metals are the most common environmental contaminants that affect the aquatic systems [3]. Indeed, the presence of trace metals in aquatic systems can provoke serious environmental issues because of their persistence in the environment, as well as their bioavailability and toxicity to aquatic organisms and their ability to be incorporated into the food chain [9].

Trace metals can exist in water and living organisms in a different chemical forms and in combination with other materials. Alinnor and Alagoa noted that the mechanisms of accumulation and storage of trace metals in aquatic organisms vary in terms of chemical forms of the metals, modes of uptake and animal species [10]. The dose taken in will determine whether or not such trace metals will be toxic or beneficial to the body. It has been established that trace metals such as: As, Cd, Cr, Hg, Pb and Zn are the most important elements with regards to their potential toxicity effects [11]. Accordingly, it has also been established that, trace metals when in small quantities are essential for healthy growth but when in excess become hazardous. Such trace metals include: Co, Cu, Mn, Ni and Se [12, 3]. Trace metals found in an aquatic environment can come from natural and anthropogenic sources. Such sources include geological minerals, wind-blown silicate dust and volcanic emissions. According to Udosen, human activities such as mining, industrialization and sewage treatment discharges as well as discharges of electronic wastes (computers, printers, photocopy machines, television sets, mobile phones and metallic toys) and discharges of agricultural wastes are some of the few examples of man-made sources which contribute to the increased levels of trace metals in aquatic environment [1].

Ekere *et al*., and Uwah *et al*., noted that in Nigeria, especially among the rural settlements, where safe and suitable potable water supply for drinking and other uses are lacking, the people depend on rivers, streams, ponds, lakes, shallow hand-dug wells for their water needs and also depend on aquatic animals which are capable of bio-accumulating pollutants like trace metals, for food. So, pollution of the aquatic environments could pose serious threat to man [13, 3]. Indeed, in the aquatic systems, sediment is considered as potential sink for different pollutants, particularly trace metals [14]. It is reported that, sediment plays an important part in remobilisation of trace metals and other contaminants in aquatic systems, under favourable conditions. Obviously, Rasheed, noted that, sediment also enhances interactions between water and trace metals in the aquatic systems [15].

Atabong River in Okobo, is one of the most frequently traversed water routes in Akwa Ibom State, Nigeria. This is because it serves as a site for fishing, transportation, lumbering activities and forestry operations. Communities within the area depend directly on the river for their agricultural and recreational activities, food and sometimes, domestic water supplies. However, surface run-off occasioned by erosion, lumbering activities and forestry operations and domestic sewage discharges, could cause a wide scale contamination of the river. Such a polluted aquatic environment could impact negatively on the aquatic organisms as bioaccumulation of toxic trace metals could occur. In fact, trace metal pollution could lead to environmental health problems because of the persistence and non-biodegrability of the metals in the environment [1].

Data and information on trace metals in water, fish and sediment of Atabong River are either insufficient or absent. There is therefore every need for this study which is aim at determining the levels of some trace metals (Pb, Ni, Mn, Cr and Cd) in water, fish (*Brycinus nurse*) and sediment from Atabong River in Okobo, Nigeria, with a view to ascertain the suitability of the fish for human consumption and the water for domestic purposes in terms of trace metals contamination.

2. Materials and Methods

2.1. Study Area

This study was carried out in Atabong River. Atabong is situated in the eastern part of Okobo Local Government Area of Akwa Ibom State, Nigeria. The area is located within

latitudes 4° 4′ and 4° 49″ North of the Equator, and longitudes 8° 10″ and 8° 14″ East of Greenwich Meridian. The area is on gentle undulating plains and could best be described as lowland. Most of the inhabitants of the area depend on the river for their domestic needs, recreational activities and fishing. The river is highly accessible to surface run-off from all kinds of human activities including wastes from boat repairing shops, domestic wastes, open dump site, and agrochemical wastes from agricultural farmlands as well as human feaces from open defecation. All these activities of man can result to the contamination of the river which in turn could increase the trace metal loads in the water, living organisms and of course the sediment. The study area is shown in Figure 1.

