

Levels of Heavy Metals in *L. falcipinnis* from Woji-Elelenwo Creek, River State, Nigeria, and Health Implications.

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Abstract

This research is aimed at assessing the levels and the health implications of heavy metals in *L. falcipinnis* from Woji- Elelenwo Creek, Rivers State, Nigeria in relation to seasonal variations. The health implications were expressed in Estimated Daily Intake (EDI), Hazard Quotient (HQ), Total Hazard Index (THI). The bioaccumulation factor of heavy metals in fish was calculated using standard methods. Correlation of concentration of heavy metals in fish versus concentration of heavy metals in water was plotted. The fish and water samples were collected simultaneously from four sampling stations along the study area for a period of one year in tandem with recommended methods and transported to the laboratory for analysis. Atomic Absorption Spectrophotometer (AAS) (model AANALYST 400 Perkin Elmer) was used for metal analysis. SPSS version 23 was used for data analysis at $p > 0.05$. Result showed heavy metals concentrations in water were within recommended limit by FMEnv except Cd that had a higher concentration of 0.034mg/l against 0.001mg/l by FAO/WHO (2005). Heavy metal concentration in biota was in descending order of Fe = Zn > Mn > Ni > Cr = Cd; (0.06 > 0.04 > 0.0347 > 0.03 > 0.02). Mn, Fe and Cd had no significant difference in mean concentration across the stations at $p > 0.05$. Zn in water showed a significant correlation with Zn in fish. Mn in water showed a significant correlation with Mn in fish. Mn in water showed a significant correlation with Cr in fish. Pb, Mn, Ni and Fe had BAF < 1. The EDI and THI for metals were less than 1, indicating less health risk for food consumption of biota from sampled area. However, consistent and persistent consumption of biota from studied area may lead to bio-magnification across the food chain and in turn pose health risk to higher organisms. Therefore, it is imperative that periodic monitoring of aquatic ecosystem should be practiced and anthropogenic activities in the studied area minimized.

Keywords: Heavy metals, Water, *L. falcipinnis*

1. Introduction

Water is one of the most important natural resources, and there are many different demands for it. Skillful management of water bodies is required if they are to be used for such diverse purposes as domestic, industrial supply, crop, irrigation, transport, recreation, sport, commercial fisheries, power generation and waste disposal.

Water and its management will continue to be a major issue as the world is ushered into the era of modern civilization, which will definitely have profound impact on our lives and that of our

planet Earth than ever before (WHO, 2013). Unequivocally, water is essential for the development and the maintenance of the dynamics of every ramification of society (UNESCO, 2003).

The pollution of water is of grave consequence because both terrestrial and aquatic life may be poisoned. The presence of some hazardous substances may cause diseases, which may add dour, change the water quality and significantly hinder economic activities (Asonye *et al.*, 2007).

Heavy metals are pollutants of particular interest in this study because they are amongst the most toxic substances. Heavy metal toxicity dates back to the ancient periods, the lead toxicity that resulted in mental retardation for the rulers and the decline of the Roman Empire (Asonye *et al.*, 2007).

Heavy metals behavior in the aquatic environment (streams, lakes and rivers) is surprisingly similar to that outside a water body. Streamed sediments exhibit the same binding characteristics found in the normal soil environment. As a result of this, many heavy metals tend to be impounded at the bottom of water bodies. Some of these metals will dissolve. The aquatic environment is more vulnerable to the effects of heavy metal pollution which is harmful because aquatic organisms are in close and prolonged contact with the soluble metals (Meybeck and Helmer, 1996).

2. Methodology

Study Area

The study area (sampling stations) were mapped out with GPS and the coordinates are recorded as follows; Station 1 (**Elelenwo Abattoir Waterfront**) latitude 4°51'2.94" and longitude 7° 3'35.84", station 2 (**Oil Servicing Company Waterfront**) latitude 4°50'2.16" and longitude 7° 3'40.55", station 3 (**ABEC International Secondary School Waterfront**) latitude 4°49'28.17" and longitude 7° 4'9.43", station 4 (**Elelenwo by Akpajo Waterfront**) latitude 4°48'12.53" and longitude 7° 4'10.84".

