SPATIAL AND TEMPORAL VARIATIONS OF HEAVY METALS CHARACTERISTICS OF ANYA RIVER, IKWUANO LOCAL GOVERNMENT, ABIA STATE.

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Abstract
This study investigated eight heavy metals (Mn, Cu, Pb, Fe, Zn, Cd, Cr and Ni) characteristics of Anya River with respect to season and anthropogenic activities. Eight (8) heavy metals were assessed between February and September 2019 in 3 stations, using atomic absorption spectrometer, and compared with Nigerian drinking water standards. Data were subjected to analysis of variance (ANOVA). Results obtained revealed that there were no significant difference (P>0.05) across the three stations for the investigated heavy metals. The result showed that Anya River is contaminated with heavy metals in order of Fe > Zn >Mn> Cr > Cu >Pb> Cd >Ni. All the heavy metals investigated were quite above the allowable limit set by SON and FMEnv for drinking water and healthy environments especially during the rainy season. It is strongly recommend that holistic investigation involving health risk assessment, bio-accumulation, magnification, DNA disruption of heavy metals in organisms living in this River should be carried out.

Key words: Heavy metals, surface water, concentrations, variation, water quality

Introduction

Activities aimed at sustaining human population such as intensive farming and industrialization, activities, and waste discharge into surface water bodies have been a threat to the availability of good drinking water and water for agricultural purposes. Surface water bodies have been the major sources of drinking water for numerous rural communities in Nigeria; and the quality of the water has been greatly affected by upsurge in the indiscriminate use of agro-chemical, dumping and disposal of wastes into land and water bodies (Enitan *et al*., 2018).

These anthropogenic activities can also alter heavy metal characteristics of any receiving surface water body. The heavy metal characteristic of Anya river is suspected to be deteriorating day by day due to numerous anthropogenic such as washing of motorcycles, kitchen utensils, application of heavy metal contained pesticides, and other unsustainable agricultural practices within and along floodplain of the river (Field Observation, 2019).

Although some heavy metals at trace level are essential for humans, they can be dangerous at relatively high exposure levels (Goorzadi *et al*., 2009; Govind and Madhuri, 2014; Onyele and Anyanwu, 2018; Adaka, et al., 2017). Heavy metals are considered as severe pollutants owing to their toxicity, persistence and bio- accumulative nature in the environment. Heavy metals are very hazardous due to their recalcitrant to degradable and have long biological half- lives (Olgunoğlu *et al*., 2015).The incipient effects of drinking heavy metal contaminated water could manifest, and could cause health challenges. Heavy metal related diseases are usually severe. Many people were reported killed by a rheumatic ailment known as ittai-ittai in just one catastrophic episode of cadmium poisoning in Japan (Akporido and Ipeaiyeda, 2014). Chronic exposure to heavy metal through consumption of food/ drinking contaminated water could cause different type of disease.

Chronic exposure to cadmium has been found to cause serious damage to kidney, liver, bone.

Many authors have enumerated the adverse effects of heavy metal on humans including, cadmium (Dabai *et al*.,2013; Muhammad *et al*., 2014),chromium (Muhammad *et al*., 2014), copper (Chinedu *et al*., 2011; Muhammad *et al*., 2014), iron, lead (Idris *et al*., 2013; Dabai *et al*., 2013; Nwaichi and James, 2012; Muhammad *et al*., 2014) Despite all the anthropogenic activities that are capable releasing heavy metals into Anya River and their associated adverse effects listed, little or no work has been carried out to investigate the concentration of heavy metals in the surface water body to the best of our knowledge. Thus, this work investigated heavy metal characteristics of Akor River in relation to seasonal variation.

Materials and Method

Description of Study Area

Anya River, Umudike is located between N5°28 642" and5° 29'692' N and 7° 32'109' and 7° 32'432''E (Onyenwe *et al*., 2018). Activities that could impact Anya River are cocoyam farming, wastewater discharging from Michael Okpara University of Agriculture, Umudike, washing of cars and motorcycles. For the purpose of this study, three stations were also selected based on accessibility and anthropogenic activities.