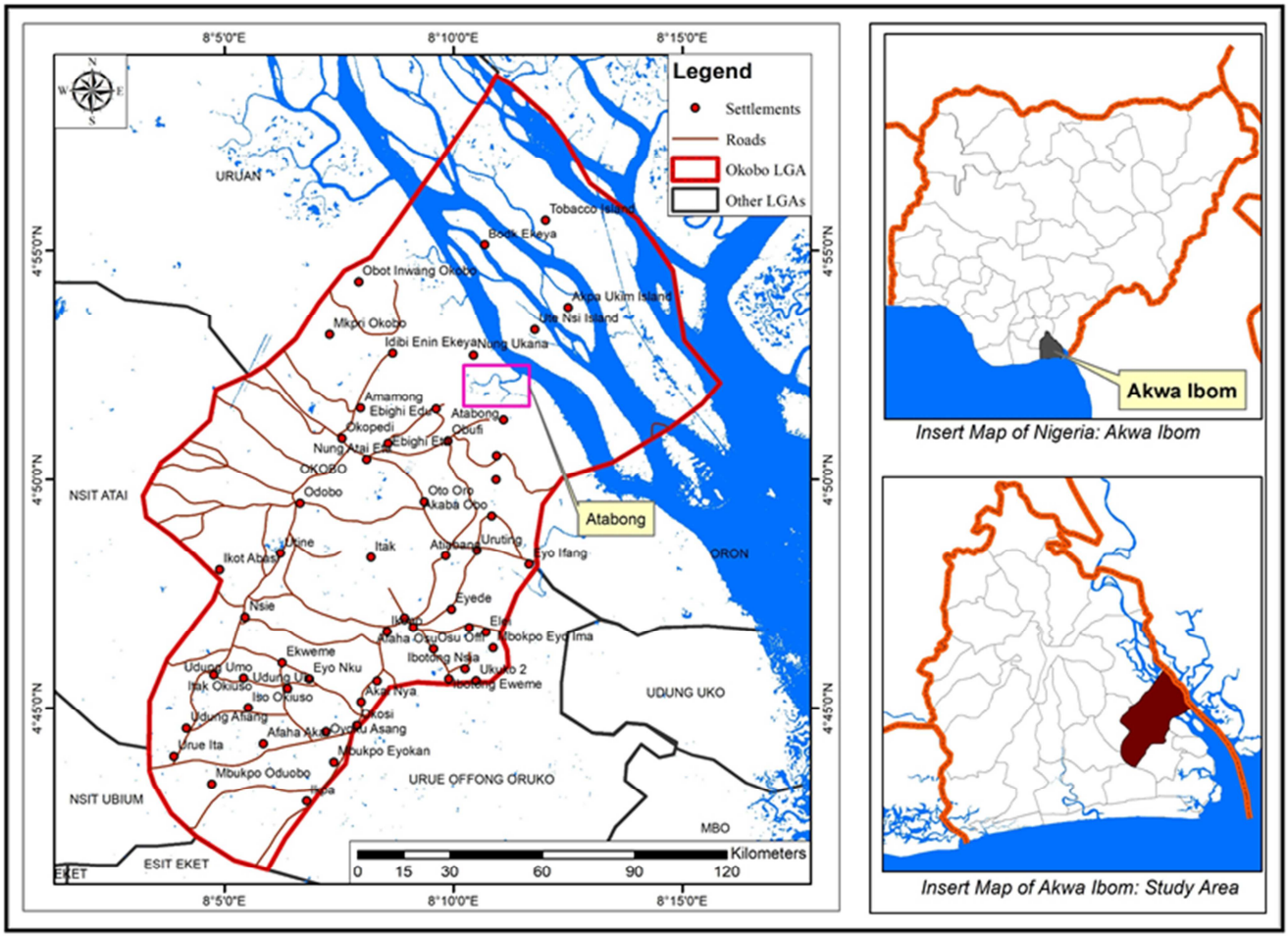

Figure 1. *The study area.*

2.2. Samples Collection

Samples (water, fish and sediment) were collected once a month, for a period of six months (January to march 2019, representing dry season and June to August 2019, representing wet season). Samples were collected at three (3) locations designated as stations 1, 2 and 3, representing downstream, midstream and upstream, respectively. Water and sediment Samples were collected according to the methods described by Udosen as well as Uwah *et al*. Water samples for trace metal analysis were collected in nitric acid pre-rinsed 1L containers and 5 mL of concentrated nitric (HNO_3) acid added immediately to minimize chemisorption. Water samples for Dissolved oxygen (DO) and biochemical oxygen demand (BOD) determinations were collected in amber bottles. In the field, the bottles were pre-rinsed with the water from the respective sampling sites. Each mouth of the sample bottles was dipped against the flow direction to avoid trapping of air bubbles in the bottles. Sufficient air spaces were left in all the bottles (except those for DO determination) to allow for expansion of water when the temperature increases. Sediment samples were collected at a depth of about 25 m using Van Veen grab sampler at three different points and made into composite samples. The sediment samples collected were stored in 1L plastic containers [1, 3]. Fish (*Brycinus nurse*) samples were collected by means of locally prepared fish traps. These traps were placed inside the water (one per sampling site) at dusk and were inspected at dawn the following day. Medium- sized fish samples were selected from the total catch early in the morning, and were stored in a locally made aquarium [1, 3].

2.3. Samples Preparation

Sediment samples were prepared according to the method

described by Uwah *et al*. The samples were air-dried and ground using porcelain mortar and pestle. The texturally equivalent petite fractions of the sediment were separated after grinding by sieving through a 2.00 mm mesh sieve. For each of the finely dried and ground sediment, 20 g were kept in an air-tight plastic bottle prior to digestion. Fish samples were washed with distilled water to remove dirt and other loosely held particles. They were then descaled, gutted and decapitated using stainless steel kitchen knife. The decapitated fish samples were filleted on both sides, placed in a porcelain crucible and dried in an oven. The dried muscles of fish samples were blended into a powder using an electric blender. The powdered fish samples were stored in a well-labeled plastic bag before digestion [3].