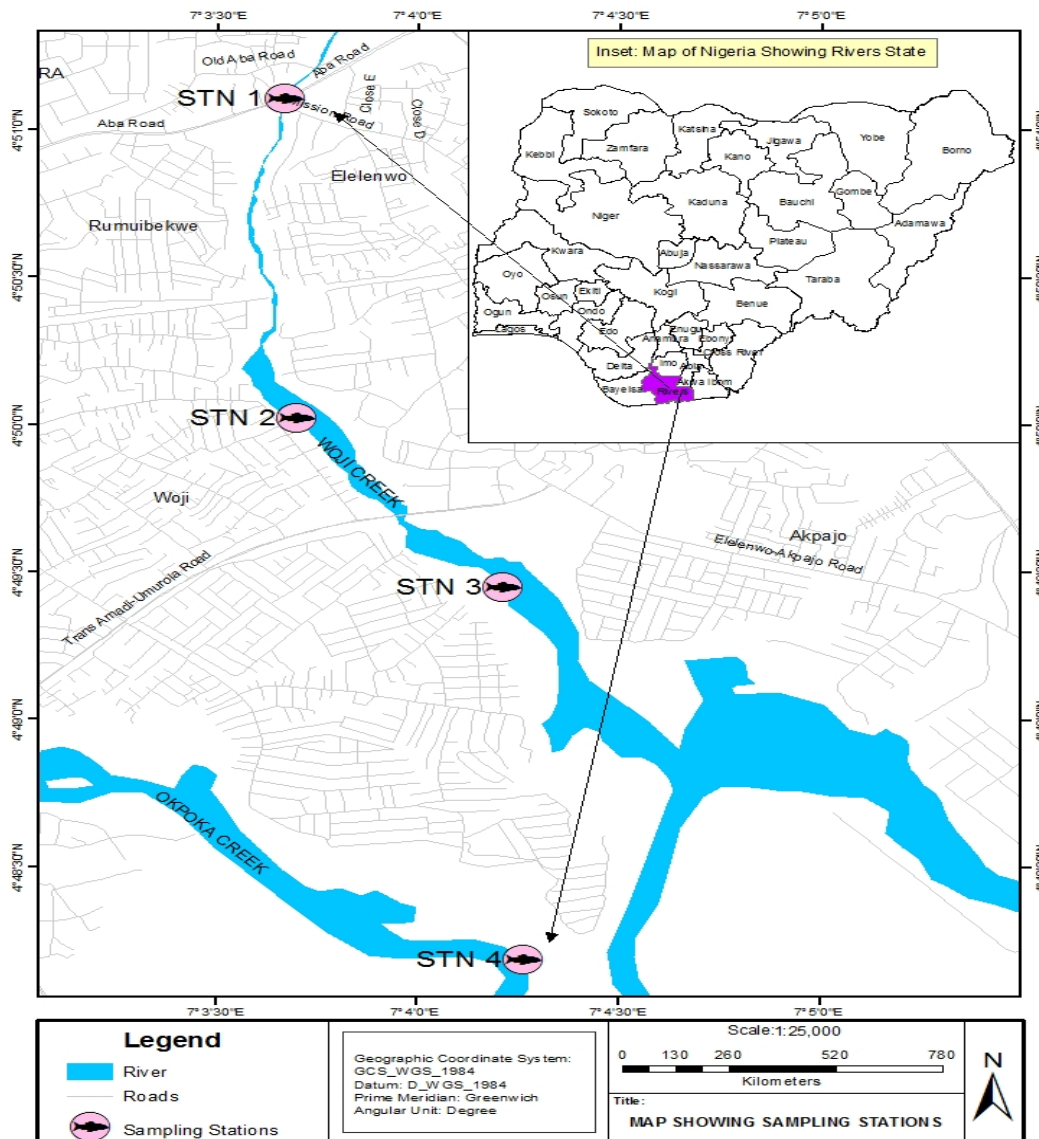


Figure 1; Map of study area

The study area is characterized by diverse industrial activities such as oil services company, abattoir, a “computer village” where electronics are sold and repaired, there is a domestic waste dump site at the bank of the Creek.

Samples collection and Laboratory Analysis

Fish samples were obtained from the sampling stations bimonthly by local fishermen using cast net during the sampling period of 12 months covering wet and dry season. The fish was

identified, washed with river water, and kept in a labeled container in an iced chest cooler and transported to laboratory for analysis.

Water samples for heavy metals analysis were collected with pre-rinsed one-liter plastic containers and acidified with 2ml of concentrated nitric acid (HNO₃) in order to stabilize the oxidation state of the metals.

Samples were transported to the laboratory for analysis. Metals concentrations were determined using Atomic Absorption Spectrophotometer (model AANALYST 400 Perkin Elmer).

Statistical Analysis

SPSS version 23 was used for the analysis and Tukey HSD was used for the mean separation. JMP version 10 was used for the correlation matrix.

Biota Accumulation Factor (BAF)

It is the transferred factor determined by quotient of heavy metal concentration in the biota to that in the water (*Hassan et al.*, 1991 in Javeed and Nazura, 2014).