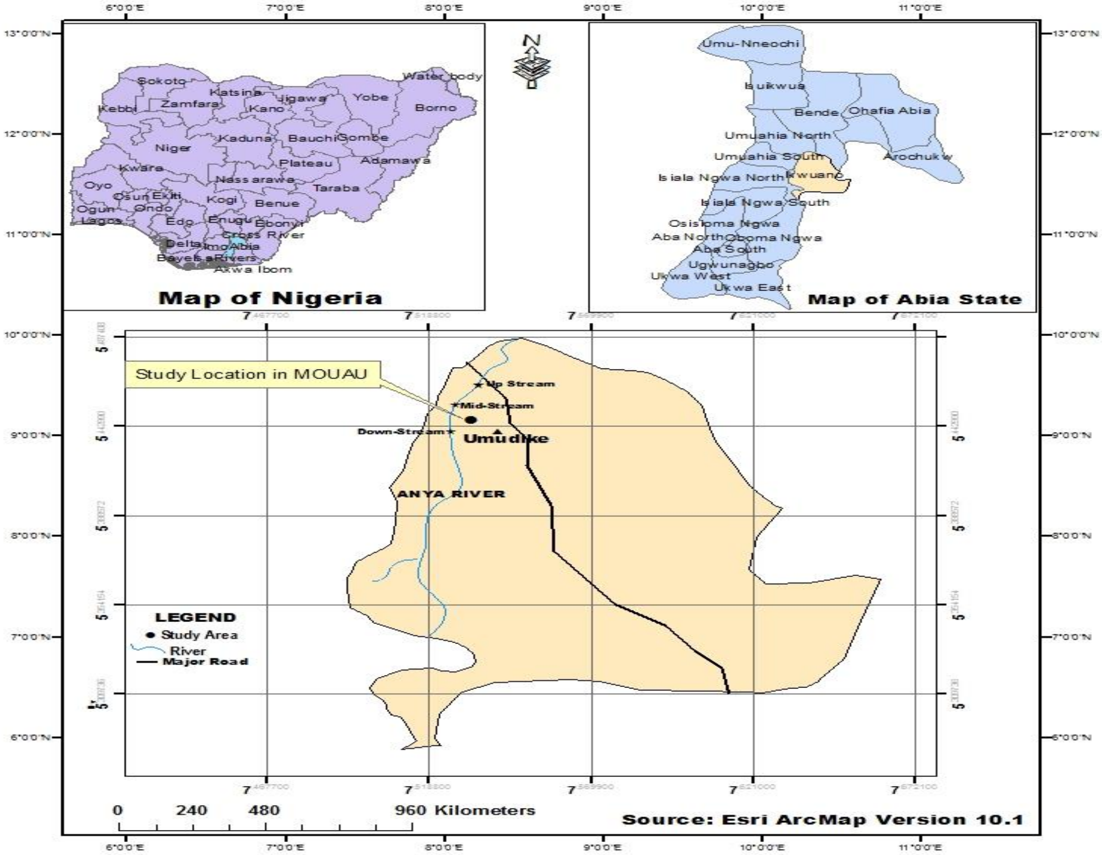

Fig. 1. Map of Abia state showing the study area and sampling locations

Station one (Upper stream): Station one is located at Abia State University (ABSU), Umudike Campus extension. The substratum is a mixture of sand and clay, leaves of trees and remains of dead macrophytes. Floating macrophytes present are *Pistia stratiotes*, *Nymphaea lotus* and *Eichhornia crassipes*. The vegetation here includes deciduous trees typified by oil Palm trees (*Elaeis guineensis*), Bamboo plants (*Bambusa vulgaris*), crop plants like plantain and banana (*Musa spp*), cassava (*Manihot esculenta*), maize (*Zea mays*), etc. The trees shade a large portion of the stream. Human activities carried out here include bathing, washing of clothes and vehicles and cultivation of crops etc.

Station two (Middle Stream): Station two is located mid-stream at NRCRI reservoir. The substratum is a mixture of sand and silts. The vegetation here includes deciduous trees such as Palm trees (*Elaeis guineensis*), crop plants like cassava (*Manihot esculenta*) and potato (*Ipomoea batatas*)etc. The trees present shade only some part of the water body. Human activities carried out here include washing of vehicles, watering of cattle and irrigation activities takes place during the dry season. Vegetation is subjected to chemical input from application of fertilizers, herbicides and pesticides.

Station three (Downstream): Station three is located in Michael Okpara University of Agriculture Umudike, along the road leading to Good luck hostels. Activities impacting the River are flash flood and wastewater from a greater part of University environment, occasional bathing and fishing

Water Samples Collection and Laboratory Analysis

Water samples were collected from Anya River monthly from February to September, 2019. One (1) litre water sampler was used to collect the water samples at three different location in replicate of three. The samples were collected transferred into a clean 250 ml plastic bottle and acidified with Nitric acid (HNO3) according to Sharma and Tyagi (2013). The water samples were digested using concentrated

Analar Nitric acid according to Zhang (2007). The UNICAM Solaar 969 atomic absorption spectrometer (AAS) which uses acetylene-air flame was used for the heavy metal determination.

Statistical Analysis

The data were subjected to get the mean, minimum, maximum and standard error of the mean using Microsoft Excel Descriptive Statistic package. One-way ANOVA was used to ascertain if there were significant differences in the heavy metal contents parameters among the stations.