2.4. Digestion of Sediment Samples

Digestions of sediment samples were done according to the method described by Uwah *et al*. From each of the finely ground sediment samples, exactly 1.0 g was digested in a mixture of nitric acid (HNO_3) and perchloric acid ($HClO_4$) in the ratio of 3:2 in a crucible and refluxed on a hot plate placed inside the fume hood at 110°C and was allowed to heat for 45 minutes till the mixture became clear. After heating, the resultant solutions and the undigested portion of the sediments were filtered using a filter paper. The filtrate was put in a volumetric flask and made up to 20 mL with deionized water. All the digested samples were stored in plastic bottles with plastic covers and labeled appropriately for trace metals analyses [3].

2.5. Digestion of Fish Samples

Digestions of fish samples were done according to the method described by Uwah *et al*. Each of the fish was dried in an oven at 80°C for 24 h and homogenised to powder form. Two (2) g of the powdered sample were taken in a beaker; 6 mL HNO_3, 2 mL perchloric acid and 30 mL distilled water added and stirred. The beaker was heated, allowed to cool and the content filtered and made up to 50 mL with distilled water in a 50 mL volumetric flask [16].

2.6. Determination of Trace Metals in the Water, Fish and Sediment Samples

The digest solutions of the water, fish and sediment samples were prepared by measuring 10 mL of each of the samples into 250 mL crucibles. The samples were digested with aqua regia reagent (HCl and HNO_3) in the ratio of 3:1 at130°C using electric hotplate for 30 minutes. Each of the filtrate was made up to 100 mL with distilled water in 100 mL volumetric flasks after filtration. Standard solutions of the metal to be analysed were prepared. The atomic absorption spectrophotometer (AAS) (model: varian spectra 100, Australia.) was set with power on for ten minutes. The standard metal solutions were injected to calibrate the AAS using acetylene gas. An aliquot of the digest solutions were injected and the concentrations obtained from the AAS.

2.7. Bioaccumulation Factors (BAF)

The bioaccumulation of the trace metals in fish was quantified from bioaccumulation factor (BAF) which is the ratio of the level of each of the trace metals in fish to the level of that trace metal in water or in sediment as modified by Arnot and Gobas, according to Equations 1 or 2 [17].

$$BAF = \frac{C_F}{C_W} \quad (1)$$

$$BAF = \frac{C_F}{C_S} \quad (2)$$

Where: C_F = Level of trace metal in fish, C_W = Level of trace metal in water, C_S = Level of trace metal in sediment

2.8. Physicochemical Parameters Determination in the Water Samples

The physicochemical parameters of the water samples were determined by standard procedures described by Ademoroti; HACH; as well as Uwah *et al*. All field meters and equipment were checked and calibrated according to the manufacturer's specifications. The pH meter was calibrated using buffers of pH 4.0, 7.0 and 10.0. Total Dissolved Solid (TDS) meter was calibrated using the potassium chloride solution provided by the manufacturer. *In situ* measurements for some of the parameters pH, and temperature (°C) were measured using WTW pH Electrode SenTix 41. While electrical conductivity (EC) and TDS was determined by using a C0150 conductivity meter [18, 19, 3].

The turbidity of the water samples was measured using a standard turbidity meter, Model 6035. After stabilising the equipment for 10 minutes, the equipment was standardised on the appropriate scale and the turbidity of the samples measured using 5 mL of the sample. This model operates over a range or 0.00 to 199.0 NTU 18, 19, 3].

Dissolved oxygen (DO) in the water sample was determined by the Winkler's method. The biochemical oxygen demand **(**BOD) determination was done by keeping the water samples in an incubator in the dark for five days, after which the DO test was repeated and the BOD calculated by taking the difference between the initial and final concentrations of oxygen present after incubation as shown in Equation 3 [18, 19, 3].

$$BOD_5\,(mg/l) = DO\,(initial) – DO\,(final) \quad (3)$$

The chloride content in water samples was determined by the Mohr's titration method. Exactly 1 cm^3 of 5% K_2CrO_4 was added to 10 cm^3 of water and titrated by constant stirring with 0.0282M $AgNO_3$ to brownish colour and compared with the blank. The chloride content was calculated using Equation 4.

$$Cl\,(mg/L) = \frac{(A-B)\times M \times 70900}{Volume\ of\ sample\ (mL)} \quad (4)$$

Where: A = volume of $AgNO_3$ used for titrating the sample, B = volume of $AgNO_3$ used for titrating the blank and M = Molarity of $AgNO_3$.

Nitrite determination was done by measuring 10 m L of the water sample into a 25 mL conical flask and 1 mL of sulphanylamide solution added and allowed to stand for 2–8 minutes. An exact volume of 1 m L of 1-naphthylethylene diamine reagent was added to the mixture and allowed to stand for about 20 minutes and then made up to the 25 mL mark with deionised water. The absorbance was read at 543 nm using Jenway 7305 visible spectrometer [18, 19, 3].

Nitrate determination was done by measuring 10 m L of the water sample into a 25 mL conical flask and 2 mL of bruccine reagent added and followed with the addition of 10 m L concentrated H_2SO_4, mixed for about 30 seconds and allowed to stand for 20 minutes and then made up to the 25 mL mark with deionised water. The absorbance was read at 420 nm using jenway 7305 visible spectrometer. The Bruccine reagent was prepared by dissolving 1.0 g of bruccine sulpahte and 0.1 g of sulphanilic acid in 70 mL of hot distilled water and 3 cm^3 concentration HCl added and the volume made up to 100 mL with distilled water [18, 19, 3].