Biological Accumulation Factor (BAF) was calculated for *L. falcipinnis* across the four sampled stations as reported by Li *et al.*, (2007)

$$\text{BAF} = \frac{\text{concentration of metal in organ}}{\text{concentration of metal in water}} \dots\dots\dots(1)$$

Estimated Daily Intake (EDI)

EDI was calculated using the generic equation proposed (USEPA, 1993) was used:

$$\text{“EDI} = E_F \times E_D \times F_{IR} \times 10^{-3} \times C_F \times C_M / W_{AB} \times T_A \text{”} \dots\dots\dots(2)$$

Where,

EDI = Estimated Daily Intake

E_F = Exposure frequency (365 days/year or days of exposure / week per 52 weeks / year)

E_D = Exposure duration (average life expectancy of 51 years by World Bank, 2017)

F_{IR} = Fish ingestion rate (person/day) was considered 40g/day (and converted to be 0.04mg/day for a healthy adult in Niger Delta Region of Nigeria (Maximilian *et al.*, 2015).

C_F = Conversion factor from dry fish weight to fresh fish weight (1-moisture content) (Rattan *et al.*, 2005; USDA, 2007)

C_M = Heavy metal concentration in biota studied. (mg/kg)

W_{AB} = Average body weight (70kg) (IRIS, 2013).

T_A = Average Exposure time for non-carcinogens (EF X ED) (Wang *et al.*, 2012; World Bank, 2017).

Hazard Quotient (HQ)

Potential risk assessment of the toxicant was interpreted based on the values of Hazard Quotient (HQ) being the exposure dose divided by the Reference dose.

Where;

$$HQ = EDI / R_{fdo} \dots\dots\dots(3)$$

EDI = Estimated Daily Intake

R_{fdo} = Reference dose (Pb = 004, Mn = , Cr = , Ni = , Fe = 0.7 , Zn = and Cd = 0-001) (IRIS 2013; USEPA, 2018).

Hazard Index (HI)

To assess the overall potential health risk posed by more than one metal, THQ of every heavy metal is summed up and known as hazard index (HI). The HI was calculated by the sum of the target hazard quotients of each heavy metal (USEPA 2011).

$$HI = HQ_{Mn} + HQ_{Fe} + HQ_{Cd} + HQ_{Ni} + HQ_{Cu} + THQ_{Zn} \dots\dots\dots(4)$$

Where;

THI = Total Hazard Index. HQ_{Pb} = Hazard Quotient of Lead. HQ_{Mn} = Hazard Quotient of Manganese. HQ_{Cr} = Hazard Quotient of Chromium. HQ_{Ni} = Hazard Quotient of Nickel. HQ_{Fe} = Hazard Quotient of Iron. HQ_{Zn} = Hazard Quotient of Zinc. HQ_{Cd} = Hazard Quotient of Cadmium. Any THI above 1.0 is indicative of potential health risk.

3. Results

Fig 1-7 showed that showed seasonal variation of heavy metals concentration in water by stations. Pb and Mn had highest concentration in wet season station 1 followed by 2, 3 and 4. Ni had highest concentration in wet season in station 2 followed by station 1, 3,4 and 2 Cr had the highest concentration in station 2, followed station 1, 3 and 4. Zn had the highest concentration in dry season in station 4, followed station 2, 3 and 1. Cd had the highest concentration in wet season in station 2.

Table 2, 3 and 4 showed a metal concentration in L. fa was in descending order of Fe = Zn > Mn > Ni > Cr = Cd; (0.06 > 0.04 > 0.0347 > 0.03 > 0.02). Mn, Fe and Cd had no significant difference in mean concentration across the stations at p > 0.05.

Table 4.1 Mean and Standard Deviation Concentration of Metals in water

Parameter (mg/l)	Mean	Standard Deviation	Range	Standard Limit	Reference
Pb	0.014	0.00079	0.005-0.042	0.04	DPR, 2018 FMEnv.,2001

Mn	0.033	0.0045	0.020-0.053	0.4	DPR, 2002 FEPA,2003
Cr	0.023	0.0021	0.011-0.039		DPR, 2018, FMEnv., 2001
Ni	0.23	0.0230	0.1-0.42	0.07	USEPA, 2018 FAO/WHO, 2007
Fe	0.057	0.0067	0.02-0.091	0.7	DPR, 2018 FMEnv., 2001
Zn	0.070	0.0062	0.01-0.117	3 – 5	FAO/WHO, 2008
Cd	0.034	0.0043	0.02-0.064	0.001	FAO/WHO, 2008