Results and Discussion

Table 1: The summary of the heavy metals parameters measured in the Anya River

Parameter	Unit	Min.	Max.	Station 1	Station 2	Station 3	P-value	FM-Env. (2011)	SON (2015)
Iron (Fe)	mg/l	1.63	4. 16	2.30±0.18	2.72±0.27	3.0 5±0.32	P>0.05	20	0.30
Copper (Cu)	mg/l	0.11	2.25	0.85±0.19	0.99±0.22	1.13±0.24	P>0.05	0.05-1.5	1.00
Zinc (Zn)	Mg/l	1.01	3.70	1.96±0.32	2.22±0.39	2.60±0.36	P>0.05	0.5-15	3.00
Lead (Pb)	mg/l	0.20	1.85	0.82±0.13	0.91±0.19	1.00±0.20	P>0.05	0.01-1.0	0.01
Manganese (Mn)	mg/l	0.82	2.84	1.57±0.31	1.55±0.14	1.79±0.30	p>0.05	0.05-0.50	0.20
Chromium (Cr)	mg/l	0.21	1.97	0.94±0.22	1.03±0.13	1.07±0.20	p>0.05	0.05	0.05
Nickel (Ni)	mg/l	0.13	1.4	0.59±0.11	0.75±0.16	0.52±0.12	p>0.05	0.05	0.02
Cadmium (Cd)	mg/l	0.21	1.61	0.66±0.11	0.68±0.15	0.81±0.18	P>0.05	0.03	0.03

Iron (Fe): The spatial and temporal variation of iron (Fe) ranged between 1.63 and 4.16 mg/l (Table 1). The highest value was recorded in station 2(July) while the lowest was recorded in station 1(July) All the values of Fe recorded during this study period were far above permissible limit of 0.3 mg/l set as by SON (2015) and WHO (2017) for drinking water; thus extracting water from Anya River for community drinking may pose danger to the community. However, the values were lower than permissible level (20 mg/l) set by FMEnv. (2011) for environments. There was no significant difference (*P*> 0.05) in the Fe values across all stations.). The high values of Fe could be attributed to numerous anthropogenic activities along the rivers. Higher iron values could result to neurological effects (Zheng *et al*., 2003) and long-term iron toxicity may cause iron-mediated oxidative damage to the mitochondrial genome leading to progressive dysfunction (De Freitas and Meneghini, 2001). The iron values recorded in this study were within or little higher than results obtained by Anyanwu (2012) who recorded a range between 1.00 and 3.95 mg/L in Ogba River, Benin City, but Oluyemi *et al*. (2010) in other hand recorded higher Fe valuesthat this present study with mean value of 6.00 ± 0.21 31.75 ± 0.80 mg/L in

Olubo stream in Ife North Local Government Area of Osun State, both in Nigeria.

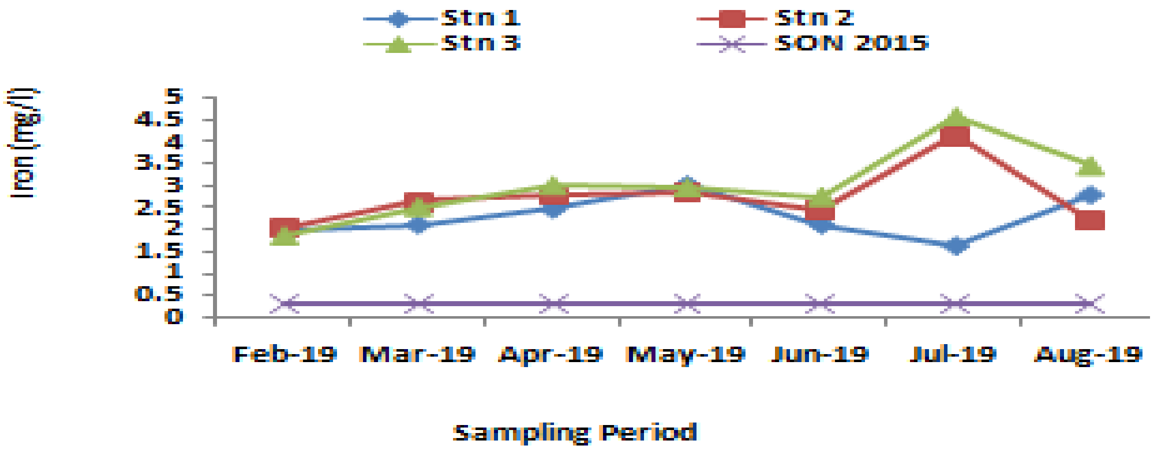

Figure 2: Spatial and temporal variations of Fe at the study stations of Anya River

Copper (Cu): The spatial and temporal variation of Cu ranged between 0.11 and 2.25 mg/l (table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 1(February). Almost all the values of Cu recorded during this study period were within the permissible limit of 1 mg/l set by SON (2015) and 0.5 – 1.5 mg/l set by FMEnv.(2011) for drinking water and environments, hence may not pose any danger to the community and environments. There was no significant difference ($P > 0.05$) in the Cu values across all stations. Copper toxicity enhances Zn deficiencies due to anxiety state through over-production of catecholamine. The present study recorded higher Cu values than the recent studies conducted in some surface water bodies in Nigeria. Aloke *et al*. (2019) and Nnabo (2015) who reported a range between 0.97 and 0.075 mg/L and 0.02 and 0.08 mg/L in Enyigba stream. Enitan *et al*. (2018) reported a range between 0.139 mg/L and 0.164 mg/L in Ndawuse River, Abuja, Uzairu *et al*. (2014) recorded a range between 0.01 and 0.51 mg/L in River Challawa, Kano and Anyanwu (2012) with values between 0.09 and 0.12 mg/L in Ogba River, all in Nigeria. However, the present findings were lower than results of Ekpete *et al.* (2019) with range between 2.17 and 3.69 mg/L in surficial water of Silver River, southern ijaw, Bayelsa State, Niger Delta, Nigeria. Although, raining season months had higher values than dry season months, and may be attributed to indiscriminate farming activities around the water courses. The trend observed in this present study was not in line with Uzairu *et al*. (2014) who observed higher Cu values during the dry season