Sulphate determination was done by the Gelatin method by measuring 10 mL of the water sample into a 25 cm^3 conical flask and 1 mL of gelatin-$BaCl_2$ reagent added. The sulphate was precipitated out as $BaSO_4$ and the volume made up to the 25 mL mark with deionised water. The absorbance was read at 420 nm using jenway 7305 visible spectrometer [18, 19, 3].

Phosphate determination was done by the molybdenum blue method by measuring 30 mL of the water sample into a 25 mL conical flask and 3 mL of molybdenum blue reagent added and the volume made up to the 25 cm^3 mark with deionised water. The absorbance was read at 885 nm using jenway 7305 visible spectrometer [18, 19, 3]..

Total suspended solids, TSS (those solids particles that do not dissolve in water), were determined by first taking the weight of filter paper (W_1) and then measured 50 mL of the water sample into a clean beaker which was filtered through the filter paper. After the filtration process was completed, the filter paper and the residue were dried and reweighed (W_2). TSS was measured using Equation 5 [18, 19, 3].

$$TSS = W_2 – W_1 \quad (5)$$

The alkalinity contents of each of the water samples were determined by adding 5 drops of methyl orange indicator to 50 mL of each water sample and each of the resulting solution titrated with 0.5 M HCl to a pink colouration at the end point. The volume of the titrant used was recorded and the alkalinity of each of the samples calculated as shown in Equation 6.

$$\text{Alkalinity (mg/L)} = \frac{V_t x\ M\ x\ 1000{,}000}{V_S} \quad (6)$$

Where: V_t = volume (mL) of titrant, V_S = volume (mL) of sample, M = molarity [18, 19, 3].

2.9. Quality Control

Quality control of the analytical data was guaranteed through the implementation of laboratory quality assurance and laboratory methods, including the use of standard operating procedures, calibrations with standards and reagent blanks. Samples were analysed in triplicates, all chemicals and reagents used were of analytical grade.

2.10. Health Risk Assessment

According to USEPA as well as Uwah *et al*., exposure assessment is the determination of the magnitude, frequency, duration and route of exposure with respect to particular chemical contaminants [20, 16]. To assess human health risk of any chemical contaminant, risk assessment procedures, which involve a four-step process, were followed. The first step (the hazard identification was achieved by measuring the concentrations of trace metals in water, fish and sediment). The second step (the exposure assessment for the inhabitant of the area), was estimated for two categories (adult and children) and examined through ingestion (water and fish) and dermal absorption (water) routes based on the USEPA risk assessment methodology [20, 21]. The exposure doses for water ingestion and dermal absorption were calculated from Equations 7 and 8, respectively.

$$\text{EXP}_{\text{Ingestion}} = \frac{\text{CW} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (7)$$

$$\text{EXP}_{\text{Dermal}} = \frac{\text{CW} \times \text{SA} \times \text{KP} \times \text{ABS}_{\text{D}} \times \text{ET} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}} \quad (8)$$

Where: $\text{EXP}_{\text{Ingestion}}$ is the exposure dose through ingestion of water (mg/kg/day), $\text{EXP}_{\text{Dermal}}$ is the exposure dose through dermal absorption (mg/kg/day), CW is concentration of trace metals in water (mg/L), IR is water ingestion rate (l/day), EF is the exposure frequency (days/year), ED is exposure duration, BW is the average body weight (kg), AT is the average time (days), SA is the exposed skin area (cm^2), ET is exposure time (hour/day), CF is the conversion factor (l/mL), KP is the dermal permeability coefficient (cm/hour) and ABS_{D} = Dermal absorption factor (no unit) [20, 21].

The exposure dose for fish consumption was evaluated by calculating the level of exposure resulting from the consumption of a particular metal in fish using Equation 9.

$$\text{EXP}_{fish} = \frac{\text{CC} \times \text{IR} \times \text{FI} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (9)$$

Where: CC is the concentration of trace metals in winkles tissue (mg/kg), IR is the ingestion rate, FI is the fraction ingested (no unit), EF is the exposure frequency (days/year), ED is the exposure duration over a life time, BW is the body weight and AT is the average life time (70 years x 365 days) [20, 21].

Dose–response, also known as reference dose (RfD), is the third process which is based on the existing toxicity information developed for different chemical pollutants. Oral reference dose (RfD) is employed in this study for the metals as suggested by the United Nations Food and Agricultural Organization (FAO) and WHO [22]. The final step (the risk characterization), was carried out by evaluating the non-cancer risk in terms of hazard quotient (HQ). In order to

develop HQ, comparison of the calculated contaminants from each exposure route (ingestion and dermal) with the reference dose was carried out using Equations 10 and 11, respectively.

$$HQ_{Ingestion} = \frac{EXP_{Ingestion}}{RfD_{Ingestion}} \quad (10)$$

$$HQ_{Dermal} = \frac{EXP_{Dermal}}{RfD_{Dermal}} \quad (11)$$

Where: $HQ_{Ingestion}$ is the hazard quotient through ingestion and HQ_{Dermal} is the hazard quotient through dermal contact, $RfD_{Ingestion}$ is the oral reference dose ingestion and RfD_{Dermal} is the dermal reference dose (mg/kg/day) [23, 24, 21]. HQ for fish consumption was determined by expressing it as the ratio of intake of fish to the RfD of the metal of concern according to Equation 12 [25].