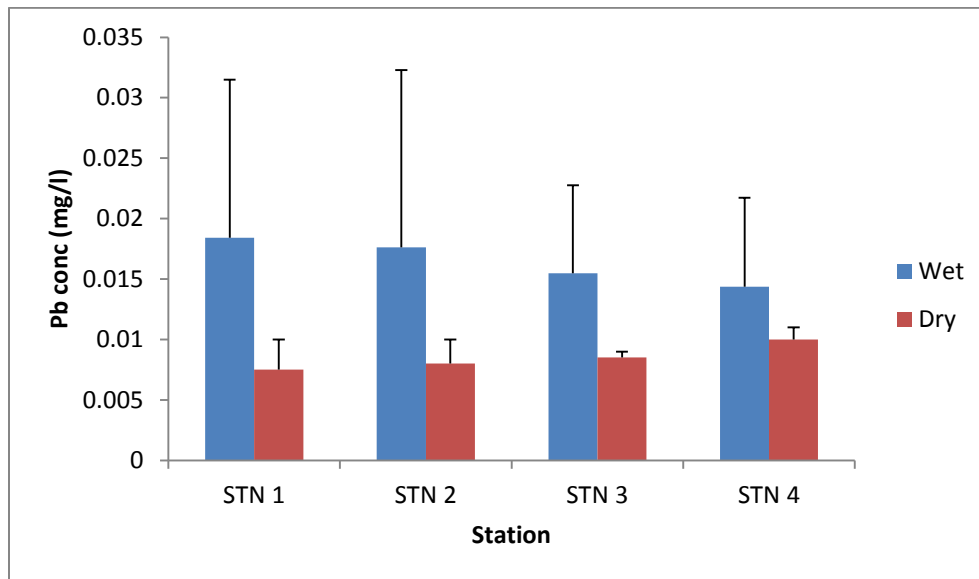


Fig 1. Spatial and Seasonal Variations (Mean ± SE) of Pb in water

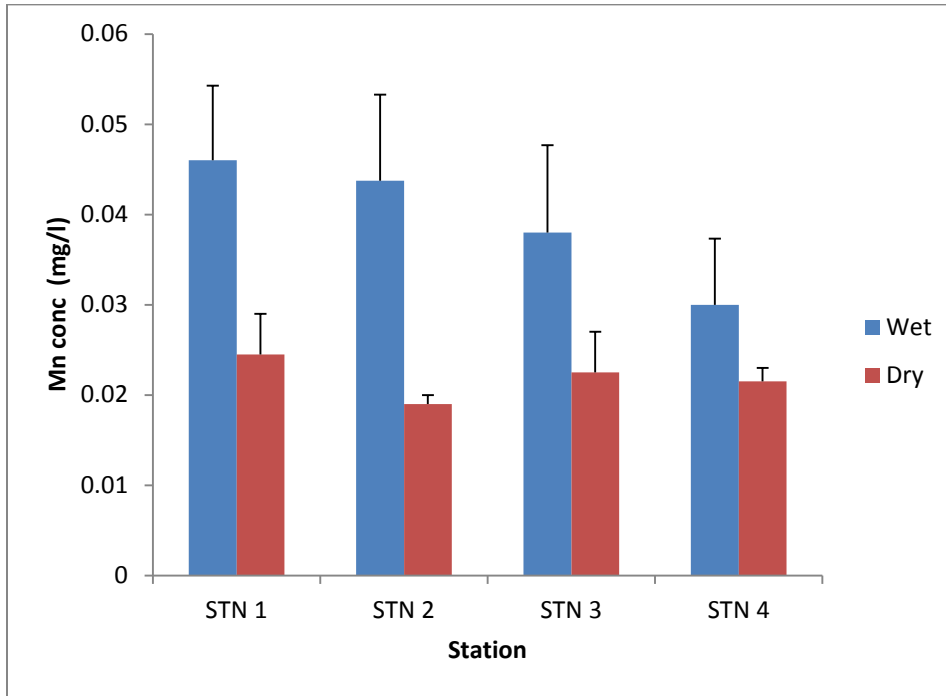


Fig 2. Spatial and Seasonal Variations (Mean ± SE) of Mn in water

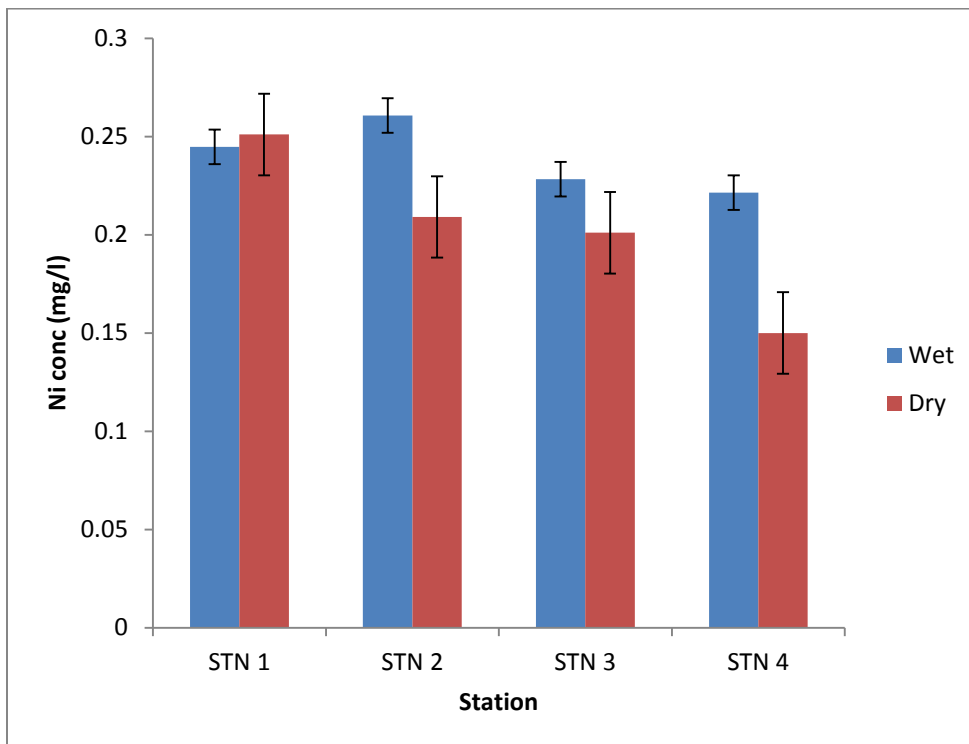


Fig 3. Spatial and Seasonal Variations (Mean ± SE) of Ni in water

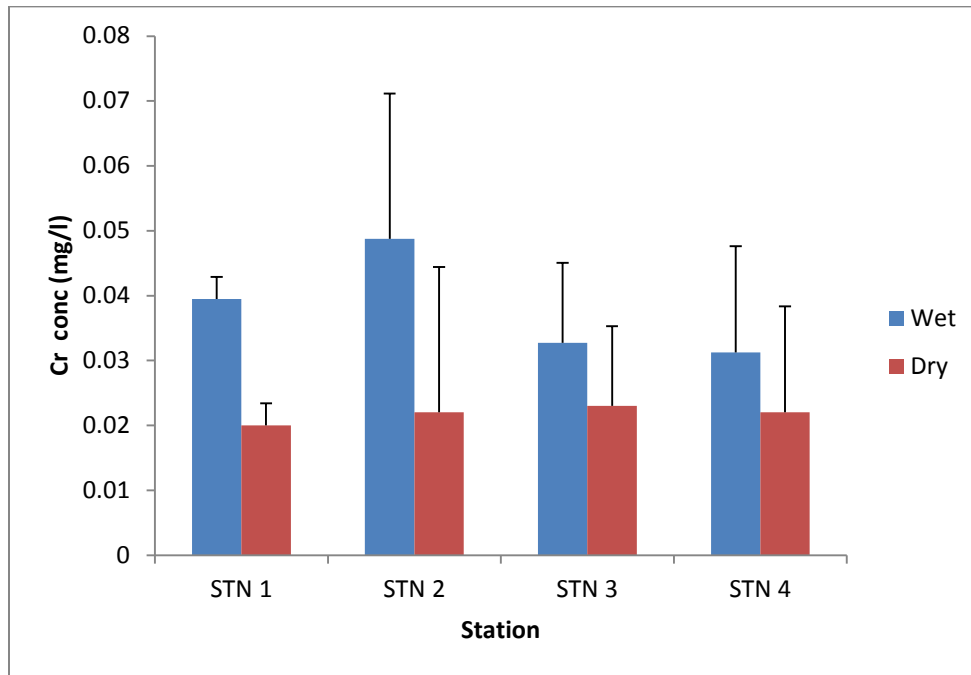


Fig 4. Spatial and Seasonal Variations (Mean \pm SE) of Cr in water

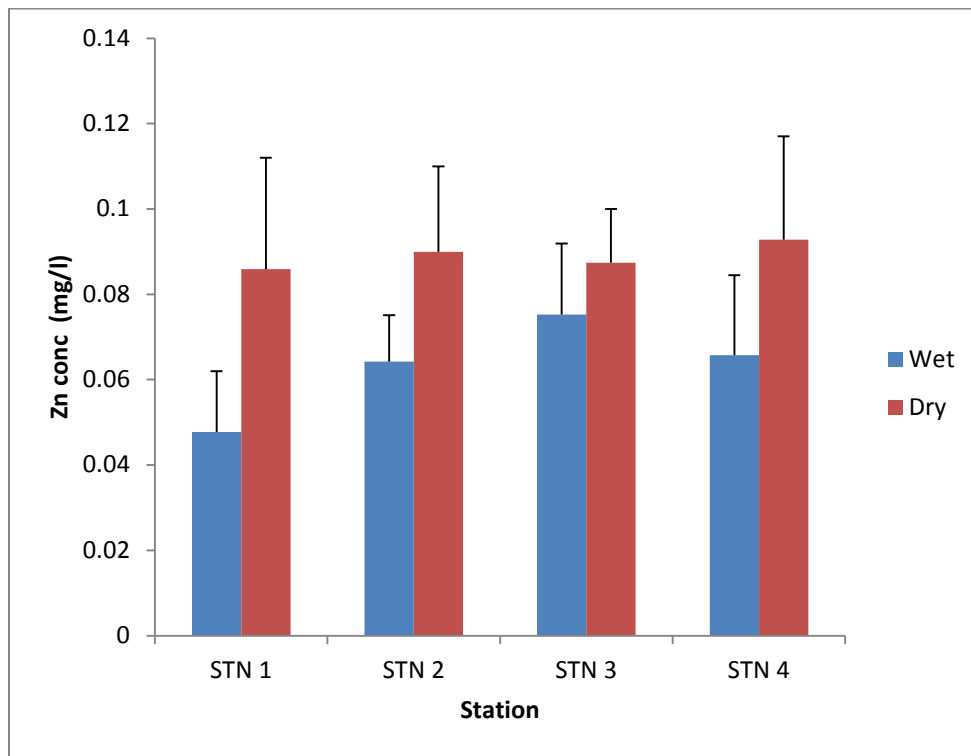


Fig 5. Spatial and Seasonal Variations (Mean \pm SE) of Zn in water

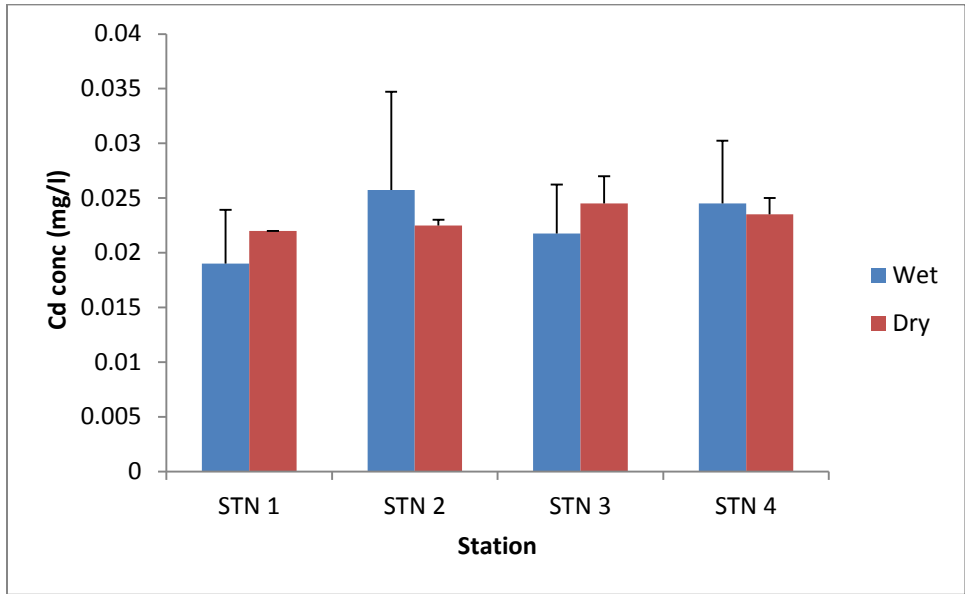


Fig 6. Spatial and Seasonal Variations (Mean \pm SE) of Cd in water

