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Heavy metals contamination of Anambra River

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Abstract *The need for continuous monitoring of the influence of heavy metal rich waste on the quality of water from Anambra is necessary because the river plays major roles in the life of the people. Concentrations of some heavy metals (Cr, Cu, Ni, Zn, As, Cd, Pb, Ni, Mn and Hg) were determined using atomic absorption spectrophotometer Cd and the results obtained were compared with permissible limits stipulated by some regulatory bodies (Standard Organization of Nigeria, European Union and World Health Organization standards). The results obtained indicated observable mean concentrations of 0.046, 0.032, 0.032, 0.151, 0.032, 0.053, 0.031, 0.032, 0.060 and 0.030 mg/L for Cr, Cu, Ni, Zn, As, , Pb, Ni, Mn and Hg respectively. The measured concentrations of Cd, Pb, Ni, Mn and Hg were comparable higher than WHO, SON and EU permissible limits. The concentration of Cr, Cu, Ni, Zn and As were lower than WHO maximum contamination levels. The pollution index of Cd, Pb, Ni, Mn and Hg were above threshold value of 1.0, indicating high level of contamination of water samples from Anambra River.*

Key Words: *Anambra River, contamination, heavy metals, pollution index*

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1.0 Introduction

Water pollution is a global problem and has the potential to adversely impact public health (Khan and Ghouri, 2011). Portable water is essential for human survival and public health. This implies that such water should be safe for human consumption. The safety of water from rivers and other sources depends on the values of water quality parameters including physicochemical, bacteriological, organoleptic, heavy metals, radioactive and other indices (Kappor, 2001; Ogoko, 2015a; Ogoko and Donald, 2018). Water bodies are repositories of toxic organic and inorganic substances, biodegradable and non-biodegradable matters as well as pathogenic microorganisms that can initiate or increase toxicological risk to the ecosystem (Mgbemena, 2014; Mgbemena *et al*., 2011). Risk factors have been found to be strongly dependent on level of anthropogenic, industrial and other activities including urbanization, agricultural activities, mining activities and indiscriminate dumping of contaminated wastes (Eddy *et al*., 2006). Among all water quality indices, the presence of heavy metal ions has been found to be one of the greatest challenges because they are toxic within certain concentration, easily transfer to higher organism through the food chain, non-biodegradable and can bioaccumulate and be magnified (Odoemelam and Eddy, 2009). Heavy metals are those metals whose density is greater than 5 g/cm^3 and are toxic above certain concentration (Adnan *et al*., 2015; Ogoko *et al.,* 2015). Generally, background concentration of heavy metals in the universe is within tolerable concentrations but in several environment (including aquatic environment), abnormal increase in concentrations of heavy metal ions (especially in water), have been reported (Eddy *et al.,* 2004).

Scanty data has been published on the presence of some heavy metals in the Anambra River. Nwani *et al*. (2009)

identified significant concentration of heavy metals in some commonly consumed fishes from the Anambra Rivers and established the following concentration order, Fe>Zn>Cu>Mn>Cr>Pb. Nsofor *et al*. (2014) observed the concentration of heavy metals in shell fish tissue from the lower Niger River (i.e Anambra River) at Onitsha to include Zn (4.35±1.2), Cu (1.35±0.43), Cd (0.31±0.0421), Hg (0.16±0.0011) and As (0.04±0.001) in mg/l . Ujah *et al*. (2017), observed significant concentration of some heavy metals in water, fish and sediment from the Anambra River and noted that iron concentration was highest followed by lead with antimony and cadmium. Observed variations in the analysed parameters were found to be statistically significant at $p<0.05$.