$$HQ = \frac{Intake_{(fish)}}{RfD} \quad (12)$$

All exposure assessment parameters for ingestion and dermal absorption of metals in water and ingestion of metals in fish, used in this study are as provided by USEPA; Naveedullah *et al.*; Wu *et al.*; Iqbal and Shah as well as Ijeoma *et al* [22–24, 26, 27]. The parameters include: SA = 18, 000 cm^2, KP (cm/hour) = (Pb = 1.0E-4; Ni = 2.0E-4; Cu = 1.0E-3; Cr = 1.0E-3; Cd = 1.0E-3; As = 1.0E-3), ABS_D (no unit) = 0.001, ET (hour/day) = 0.6, EF (days/year) = 365, CF = 1/mL, BW (kg) = 70, ED (years) = 70, IR (kg/day) = 0.040, FI (no unit) = 1 (assuming that the whole muscle fillet of the fish is consumed), AT (days) = ED × EF, $RfD_{Ingestion}$ (mg/kg/day) = (As = 0.0003; Cd = 0.01; Cu = 0.04; Pb = 0.036; Cr = 0.03; Ni = 0.02; Zn = 0.3), RfD_{Dermal} (mg/kg/day) = (Pb = 5.25E-4; Ni = 5.4E-3; Cu = 1.2E-2; Cr = 6E-5; Cd = 1E-5; As = 1.23E-4; Hg =2.10E-5) [22–24, 26, 27].

The HQs for each sample were summed up to obtain overall toxic risk, i.e. the hazard index (HI) as indicated in Equation 13.

$$HI = \Sigma HQ_i,\ i = 1...n \quad (13)$$

Where: i = the number of trace metals. If the calculated HI is less than one, then the non-carcinogenic adverse effect due to the exposure pathway or toxicant was assumed to be negligible.

Data generated in this study were subjected to statistical analyses using statistical package for social sciences (SPSS).

3. Results and Discussion

3.1. Levels of Trace Metals in Water, Fish and Sediment Samples

Levels of the investigated trace metals in water, fish and sediment, analysed in this study are as presented in Tables 1 to 3. The trace metals levels in water are presented in Table 1. Those in fish are presented in Table 2, while those in sediment are presented in Table 3.

Table 1. *Trace metal levels (mg/L) in water from Atabong River during dry and wet seasons.*

Metal	Dry season				Wet season			
	Station 1	Station 2	Station 3	Mean	Station 1	Station 2	Station 3	Mean
Cr	0.018	0.018	0.018	0.018	0.022	0.023	0.024	0.023
Mn	0.005	0.005	0.005	0.005	0.012	0.013	0.014	0.013
Pb	0.000	0.000	0.002	0.001	0.000	0.000	0.003	0.001
Cd	0.005	0.005	0.005	0.005	0.016	0.016	0.013	0.015
Ni	0.010	0.010	0.010	0.010	0.021	0.018	0.021	0.020

Table 2. *Trace metal levels (mg/kg) in fish from Atabong River during dry and wet seasons.*

Metal	Dry season				Wet season			
	Station 1	Station 2	Station 3	Mean	Station 1	Station 2	Station 3	Mean
Cr	0.005	0.002	0.007	0.005	0.014	0.011	0.011	0.008
Mn	0.004	0.006	0.003	0.004	0.031	0.030	0.020	0.014
Pb	0.001	0.00	0.003	0.001	0.004	0.004	0.004	0.002
Cd	0.003	0.005	0.003	0.004	0.015	0.013	0.013	0.008
Ni	0.003	0.002	0.002	0.002	0.017	0.018	0.016	0.009

Table 3. *Trace metal levels (mg/kg) in sediment from Atabong River during dry and wet seasons.*

Metal	Dry season				Wet season			
	Station 1	Station 2	Station 3	Mean	Station 1	Station 2	Station 3	Mean
Cr	0.031	0.030	0.033	0.031	0.457	0.458	0.459	0.458
Mn	0.04	0.04	0.05	0.043	0.050	0.054	0.052	0.052
Pb	0.003	0.001	0.003	0.002	0.013	0.013	0.014	0.013
Cd	0.043	0.041	0.042	0.042	0.318	0.318	0.318	0.318
Ni	0.026	0.022	0.024	0.024	0.126	0.125	0.124	0.125

As presented in Table 1, the mean levels of the investigated trace metals in water samples obtained from the three stations during the dry season ranged from 0.002 mg/L Pb to 0.018 mg/L Cr, while in the wet season water samples,

the mean levels of the investigated trace metals ranged from 0.001 mg/L Pb to 0.023 mg/L Cr. From Table 2, the mean levels of the investigated trace metals in fish obtained from the three stations during the dry season ranged from 0.001 mg/kg Pb to 0.005 mg/kg Cr, and in the wet season fish samples, the mean levels of the investigated trace metals ranged from 0.002 mg/kg Pb to 0.009 mg/kg Ni. As seen in Table 3, the mean levels of the investigated trace metals in sediment samples obtained from the three stations during the dry season ranged from 0.002 mg/kg Pb to 0.043 mg/kg Mn, while in the wet season sediment samples, the mean levels of the investigated trace metals ranged from 0.013 mg/kg Pb to 0.458 mg/kg Cr.