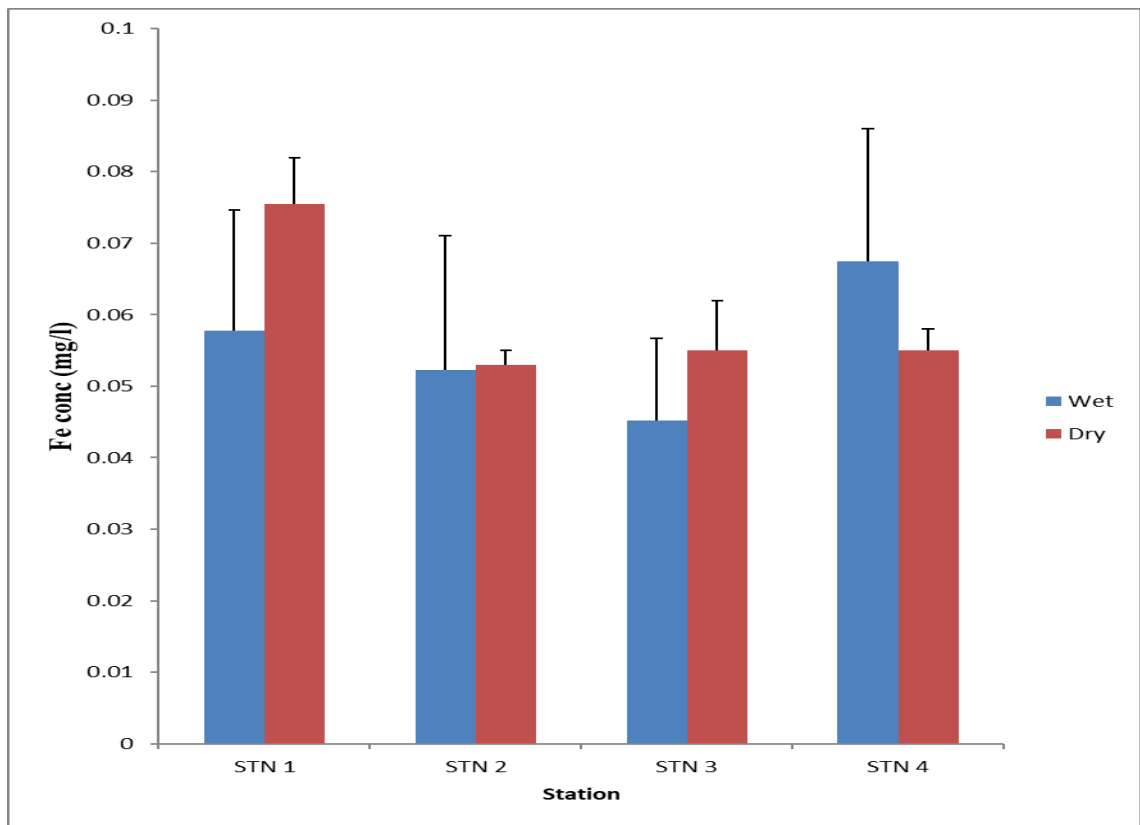


Fig 7. Spatial and Seasonal Variations (Mean \pm SE) of Fe in water

Table 2 Mean and Standard Deviation Concentration of Heavy Metals in fish

Pb	M	Cr	Ni	Fe	Zn	C
n						d
0.03±0.02	0.04±0.01	0.02±0.02	0.34±0.05	0.06±0.02	0.06±0.03	0.02±0.01

Table 3. Mean and Standard Deviation Concentration of Metals in fish by Months

Parameter (mg/kg)	April 2018	June 2018	August 2018	October 2018	December 2018	February 2019
Pb	0.0363±0.0028 ^b	0.0548±0.0038 ^a	0.0128±0.0035 ^c	0.0120±0.0020 ^c	0.0210±0.0135 ^{bc}	0.0183±0.0133 ^{bc}
Mn	0.0333±0.0108 ^a	0.0350±0.0064 ^a	0.046±0.0094 ^a	0.0315±0.0071 ^a	0.0335±0.0051 ^a	0.0325±0.0110 ^a