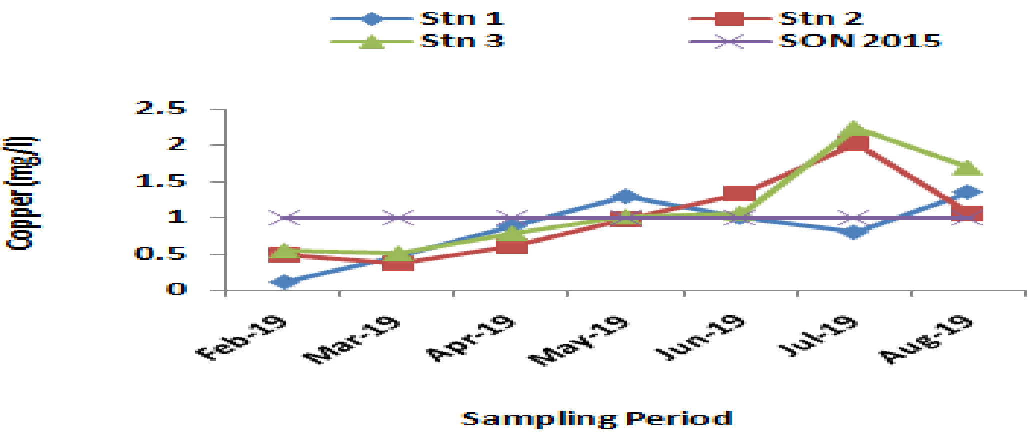

Figure 3:Spatial and temporal variations of Cu at the study stations of Anya River

Zinc (Zn): The spatial and temporal variation of Zn ranged between 1.01 to 3.70 mg/l (table 4.5). The highest value was recorded in station 3 (July) while the lowest was recorded in station 1 and (March). The values obtained during dry season months and August in all stations were within acceptable level (3.00 mg/l) of zinc (SON, 2015) whereas the concentration recorded in Rainy season months, May June and July are slightly higher than the permissible limit. The values obtained were below the standard level of 5 mg/l set by FMEnv. (2011) for environments. Extracting water from Anya River for drinking during the rainy season may lead to community health issue(s) but the level of Zn may not be an issue to the environment. There was no significant difference (*P*> 0.05) in the Zn values across all stations. In this study, the values of Zn were lower than results of Ekpete *et al*., (2019) who recorded a range between 5.17 and 8.23 mg/L in surface water of Silver River, southern ijaw, Bayelsa State, Niger Delta. In other hand, the values of Zn recorded in this study were higher than reports of most recent studies in Nigerian river. Aloke *et al*., (2019) reported a range between 1.555 mg/L and 2.015mg/L in Enyigba stream in Ebonyi state, Enitan *et al*. (2018) with concentration values between 0.165 and 0.262 mg/L in Ndawuse River, Abuja. However, the findings align with similar work by Olatunji and Osibanjo, (2012) who recorded a range between 1.65 and 3.36 mg/L in inland fresh water of lower River Niger drainage in North Central Nigeria. The observation in this present study contradicts most studies of river in other geo-polical zones in Nigeria with respect to seasonal variation. Olatunji and Osibanjo, (2012) in inland fresh water of lower River Niger drainage in North Central, Adesiyan *et al*. (2018 in River in Southwest and Uzairu *et al*. (2014) n Challawa River Kumbotso, Kano Northeast, all observed higher Zn concentrations during the dry season than rainy season unlike this present study which recorded higher concentrations during rainy season. High concentrations of Zn in during rainy (Planting) season could be due to run-off from agriculture activities where agro-chemicals are applied for pests, herbs and disease control.

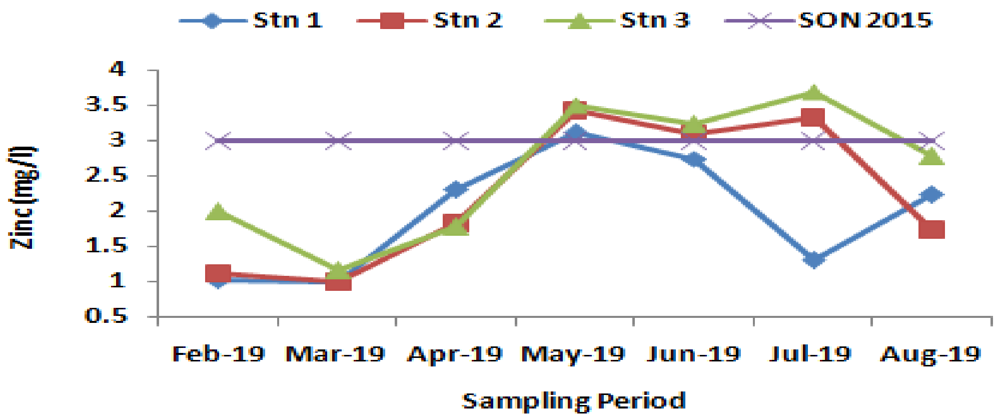

Figure 4:Spatial and temporal variations of Znat the study stations of Anya River