As noted by Li and Zhang, that the levels of trace metals in an aquatic or terrestrial environment and their consequent accumulation in organisms affect the survival of aquatic organisms in such environment and hence the toxic index of consumption of such aquatic organisms by humans [28]. According to ATSDR, Cr is an essential trace nutrient and a vital component of glucose factor, but its toxicity damages the liver, lungs and causes organ haemorrhages [29]. Generally, the results obtained for the levels of the investigated trace metals in water, fish and sediment, in this study are comparable with those reported by Addo *et al*., in fish obtained from Kpeshie Lagoon, Accra [30]. The elevated level of Cr in sediment during the dry season, in this study, suggested a reduction in the volume of water which could leads to an increase in the level of the trace metal in sediment. The elevated value of Cr in fish during the wet season could be attributed to increase in the level of the trace metal in the surrounding water and sediment, thereby, leading to higher absorption by the fish. However, the mean level of Cr in each of the samples analysed, did not exceed the recommended limits by international and national bodies.

Pb is a toxic trace metal with no metabolic benefits to humans and aquatic biota and it is known that the presence of Pb in any compartment of the aquatic ecosystem indicates contamination [31]. The level of Pb in the analysed samples in this study, agreed with that reported by Dan *et al*. from Qua Iboe River Estuary, Nigeria [32]. The level of Pb reported in each of the samples in this study, was generally low.

3.2. Bioaccumulation Factors (BAFs) of Trace Metals in Fish

For both the dry and wet seasons, the BAFs of trace metals from water to fish are presented in Table 4, and those from sediment to fish are presented in Table 5. From Table 4, Pb recorded the BAFs values of 1.0 and 2.0, in fish from water in the dry and wet seasons, respectively. Mn and Ni recorded the BAFs values of 2.8 and 1.6, in fish from water respectively, in the wet season. From Table 5, Pb equally recorded the BAFs value of 1.5 in fish from sediment during the dry season and 0.29 during the wet season. The other trace metals had BAFs values in the fish from either water or sediment lower than unity in the two seasons. The BAFs were generally elevated in the wet season compared to those of the dry season. These could be attributed to higher activities and feeding regimes by the fish. According to Dan *et al*, the actions tend to lower oxygen affinity of the blood and increase the rates of feeding and pollutants accumulation [32]. The BAFs values of the studied trace metals in the fish were in the order: Pb > Mn > Ni > Cr> Cd for dry season, and Mn > Pb > Ni > Cd> Cr for wet season. The rate of accumulation of trace metals in an organism depends on the ability of the organism to eliminate the trace metals and the levels of the trace metals in the surrounding [33].

Table 4. *BAFs of trace metals from water to fish.*

Metal	Dry season			Wet season		
	Level in fish	Level in water	BAFs	Level in fish	Level in water	BAFs
Cr	0.005	0.020	0.250	0.008	0.018	0.444
Mn	0.004	0.008	0.500	0.014	0.005	2.800
Pb	0.001	0.001	1.000	0.002	0.001	2.000
Ni	0.004	0.009	0.444	0.008	0.005	1.600
Cd	0.002	0.014	0.143	0.009	0.010	0.900

Table 5. *BAFs of trace metals from sediment to fish.*

Metal	Dry season			Wet season		
	Level in fish	Level in sediment	BAFs	Level in fish	Level in sediment	BAFs
Cr	0.007	0.031	0.226	0.008	0.214	0.037
Mn	0.003	0.043	0.070	0.014	0.047	0.298
Pb	0.003	0.002	1.500	0.002	0.007	0.286
Ni	0.003	0.042	0.071	0.008	0.160	0.050
Cd	0.002	0.024	0.083	0.009	0.067	0.134

3.3. Levels of Physicochemical Parameters in the Water Samples

The results of the investigated physicochemical parameters in the water samples analysed in this study are as presented in Table 6. It has been established that, the toxicity level of a given biota is dependent on both the pollution sources of the biota and the physicochemical properties of the given

environment [33, 3]. From the table, temperature (the degree of hotness or coldness of the water system), ranged from 29.0 to 29.49°C across the sampling stations in both the dry and wet seasons, with the mean values of 29.30 and 29.11°C, for dry and wet seasons, respectively. Temperature is regarded as an important factor which influences the chemical and biological characteristics of the aquatic system [30]. Having the knowledge of the temperature of a water body is important because different aquatic organisms show different behavioural changes at different temperatures. As noted by [34], temperature range of 25 to 30°C are favourable for survival of aquatic organisms. Accordingly, the pH (which is a measure of the hydrogen ions concentration in the water) gave the mean values of 6.67 and 6.83, for dry and wet seasons, respectively. pH has implication on the bioavailability of trace metals in an aquatic body. It has been reported that high or low pH of a river, is capable of affecting the aquatic lives and alters the toxicity of pollutants in one form or the other in the river [34].