Cr	0.0095±0.0031 ^b	0.0085±0.0002 ^b	0.0523±0.0043 ^a	0.0198±0.0276 ^{ab}	0.0135±0.0034 ^{ab}	0.0168±0.0069 ^{ab}
Ni	0.3953±0.0128 ^a	0.3603±0.0417 ^{ab}	0.3603±0.0417 ^{ab}	0.3180±0.0308 ^{ab}	0.2973±0.0648 ^b	0.3325±0.0419 ^{ab}
Fe	0.0443±0.0020 ^a	0.0530±0.0131 ^a	0.0738±0.0316 ^a	0.0518±0.0202 ^a	0.0605±0.0205 ^a	0.0588±0.0131 ^a
Zn	0.0320±0.0109 ^b	0.0370±0.0155 ^b	0.0633±0.0172 ^{ab}	0.0490±0.0132 ^b	0.0953±0.0041 ^a	0.0920±0.0022 ^a
Cd	0.0240±0.0016 ^a	0.0133±0.0002 ^a	0.0228±0.0340	0.0205±0.02 ^a	0.0198±0.0033 ^a	0.0258±0.0033 ^a

Alphabets of different letters within a row showed significant difference

Table 4. Mean and Standard Deviation Concentration of Metals in fish by Stations

Parameter (mg/kg)	Station 1	Station 2	Station 3	Station 4
Pb	0.0355±0.0163 ^a	0.0237±0.0170 ^a	0.0222±0.0184 ^a	0.0220±0.0173 ^a
Mn	0.0388±0.0063 ^a	0.0390±0.0048 ^a	0.0363±0.0060 ^a	0.0270±0.0065 ^a
Cr	0.0230±0.0030 ^a	0.0315±0.0029 ^a	0.0190±0.0211 ^a	0.0070±0.0024 ^a
Ni	0.3777±0.0193 ^a	0.3658±0.0398 ^a	0.3333±0.0422 ^{ab}	0.2988±0.0547 ^b
Fe	0.0767±0.0067 ^a	0.0620±0.0190 ^a	0.0553±0.0195 ^{ab}	0.0340±0.0066 ^b
Zn	0.0617±0.0285 ^a	0.0713±0.0332 ^a	0.0608±0.0294 ^a	0.00518±0.0270 ^a
Cd	0.0273±0.0053 ^a	0.0228±0.0094 ^{ab}	0.0180±0.0100 ^a	0.0158±0.0070 ^b