Lead (Pb): The spatial and temporal variation of Pb ranged between 0.20 and 1.85 mg/l (table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 2 (February). All the values of Pb recorded during this study period were far higher than the permissible limit of 0.01 mg/l set by SON (2015) for drinking water but within the permissible limit between 0.1-1.0 mg/l set by FMEnv. (2011) for healthy environments. The level of Pb in Anya River may lead to the community/public health issues if the community continued to extract the water from the River for drinking. There was no significant difference (*P*> 0.05) in the Pb values across all stations. In this study, the surface water contained high Pb especially during rainy season. The level of values obtained during this study period were lower than the range recorded by Ekpete *et al*. (2019) who obtained values between 1.742 and 3.812 mg/L in surficial water of Silver river, southern ijaw, Bayelsa State, Niger Delta Southeast and Uzairu *et al*. (2014) obtained a range between 1.25 and 9.05 mg/L in river Challawa in Kumbotso, Kano North East. But the values of Pb obtained in this present study were higher than the results recorded in Nigerian river, Aloke et *al*., (2019) recorded a range between 0.272 and 0.571 mg/L in Enyigba, southeast, Enitan *et al*. (2018) who reported a range between 0.133mg/L and 0.303 mg/L in Ndawuse River, Abuja North centeral, Adesiyan *et al*.(2018) reported values between 0.002 and 0.28 mg/L in in River in Southwest, Nnabo (2015) observed a range between 0.10 and 0.70 mg/L in river and streams in Ebonyi, Southeast. Olatunji and Osibanjo (2012) obtained values between 0.01 and 0.16 mg/L in inland fresh water of lower river Niger drainage in North Central and Anyanwu (2012) recorded concentration of Pb between 0.012 and 0.20 mg/L in Ogba River, Benin City Southeast, all in Nigeria. Both higher concentration and seasonality variation in this study could be attributed anthropogenic and climatic variables influences. Higher concentrations of Pb recorded during rainy season are not in line with some of observation by most researchers, who obtained higher concentration during dry season (Olatunji and Osibanjo, 2012; Uzairu *et al.* 2014; Adesiyan et *al*. 2018).

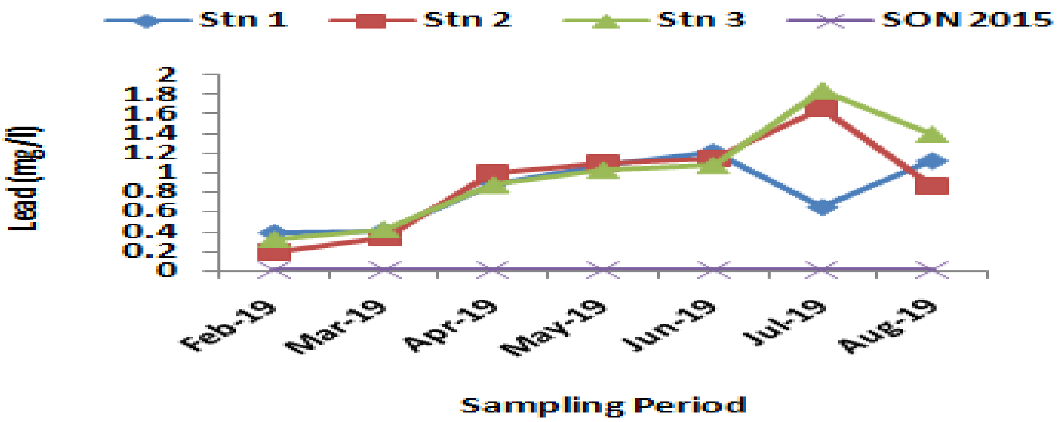

Figure 5:Spatial and temporal variations of Pbat the study stations of Anya River

Manganese (Mn): The spatial and temporal variation of Mn ranged between 0.82 and 2.84 mg/l (table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 3 (February). All the values of Mn recorded during this study period were far above the permissible limit of 0. 02 mg/l set by SON (2015) (fig.5) for drinking water and standard of 0.05 - 0.5 mg/l set by FMEnv., 2011) for healthy environments. Extraction of water from Anya River for drinking may cause diseases to the communities. There was no significant difference (*P*> 0.05) in the Mn values across all stations. The values of Mn observed during this study period were within the range of values observed in Enitan *et al*. (2018) who reported a range between 0.215 and 1.478 mg/L in Ndawuse River, Abuja, Ekpete *et al.* (2019) who reported a range between 0.34 and 2.89 mg/L in surface water of Silver river, southern ijaw, Bayelsa State, Niger Delta. The values recorded in this study were quite higher than results of Nnabo (2015) who recorded a range between 0.02 and 0.42 mg/L and Anyanwu (2012) who reported values between 0.22 and 0.53 mg/L in Enyigba stream and Ogba river respectively, all in Nigeria. However, the Mn values recorded during the study period were lower than Olatunji and Osibanjo (2012) who obtained values with a range between 1.74 and 8.37 mg/L in inland fresh water of lower River Niger drainage in North Central Nigeria.