It is utmost indicative that heavy metal concentrations in the water is a strong index to its usefulness to drinking, quality of aquatic life and other applications. This indicates that without the knowledge of their concentrations in the environment, information cannot sustain about their toxicity or safe indices (Adnan et al., 2015). Therefore, the present study is aimed at investigating the concentration of heavy metal ions in Anambra River, which is a river exposed to several contamination sources (Ujah *et al*. 2017). There are substantial literatures on the contamination of several Rivers in Nigeria. Ogoko and Donald (2018) noted that the concentrations of Pb, Cu, Zn and Mn in Imo River were higher than the WHO permissible values, indicating that the water was polluted. In a similar study on Jabi Lake, Ogoko and Ajayi (2020) observed that the pollution index of manganese, iron, cobalt, lead and chromium were above unity (1.0), which pointed towards a very high level of pollution and that the water was not suitable for drinking. Keziah *et al.* (2019) observed significant bioaccumulation of cadmium (Cd), zinc (Zn), lead (Pb) and mercury (Hg) in the gills, muscles and intestine of *Tilapia zillii, malapterurus electricus* and *clarias gariepinus* obtained at Onitsha shelf of Niger River. The attributed the sources of the heavy metals in the lower organism to continuous discharge of heavy metal rich wastes into the river. Hector *et al*. (2014) observed that the concentrations of Cd, Cr, Co, Hg, As, Fe, and Pb in Warri River were in excess of the WHO recommended limit for safe water and aquatic foods. This study was undertaken in order to assess the levels of heavy metals (Cd, Cr, Cu, Fe, Pb, Ni, Zn, Mn, As and Hg) in Anambra River and to establish if the present concentration level of these metals could constitute health threats to consumers. Besides, the findings of this research could provide supplementary information on the heavy metals pollutants of surface water in south-eastern Nigeria.

2.0 Materials and methods

2.1 Sample collection and pre-treatment

In compliance to grid techniques, triplicate water samples were collected from each sampling point at the depth of 10-15 cm below the surface of water in a previously washed two liters acid plastic container. The triplicate samples were then pooled together to form composite mixtures that were stored in a labeled plastic container. Water samples were collected from eight different point or stations within four major study blocks in the Anambra River. The water sample was acidified with 2 ml of concentrated nitric acid and stored at a temperature of about 5°C prior to transportation for analysis in the laboratory.

2.2 Digestion of water sample

The water samples were shaken thoroughly in their respective plastic containers. 100 ml of water sample was measure into a 100 ml conical flask. 5ml of concentrated nitric acid was added. The conical flask and its content were heated on a hot plate and evaporated to about 20 ml in order to ensure that the water did not boil. A further 5ml of concentrated nitric acid was added and the beaker was covered with a watch glass while heating continued. Concentrated nitric acid was periodically added until the solution appeared coloured and cleared. Few drops of hydrogen peroxide were ~~then~~ added to ensure complete digestion. The solution was filtered and the filtrate was transferred to a 100 ml volumetric flask to cool and then made up to the mark with distilled water (Radojovenic and Bashkin, 2006).

2.2.1 Determination of heavy metal ions

Atomic absorption spectrophotometer (HACH DR2) was used in the analysis of metal element concentration according to American Public Health Association (APHA, AWWA, 2001). Calibration curves were prepared for each metal using serially diluted concentrations of the respective metal stock solution. From the calibration curve, concentration of the metal ion was then estimated through graphical extrapolation (Ogoko, 2019).

2.3 The study area

The study area was the Anambra River and the map of the River is shown in Fig. 1. Anambra River is located at Aguleri but cut across other communities in Anambra State Nigeria and empties at a point ~~just~~ close to east of river Niger. The river rises at Kogi State and drains through Enugu and Anambra State and eventually discharges into River Niger. The river (Oma Mbala) gives credence to the name Anambra State. Anambra River is located in South Central region of Nigeria and lies between latitudes 60º 00N and 60º 30º N and between longitudes 60º 45ºE and 70º15ºE. The Anambra River is approximately 207.4km to 210km in length (Odo, *et al*., 2009; Shahin, 2002). Aguleri community in Anambra State are highly industrious and resourceful. Anambra State is rich in natural gas, crude oil, bauxite, ceramics and high levels of arable soils. The first Nigerian private refinery, orient petroleum refinery (OPR) was located at Aguleri community. The user communities of Anambra River are involved in other activities such fishery, farming, and animal husbandry. Agrochemical waste like pesticides, herbicides and fertilizers are introduced to the river endangering aquatic lives and human that depends on this river for livelihood.