Table 6. *Physicochemical parameters of water samples during dry and wet seasons.*

Parameter	Dry Season				Wet Season			
	Station1	Station 2	Station 3	Mean	Station 1	Station 2	Station 3	Mean
Temperature (°C)	29.0	29.42	29.49	29.3	29.0	29.14	29.19	29.11
pH	6.63	6.67	6.70	6.67	6.8	6.8	6.88	6.83
TSS (mg/L)	119.0	119.1	119.8	119.3	118.3	118.7	119.5	118.8
TDS (mg/L)	126.3	126.1	126.1	126.2	146	146.8	147.9	146.9
EC (μscm^{-1})	172	173.7	175.9	173.9	100.3	101.4	102.4	101.4
Alkalinity (mg/L)	9.00	9.00	9.01	9.00	7.6	7.57	7.70	7.62
DO (mg/L)	5.13	5.20	5.23	5.19	4.2	4.9	5.25	4.78
BOD (mg/L)	2.56	2.60	2.83	2.66	3.04	3.06	3.22	3.11
Chloride (mg/L)	263.1	263	263	263	244	243.7	243.6	243.8
Nitrate (mg/L)	3	3.14	3.19	3.11	2.6	2.6	2.65	2.62
Nitrite (mg/L)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Sulphate (mg/L)	36.4	36.5	36.5	36.5	41.1	40.5	40.4	40.7
Phosphate (mg/L)	3.54	3.54	3.55	3.54	3.81	3.81	3.82	3.81
Turbidity (NTU)	2.33	2.53	2.33	2.43	3.00	3.06	3.00	3.02

The mean values for EC in the water were 101.4 and 173.9 μscm^{-1}, for dry and wet seasons, respectively. EC is the ability of an aqueous solution to carry electric current. It gives information on all dissolved ions in the solution. In this study, the dry season values for EC from each of the sampling stations were generally higher when compared with those of the wet season. These could be attributed to reduction in the volume of water during the dry season as a result of evaporation and precipitation. It could also be as a result of anthropogenic activities like farming, which involves the application of fertilizers to farmlands which are later leached into the river during the rains. EC valves from all the sampling stations in this study were however, below the WHO guideline limit of 1500 μscm^{-1}.

The mean values for TDS values were found to be 126.4 and 146.9 mg/L, for dry and wet seasons, respectively. TDS are common indicators of water pollution. The TDS values reported in this study were above the permissible level of less than 10 stipulated by WHO [35]. This could be attributed to storm water runoff and anthropogenic activities like sand mining, constantly going on in the river as well as atmospheric particles deposits. According to Ugwu and Wakama, TDS can be influenced by the pH of the water body, and noted that changes in the pH could affect the solubility of the suspended matter [36]. The TDS results reported in this study were in agreement with those reported by Ugwu and Wakama [36]. Elevated TDS values in the wet season compared to dry season were also reported by Akintoye *et al.* and Adebola *et al.* [37, 38].

The mean values for DO and BOD were found to be 5.19 and 2.66 mg/L for dry season and 4.78 and 2.11 mg/L for wet season, respectively. The level of DO in water signifies the potential for the oxidation of organic matter in the water and thus the ability of the water to support aquatic life [39]. The observed levels of DO in the water at each of the sampling stations were below the permissible limits of 8-10 mg/L given by WHO [35]. The observed levels of DO in the studied river could be attributed to high influx of domestic and agricultural wastes from surface run-offs. According to Namrata], in the systems where the rate of respiration and organic decomposition are high, DO value remains lower than the DO of the system where the rate of photosynthesis is high [34]. In this study, the decrease in DO values from one sampling point to another could be attributed to the fact that as the river flows, it carries dissolved organic matters which are oxidised by the DO in the water, thereby leading to a decrease in DO from location one to another. BOD is the amount of oxygen required to biologically break down a contaminant. BOD is an important parameter of water indicating the health scenario of fresh water bodies [40]. The BOD values reported in this study were comparable with those reported by Abdo and El-Nasharty in Ismailia Canal, Egypt [41] and below the WHO limits of 10 mg/L [35].

The mean values for alkalinity in the water were 9.00 and 7.60 mg/L, for dry and wet seasons, respectively. The acidity of water affects the quality of such water. Alkalinity in water is the ability of such water to neutralize the acids, carbonates and bicarbonates contents of the water [36]. The alkalinity contents of the water for the dry and wet seasons in this study

were below the WHO threshold value of 400 mg/L. The mean levels of nitrate, nitrite, sulphate and phosphate in the water were 3.11, 0.02, 36.5 and 3.54 mg/L, respectively, for the dry season and 2.26, 0.02 40.7and 3.81 mg/L, respectively for the wet season.