The results obtained in this study may pose a serious public threat of Mn poison for the communities who extract their drinking water from the river, if not treated before consumption. Seasonal variation obtained in this study may be attributed to run-off that emptied the fertilizer and other agro chemicals into the rivers during the rainy season and the results disagreed with Adesiyan *et al*. (2018) who reported lower Mn values in rainy season in rivers in Southwest, Nigeria.

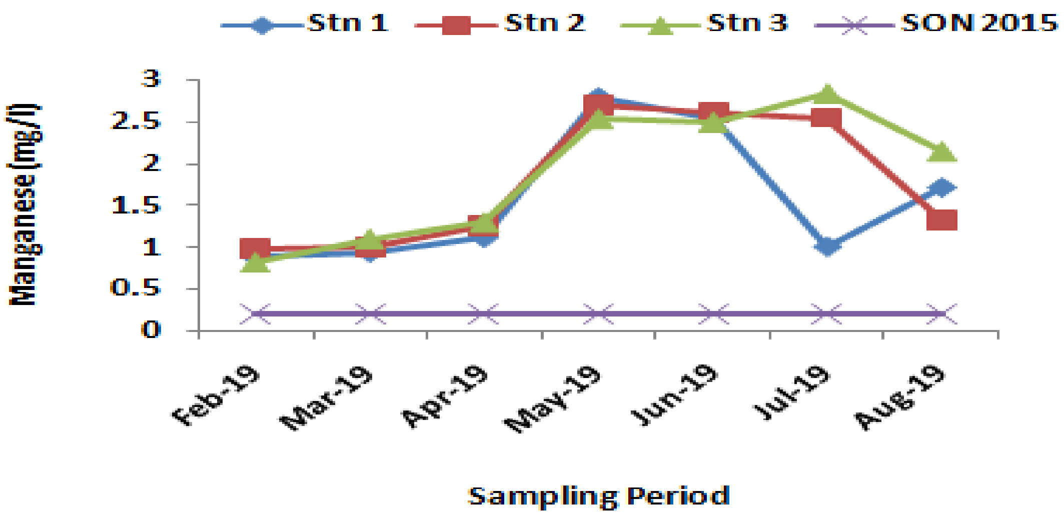

Figure 6:Spatial and temporal variations of Mnat the study stations of Anya River

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Chromium (Cr): The spatial and temporal variation of Cr ranged between 0.21 and 1.97 mg/l (Table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 2 (February). All the values of Cr recorded during this study period were within the permissible limit of 0.05 mg/l set by SON (2015) for drinking water and standard of 0.5 mg/l set by FMEnv., 2011) for healthy environments (fig.6). There was no significant difference (*P*> 0.05) in the Cr values across all stations. Chromium (Cr) concentrations in this study were lower than results obtained by Ekpete *et al*. (2019) who reported Cr concentrations between 1.694 and 3.725 mg/L, and within or lower than results recorded by Uzairu *et al*. (2014) who reported a range between 0.00 and 12.51 mg/L in river Challawa, Kano and Olatunji and Osibanjo (2012) who recorded 0.53 and 4.09 mg/L in inland fresh water of lower river Niger drainage in North Central. However, chromium (Cr) concentrations observed during the sampling period were higher than some of recent study on inland waters in Nigeria. Enitan *et al*. (2018) obtained values between 0.078 and 0.140 mg/L in Ndawuse river, Abuja; Adesiyan *et al*. (2018) reported values between 0.005 and 0. 22 mg/L in four rivers in Southwest, Amadi (2012) also recorded lower range between 0.001 and 0.078 mg/L in Aba river, all in Nigeria and allowable concentration (0.05 mg/L) pegged by SON (2015) for portable water. High concentrations of chromium in this River could pose a public health issues such as liver and kidney disease. High Cr concentration causes liver and kidney toxicity and genotoxic carcinogen (Strachan, 2010). In the rivers, concentrations of Cr were higher during the rainy season than the dry season and the results agreed with some studies of Nigerian rivers, (Adesiyan et *al*. 2018; Uzairu *et al.* 2014; Olatunji and Osibanjo, 2012) who reported lower concentration during the rainy season. The higher concentration during rainy season may be attributed to indiscriminate farming activities and other anthropogenic including run-off influence within and along the river banks.