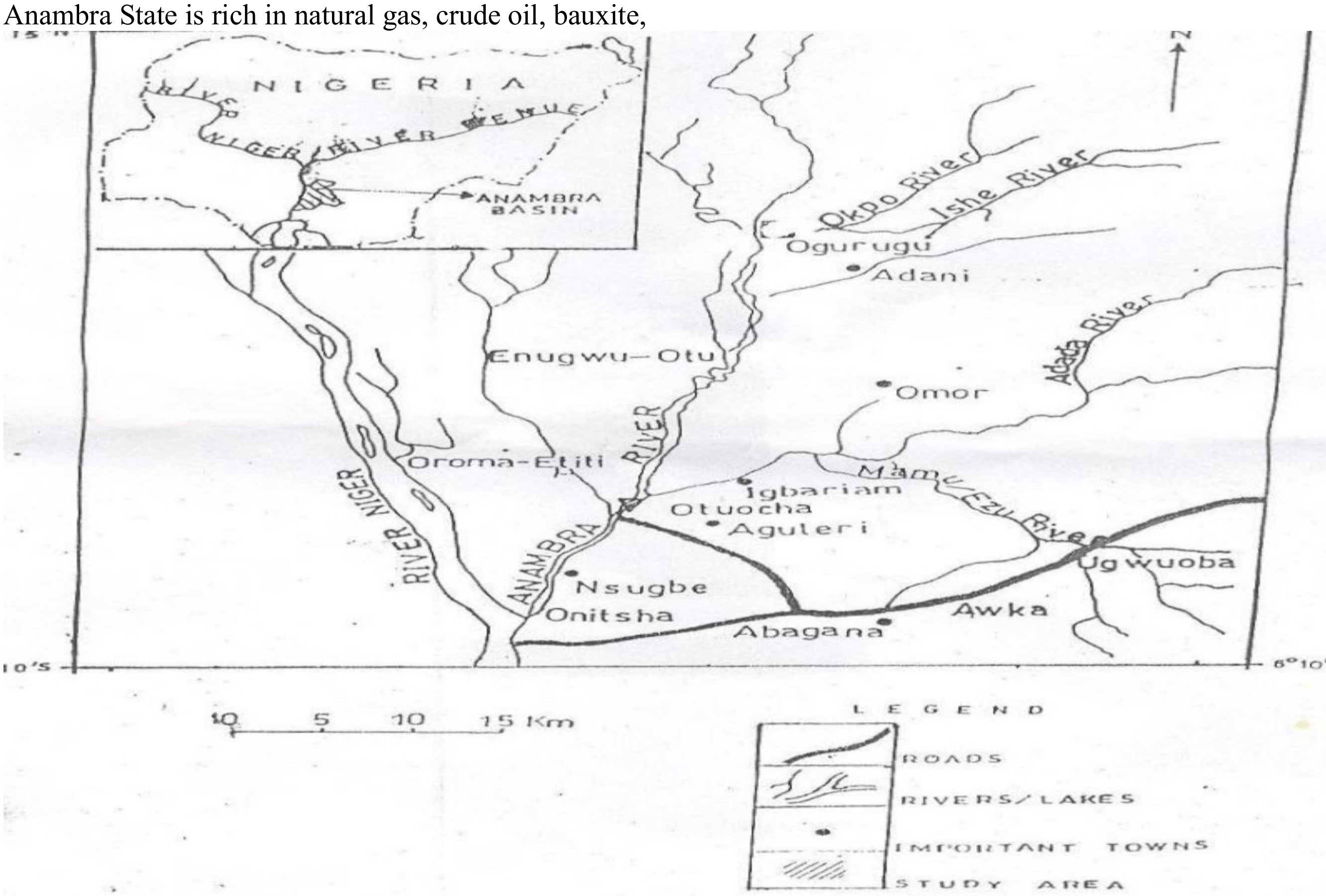

Fig. 1: Map of Anambra River

2.4 Geochemical index

2.4.1 Pollution index (Pi)

Pollution index was used to evaluate the extent of pollution in environmental water samples (Ogoko and Donald, 2018). Pollution index (Pi) is the ratio of the concentration of individual parameter evaluated to that of permissible standard. It describes the relative influence of each parameter to the total pollution. Pollution index can be expressed thus:

$$(Pi) = \frac{Concentration\ of\ individual\ parameter}{Concentration\ of\ standard} \quad (1)$$

Pollution index less than unity indicates absence of pollution but pollution index greater than unity indicates significant level of pollution has occurred.