Table 7. *Exposure of humans to trace metal contamination by oral ingestion of water.*

Metal	Dry season		Wet season	
	Adults	children	Adults	Children
Cr	7.2E-3	1.2 E-3	6.5 E-4	1.1 E-3
Mn	2.9 E-4	4.9 E-4	1.8 E-4	3.1 E-4
Pb	3.6 E-5	6.2 E-5	3.6 E-5	6.2 E-5
Cd	3.2 E-4	5.6 E-4	1.8 E-4	3.1 E-4
Ni	5.0 E-4	6.2 E-4	3.6 E-4	6.2 E-4

Table 8. *Exposure of humans to trace metals contamination by dermal contact with water.*

Metal	Dry season		Wet season	
	Adults	children	Adults	Children
Cr	7.6 E-8	1.4 E-7	6.8 E-8	1.2 E-7
Mn	3.0 E-8	5.4 E-8	1.9 E-8	3.4 E-8
Pb	3.8 E-9	6.8 E-9	3.8 E-9	6.8 E-9
Cd	3.4 E-8	6.1 E-8	1.9 E-8	3.4 E-8
Ni	5.3 E-8	9.5 E-8	3.8 E-8	6.8 E-8

Table 9. *Exposure of humans to trace metals contamination by oral ingestion of fish.*

Metal	Dry season		Wet season	
	Adults	children	Adults	Children
Cr	1.8 E-4	3.1 E-4	2.9 E-4	4.9 E-4
Mn	1.4 E-4	2.5 E-4	5.0 E-4	8.7 E-4
Pb	3.6 E-5	6.3 E-5	7.2 E-4	1.2 E-4
Cd	1.4 E-4	1.2 E-4	3.2 E-4	5.6 E-4
Ni	7.2 E-5	1.2 E-4	3.2 E-4	5.6 E-4

3.4. Health Risk due to Exposure Pathways

The exposures of humans to trace metals through oral ingestion of water, dermal contact with water and oral ingestion of fish are presented in Tables 7, 8 and 9, respectively. In all the pathways of exposures, Cr recorded high exposure, while Pb recorded the least in both adults and children in the two seasons. The exposures ranged from 3.8 E-9 Pb in the adults population from the dermal contact with water during the dry season in Table 8 to 1.1 E-3 Cr in the children population from the oral ingestion of water, during the wet season in Table 7. Generally, the exposure levels from all the pathways were higher in the children population than in the adults. This is because the body weight of a child is less than that of an adult [28, 21]. As noted by Muiruri and Nyambaka, Zn and Cr are seen as essential nutrients for humans and help in regulating the body functions [42]. The hazard quotients (HQ) of trace metals exposure to humans through the oral ingestion and dermal contact of water, and the oral ingestion of fish are presented in Tables 10 and 11, respectively. As presented in the tables, the HQ values of all the trace metals exposure to humans from each of the pathways considered were found to be less than unity (HQ < I). These are indications that, the levels of exposures from each of the pathways were not likely to cause any obvious adverse effects [43, 44, 21]. The overall toxic risk (HI), computed from the HQs was also found to be less than unity (HI < 1). This is an indication that there were no cumulative potentials of adverse health risks through ingestion of the fish and water or through dermal contact with the water by the exposed people or inhabitants of the study area.

Table 10. *HQ of trace metal contamination by oral ingestion and dermal contact of water.*

Metal	$HQ_{ingestion}$		HQ_{dermal}	
	Adult	Children	Adult	Children
Cr	2.7 E-3	8.0 E-3	4.8 E-8	7.8 E-8
Mn	1.7 E-3	2.8 E-3	1.8 E-7	3.1 E-7
Pb	9.0 E-3	1.6 E-3	9.5 E-11	1.6 E-12
Cd	2.5 E-1	4.4 E-1	2.7 E-11	4.8 E-11
Ni	2.2 E-2	3.1 E-2	2.2 E-10	4.1 E-10

Table 11. *HQ of trace metal contamination by oral ingestion of fish.*

Trace metal	HQ	
	Adult	Children
Cr	3.1 E-7	5.4 E-7
Mn	1.2 E-6	2.1 E-6
Pb	4.2 E-6	7.5 E-6
Cd	3.6 E-4	6.7 E-4
Ni	6.5 E-6	1.5 E-6

4. Conclusion

From the analyses and results, it could be concluded that the water, fish and sediment from Atabong River in Okobo, Nigeria, analysed in this study contained variable levels of the investigated trace metals and physicochemical parameters in both the dry and wet seasons. These could be attributed to all kinds of human activities in the area and excessive water run-off during the wet season, which resulted to the leaching of various kinds of wastes into the river. However, the investigated trace metals levels in the water, fish and sediment were below the permissible limits stipulated by WHO and USEPA. Bioaccumulation factors revealed the trend: Pb > Mn > Ni > Cr > Cd for dry season and Mn > Pb > Ni > Cd > Cr for wet season with regards to fish pollution status. Health risk due to consumption of the fish, water and dermal contact with the water, showed low risk as the hazard quotient and hazard index were less than unity in each case. Consumption of the fish and usage of the river water in whatever form by humans, are not likely to cause adverse health effects or risks, since the levels of contamination of the fish and water with the trace metals were below the levels that could cause toxicity in humans. However, for the purpose of monitoring and documentation, periodic investigation of the investigated trace metals in the river system is highly recommended. Accordingly, there should be periodic investigation of other trace metals not assessed in this study, in the river system. Better still, human health risk assessment of the investigated trace metals and indeed other trace metals in the Atabong River and other rivers in Akwa Ibom State, Nigeria is recommended to protect aquatic ecosystems and biodiversity in the area.

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