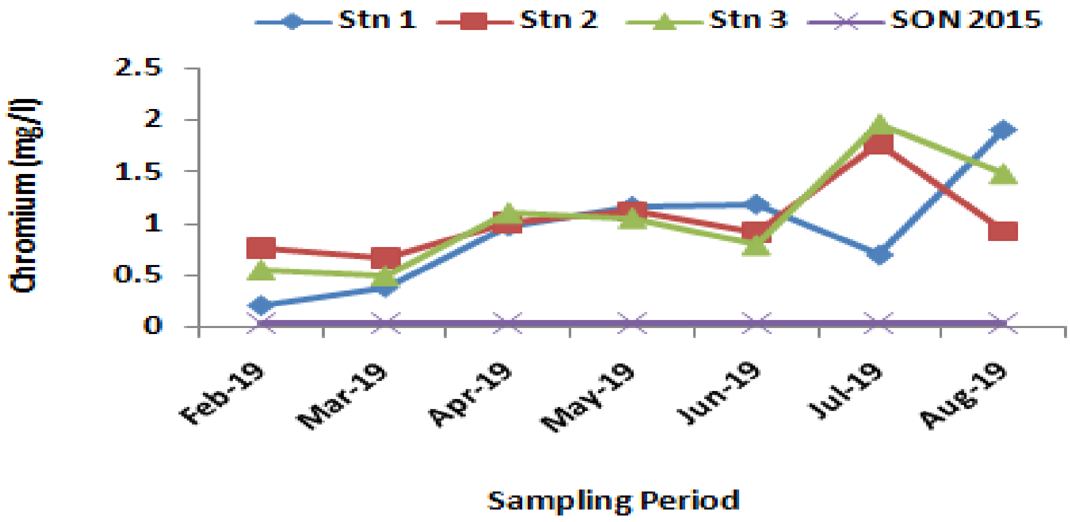

Figure 7:Spatial and temporal variations of Crat the study stations of Anya River

Nickel (Ni): The spatial and temporal variation of Ni ranged between 0.13 and 1.40 mg/l (Table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 1 (February). All the values of Ni recorded during this study period were quite higher than the permissible limit of 0.02 mg/l set by SON (2015) for drinking water and within standard of 0.5 mg/l set by FMEnv., 2011) for healthy environments except at peak of rainy season (Fig.7). Thus extraction of water from Anya River for drinking may cause nickel-related diseases to the community. There were no significant differences (*P*> 0.05) in the Ni values across all stations. The nickel values recorded in this study were quite above the results obtained by Amadi (2012) who obtained Ni concentration between 0.004 – 0.211 mg/L in Aba River, Nigeria. However, the results of Ni were within or slight lower than the concentrations range observed by Olatunji and Osibanjo (2012) who reported values between 0.59 and 1.12 mg/L in inland fresh water of lower river Niger drainage in North Central Nigeria. Nnabo (2015) also reported values between 0.42 and 1.58 mg/L in Enyigba Eboyi, South Eastern Nigeria. The concentrations of Ni were higher during the rainy season months than dry season months and could be attributed to seasonal and anthropogenic influences such flood, rain, and farming activities.

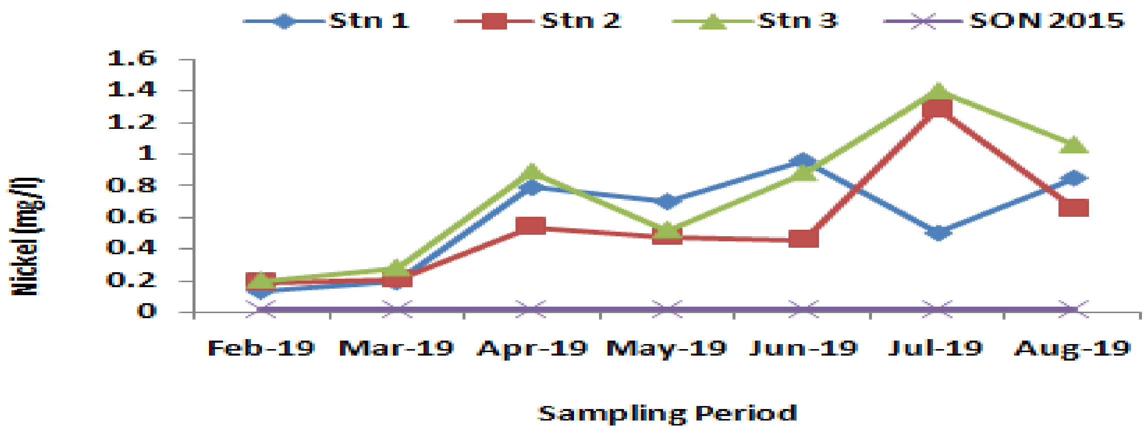

Figure 8:Spatial and temporal variations of Ni at the study stations of Anya River

Cadmium (Cd): The spatial and temporal variation of Cd ranged between 0.21 and 1.61 mg/l (Table 1). The highest value was recorded in station 3 (July) while the lowest was recorded in station 2 (February). All the values of Cd recorded during this study period were quite above the permissible limit of 0.03 mg/l set by SON (2015) for drinking water and standard of 0.03 mg/l set by FMEnv., (2011) for healthy environments. There was no significant difference (*P*> 0.05) in the Cd values across all stations.