3.0 Results and Discussion

The results of the heavy metal concentration obtained from the water sample in Anambra River are presented in Table 1. The results show that the concentration of cadmium ranged from 0.051 ± 0.01 mg/ L to 0.055 ± 0.00 mg/L. The measured concentrations of cadmium in the water samples were above the 0.003, 0.005 and 0.005 mg/L recommended as maximum permissible limits by World Health Organization (WHO, 2004), European Union and Standard Organization of Nigeria respectively (EU, 1998; SON, 2007) respectively.

Table 1: Heavy metal concentration in water samples from River Anambra

	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mn	As	Hg
S1	0.052±0.01	0.049±0.03	0.030±0.02	0.060±0.01	0.030±0.01	0.031±0.01	0.151±0.01	0.058±0.01	0.032±0.01	0.030±0.01
S2	0.054±0.01	0.043±0.01	0.034±0.01	0.066±0.02	0.032±0.02	0.033±0.02	0.150±0.01	0.062±0.02	0.033±0.02	0.031±0.01
S3	0.051±0.01	0.045±0.02	0.031±0.01	0.062±0.01	0.031±0.01	0.032±0.01	0.152±0.02	0.059±0.01	0.032±0.01	0.029±0.01
S4	0.055±0.00	0.047±0.01	0.033±0.00	0.064±0.03	0.031±0.01	0.031±0.02	0.149±0.01	0.061±0.02	0.031±0.01	0.028±0.01
S5	0.052±0.02	0.044±0.01	0.032±0.01	0.062±0.01	0.029±0.00	0.032±0.01	0.152±0.01	0.060±0.01	0.030±0.01	0.031±0.01
S6	0.053±0.01	0.046±0.00	0.032±0.01	0.062±0.02	0.033±0.02	0.033±0.01	0.152±0.03	0.061±0.01	0.033±0.02	0.031±0.01
S7	0.054±0.02	0.047±0.01	0.033±0.00	0.064±0.01	0.030±0.01	0.029±0.00	0.150±0.01	0.060±0.02	0.033±0.01	0.028±0.00
S8	0.053±0.01	0.047±0.02	0.031±0.01	0.064±0.02	0.032±0.01	0.035±0.02	0.152±0.02	0.059±0.01	0.032±0.01	0.032±0.01
Mean Conc.	0.053	0.046	0.032	0.063	0.031	0.032	0.151	0.060	0.032	0.030
SON (2007)	0.005	0.050	1.000	0.500	0.010	0.020	3.000	0.200	0.010	0.001
WHO(2004)	0.003	0.050	2.000	0.300	0.010	0.020	3.000	0.040	0.050	0.001
EU (1998)	0.005	0.050	2.000	0.200	0.010	0.200	--	0.050	0.010	0.001

****Mean of three ± Standard Deviation****

This indicate that the water is polluted with respect to cadmium. Cadmium is discharged to the atmosphere largely in the form of oxides through combustion process and is transferred to water surface by wet deposition. Other sources of cadmium include electroplating, pigments, plastics, stabilizers and battery industries (Mebrahtu and Zerabruk, 2011). In Nigeria, cadmium rechargeable batteries are poorly disposed into refused dumps and sewage sludge and can therefore constitute sources of cadmium to the aquatic environment. Cadmium has high mobility in biological systems and chronic exposure can lead to renal dysfunction, calcium metabolism disorder and high incidence of cancer (Selinus and Alloway, 2005). At lower concentrations, cadmium courses serous changes in the arteries of human kidney because it has the potential to displace zinc and initiate high blood pressure (Mebrahtu and Zerabruk, 2011).

Concentration of chromium ions in the water samples ranged from 0.043 ± 0.01 to 0.049 ± 0.03 mg/L. However, concentrations of chromium ions were within the maximum permissible limits of 0.050 mg/L (EU, 1998; SON, 2007; WHO, 2011). Therefore, it can be inferred that the water is not currently polluted with chromium ion. Sources of chromium are water erosion of rocks, power plants, liquid fuels, and coal, industrial and municipal waste. Chromium exists in compounds with variable oxidation states and not biodegradable but persistent in the environment (Adeleken and Abegunde, 2011). Exposure to high concentration of Cr^{+6} may generate lung cancer, malignant neoplasia, chromium dermatitis, skin ulcers, bronchial asthma and other severe health challenges (Sarkar, 2005). Copper concentrations ranged from 0.030±0.02 to 0.034±0.01mg/L. This is within the maximum permissible limit of 1.0, 1.0 and 2.0 mg/L recommended by Standard Organization of Nigeria, European Union, and World Health Organization respectively. This clearly suggests that the water is not contaminated with copper. The presence of copper to the river maybe from the discharge of copper laden wastes to the river or to the nearby land, which will ultimately find their ways into the river and bioaccumulate. Although the observed concentration of copper ions in the river water are within the permissible limits, continuous discharge of copper rich waste can pollute the water and lead to irritation of the nose, mouth and eyes, headache, dizziness, vomiting and diarrhea to consumer of the water. The calculated range for iron ion concentration in the water samples was 0.060 ± 0.01 to 0.066 ± 0.02 mg/L, which reveals that the water is within the permissible limits when compared to Standard Organization of Nigeria (0.50 mg/L), European Union (0.20 mg/L), and World Health