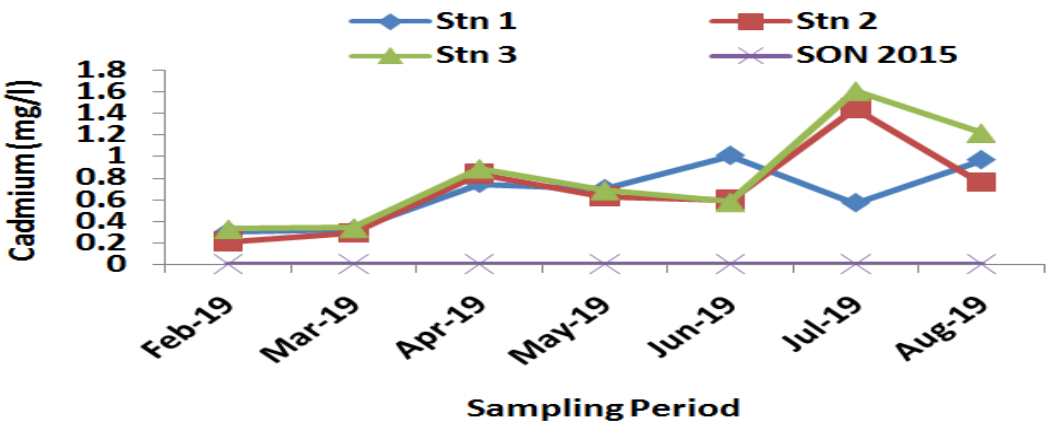

Figure 9: Spatial and temporal variations of Cd at the study stations of Anya River

The values of Cd obtained in this present study were higher than the Cd concentration of some recent studies. Aloke *et al*.(2019) obtained values between 0.002 and 0.94mg/L in Enyigba streams, Southeast, Enitan *et al*. (2018) reported a range between 0.012 and 0.021 mg/L in Ndawuse River, Abuja, Uzairu *et al*.(2014) obtained a range between 0.00 and 0.71mg/L in River Challawa in Kumbotso, Kano, Olatunji and Osibanjo (2012) recorded a range between 0.02and 0.13mg/L in inland fresh water of lower River Niger drainage in North Central, but the present Cd values were lower than the results of Nnabo.(2015) who reported Cd concentration range between 3.2and 13.5mg/L in Enyigba streams, Southeast. However, the concentrations of Cd during this study period were within the range of Cd concentration obtained by Ekpete *et al*. (2019) who reported range between 0.714and 2.414mg/L in surficial water of Silver River, southern Ijaw, Bayelsa State, Niger Delta. High values were recorded in rainy season months and this may be attributed to nature of the geological formation of the soil and run-off from agriculture activities where agro-chemical and fertilizers containing Cd as impurity may have been used to control diseases and improve crop production. Field observations have revealed that superphosphate and urea fertilizers are among agro-chemicals used by local farmers around the river which contain some levels of Cd. The level of Cd in this study may lead to public health problem. The levels of Cd recorded in this present studyare callsfor concern, as the use of the Anya water with this level of cadmium could have adverse effects on human health such as renal diseases, cancer and bone pain (Itaiitai disease)(Adesiyan *et al*.2018). Continually drinking water from theriver could result to gene mutation and teratogenic effects.

Generally, Anya River under investigated has high concentrations of heavy metals which are above permissible level for portable water; thus making the water from the River unfit for human consumption. Below are the orders of *decrease* of heavy metals in the River; Fe>Zn>Mn>Cr>Cu >Pb> Cd>Ni. The order of heavy metal agreed with Anyanwu and Umeham (2020) who claims that Fe is usually more abundant in freshwater environment than other metals in Nigeria. Similarly, the order of heavy metals in this present study was in line with Enitan *et al*. (2018) who recorded Fe as the most abundance heavy metal in Ndawuse river, Abuja Nigeria. The abundance of Fe in the river may be attributed to its high occurrence on Earth (Adefemi *et al*., 2004; Aiyesanmi, 2006; Kumar *et al*., 2010).

Conclusion

Activities aimed at sustaining human population such as intensive farming and industrialization, activities, and waste discharge into surface water bodies have been a threat to heavy metal of water bodies and surface water body in South-eastern Nigeria is not left out. In this study heavy metal characteristics were investigated. The study revealed that human (anthropogenic) activities within and around the River have negatively impacted on the heavy metal characteristics of the River and all the heavy metals investigated exceeded the permissible limit for drinking water and healthy environments; thus making the River threats to community and human health . Hence, it is strongly recommend that holistic investigation involving health risk assessment, bio-accumulation, magnification, DNA disruption of heavy metals in organisms living in this River should be carried out. The activities within and around the river should be monitored and regulated by local community leaders and Ikwuano local Government health and utility officers. A mini heavy metal treatment plants/machine could be installed in each community that extracts drinking water from Anya River.

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