Organization (0.30 mg/L) threshold values. Therefore, the water is not polluted with respect to iron. Iron is beneficial to man at low concentration, but possess treat to health if taken at a very high concentration. Studies have shown that apart from other sources, discharge of domestic and municipal wastes is one of the major sources of iron pollution (Eddy and Ukpong, 2005). The presence of iron in water can alter the pH of the water through oxidation and can also encourage the precipitation and co-precipitation of simple and complex salts respectively (Ekwemengbo *et al.,* 2011). According to Mandour (2012), significant contamination of water by iron can increase the risk of cirrhosis and lung cancer. Lead concentrations in the water ranged from 0.030 ± 0.01 to 0.033 ± 0.02 mg/L and indicated that the water is polluted with respect to lead since the permissible limit for lead in water 0.010 mg/L (EU, 1998; SON, 2007; WHO, 2011). The observed high concentration of lead in the water may be attributed to the discharge of lead laden wastes, emission from automobile, refinery waste and stationery/automobile engines emission (Ahamefuna *et al*., 2014; Mgbemena *et al*., 2014). Lead can be transferred to human body through uptake of food, water and air (Adepoju-Bello, and Alabi, 2005; Kelle *et al.,* 2020; Nduka *et al*., 2020; Ogoko and Ajani, 2020). At higher concentrations, lead can disrupt synthesis of haemoglobin, increase in blood pressure, impaired kidney function, miscarriages and subtle abortions, disruption of nervous systems, brain damage, infertility, reduced learning abilities in children and may cause behavioural disruptions of children growth (Adepoju-Bello and Alabi, 205; WHO, 2004). Nickel concentrations ranged from 0.029 ± 0.00 to 0.035 ± 0.02 mg/L and were higher than the permissible limit of 0.020, and 0.020 mg/L recommended by SON and WHO respectively (SON, 2007; WHO, 2011). Nickel concentration was however, lower than 0.200 stipulated by European Union (EU, 1998). Indiscriminate discharge of waste water such as municipal sewage and agricultural run-off are the primary route of nickel into the water. The observed contamination of the water by lead indicate that industrial, domestic and municipal wastes that are rich in nickel might have find their way to the river.

Toxicity of nickel include development of lung cancer and prostate cancer, dizziness, lung embolism, birth defect, asthma, allergic reactions, dermatitis and ulceration of skin (Emoyan *et al*., 2006). Measured concentrations of zinc ions were found to range from 0.149±0.01 to 0.152±0.03 mg/L (mean = 0.151 mg/L). However, based on SON (2007) and WHO (2011) standards (i.e 3.00 mg/L), the water is not polluted with zinc). Anthropogenic sources of zinc in the water may include discharge of smelter, slag and wastes. Zinc is needed in the body to form connective tissues such as tendons and ligaments (Miculescu *et al*., 2001). Cases of zinc toxicity is not very common. However, at concentration above 40 mg/L some adverse symptoms including irritability, muscular stiffness have been reported (Al-Weher, 2008).

The results of our water analysis also indicated the presence of manganese within the range, 0.058±0.01 to 0.062 ± 0.02 mg/L (mean = 0.060 mg/L), which indicates that the water is polluted with manganese since the values are higher than the maximum allowable limit of 0.04 and 0.05 mg/L stipulated by European Union and World Health Organization respectively (EU, 1998; WHO, 2011). Although manganese is a useful element in the human system, its toxicity depends largely on route of exposure, chemical specie, age, sex and animal species (EPA, 2004; Calkins, 2009; Kohl and Medlar, 2007). Manganese is a syndrome which results from chronic exposures of manganese (EPA, 2004; Calkins, 2009).

Arsenic concentration ranged from 0.030 ± 0.01 to 0.033 ± 0.02 mg/L with a mean value of 0.032 mg/L. Although these concentrations of arsenic were higher than the maximum permissible limits of 0.01 mg/l recommended by Standard Organization of Nigeria and European Union respectively, it was within the permissible limits of 0.05 mg/l stipulated by World Health Organization. Arsenic occur naturally in the soil and minerals and may be transfer to the river by surface run off. However, in several locations, concentrations of arsenic ions have been found to exceed the background concentration due to discharge of agricultural, industrial, domestic and municipal wastes to the River. Exposure to arsenic can occur through consumption of contaminated food and water as well as through skin contact. Mild exposure to inorganic arsenic leads to stomach and intestines irritation, skin changes, lungs irritation and reduced red and white blood production. Excessive exposure to arsenic has been reported to be characterized with symptoms such as infertility, miscarriages in women, heart and brain damage.

The concentration of mercury ranged from 0.028±0.00 to 0.032±0.01 mg/L with a mean value of 0.030 mg/L, been higher than 0.001 mg/L recommended by European Union, Standard Organization of Nigeria and World Health Organization respectively (EU, 1998;

SON, 2007; WHO, 2011). This indicates that the water is contaminated with mercury. Mercury maybe released through industrial discharge of effluent into the water bodies. Mercury in its different forms are toxic. Impact of mercury toxicity includes damage to the brain, kidney and lungs. Others diseases associated with mercury poisoning are acrodynia, Hunter-Russell syndrome and Minamata disease. The observable symptoms of these diseases ranged from sensory impairment, disturbed sensation and lack of coordination. Individual toxin, as well as methods and duration of exposure are the factors that determine the type and degree of symptoms exhibited.

The pollution index of the metal elements was computed in order to ascertain the degree of pollution of the river by heavy metal. Calculated values of the pollution index are presented in Table 2.

Table 2: Pollution Index of Heavy metal concentration in water samples from River Anambra

	Cd	Cr	Cu	Fe	Pb	Ni	Zn	Mn	As	Hg
S1	17.33	0.98	0.015	0.210	3.00	1.55	0.050	1.450	1.001	30.01
S2	18.00	0.86	0.017	0.220	3.20	1.65	0.051	1.550	0.660	31.00
S3	17.00	0.90	0.016	0.207	3.10	1.60	0.051	1.475	1.001	29.03
S4	18.33	0.94	0.017	0.213	3.10	1.55	0.049	1.525	0.620	28.00
S5	17.33	0.88	0.016	0.207	2.90	1.60	0.051	1.501	1.001	31.00
S6	17.67	0.92	0.016	0.207	3.30	1.65	0.051	1.525	0.660	31.00
S7	18.00	0.94	0.017	0.213	3.00	1.45	0.051	1.501	1.001	28.00
S8	17.67	0.94	0.016	0.213	3.20	1.75	0.051	1.475	0.641	32.00
mean	17.67	0.92	0.016	0.211	3.10	1.60	0.051	1.500	0.823	30.00

It is interesting to note that Cr, Cu, Fe, Zn and As had mean pollution index of 0.920, 0.016, 0.211, 0.051, 0.823 respectively, which are less than the threshold value of 1.0. Therefore, there is no significant pollution of Anambra River by Cr, Cu, Fe, Zn and As. However, since the calculated pollution index for Cd (17.67), Pb (3.10), Ni (1.60), Mn (1.50) and Hg (30.0) are greater than unity, the Anambra River is polluted by these heavy metals.

4.0 Conclusion

The study revealed that there is marked variation in the concentration of the heavy metals from one sampling station to another, however the differences is not strongly significant. The concentrations and computed mean pollution index of Cd, Pb, Ni, Mn and Hg were above stipulated permissible limits and threshold pollution index of 1.0 respectively, indicating high level of contamination of water samples from Anambra River. There is therefore obvious need for the relevant regulatory agencies to double efforts in its monitoring activities to discourage indiscriminate discharge of domestic and industrial wastes into rivers and other water bodies. Affordable treatment measures should be adopted for use in decontamination process in order to lessen public health problem as a consequence of heavy metal contamination of source of drinking water.

5.0 References

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