Alphabets of different letters within a row showed significant difference

Table 5 showed correlation matrix between metals concentrations in fish versus metals concentration in water. Zn in water showed a significant correlation with Zn in fish. Mn in water showed a significant correlation with Mn in fish. Mn in water showed a significant correlation with Cr in fish

Table 5. Correlation Matrix of Concentration of Metals in fish versus Concentration metals in water

	<u>Pb_water</u>	<u>Cd_water</u>	<u>Cr_water</u>	<u>Ni_water</u>	<u>Fe_water</u>	<u>Zn_water</u>	<u>Mn_water</u>
<u>Pb_fish</u>	0.3138						
<u>Cd_fish</u>	0.1462	0.1384					
<u>Cr_fish</u>	-0.1330	0.0930	0.1331				
<u>Ni_fish</u>	0.5153	-0.0365	0.4237	0.6852			

	Pb_water	Cd_water	Cr_water	Ni_water	Fe_water	Zn_water	Mn_water
Fe_fish	-0.1345	-0.1514	0.1318	0.0638	0.2083		
Zn_fish	-0.4758	0.0211	-0.2793	-0.3096	0.2274	0.5837*	
Mn_fish	0.0852	0.1432	0.5242*	0.2817	0.2174	-0.2162	0.4392*

Bioaccumulation Factor is the ratio of metal concentration in biota to the concentration of metal in water. Pb, Mn, Ni and Fe had BAF < 1 as shown in the table 6 below.

Table 6 Bioaccumulation Factor of Heavy metals in fish

Heavy metals (mg/kg)	Fish	Water	BAF
Pb	2.58E-02	1.38E-02	1.87E+00
Mn	3.53E-02	3.36E-02	1.05E+00
Cr	2.00E-02	3.26E-02	6.14E-01
Ni	3.44E-01	2.27E-01	1.52E+00
Fe	5.70E-02	5.70E-02	1.00E+00
Zn	6.14E-02	6.83E-02	8.99E-01
Cd	2.10E-02	2.29E-02	9.18E-01

Table 7 represents the health risk assessment expressed in EDI, HQ and THI. EDI for all the metals were below the 1, indicating less health risk of metals assessed. The THI for individual metals was less than 1.

Table 7 Health Risk Assessment of Heavy metals in fish

Heavy metals (mg/kg)	EDI	HQ	THI
Pb	0.012	3.33E+00	0.003431
Mn	0.016	1.14E-00	0.000118
Cr	0.008	2.67E+00	0.027444

Ni	0.136	6.80E+00	0.006998
Fe	0.024	3.43E+00	0.003529
Zn	0.024	8.00E-02	8.23E-05
Cd	0.008	1.60E+01	0.016467
			0.058069

4. Discussion

Pb is a non-essential heavy metal, the concentration of lead in surface water of the study area ranged from 0.005-0.042mg/l with a mean concentration of 0.014 ± 0.007 mg/l. This value was higher than the standard limit of 0.004mg/l (FMEnv, 2001: USEPA, 2000) and 0.05mg/l (DPR, 2018). Similar results were reported by Ogaga *et al.*, (2018) for Tombia and Gbarantoru axis of Nun River in Bayelsa State Nigeria, Nwankwoala and Angaya (2017) also obtained similar result from Choba section of the New Calabar River in Eastern Niger Delta. The result of Cr obtained during this study was similar to the results obtained by Nwineewii and Edem (2014) in Eleme creek in Rivers State, which reported a mean concentration of 0.172mg/l of Cr in surface water. Ekweozor *et al.*, (2017) reported higher concentrations of Cr in surface water at Azuabie Creek in Port Harcourt which was higher than the results obtained in this study, The mean concentration of Zn recorded in this study was 0.070mg/l. It was below the permissible limit of 3-5mg/l by WHO (2008). Ekweozor *et al.*, (2017) recorded similar lower value in surface water at Okujagu creek in Port Harcourt.

The result of heavy metal concentration in biota obtained in this study was in agreement with other results from (Ijeomah 2005) that recorded a mean concentration of 0.72, 0.74, and 0.63mg/kg in watersnail at Burutu, Bomadi and Warri Southwest respectively.

Similar result of this present study was observed by Moslen and Miebaka (2017) who reported high concentration of Cd (0.73 ± 0.14) in *Callinectis amnicola* from Estuarine Creek in the Niger Delta, Nigeria.

In this study, the BAF of most heavy metals were > 1 (Table 6) indicating high accumulative factor. Pb, Mn, Fe and Ni showed accumulation in fish. This result is in agreement with the result obtained by Ekweozor *et. al.*, (2017) that, reported bio-accumulation of fish at Okujuagu-Ama. The variation in accumulation factor of heavy metals in same species is a function of many factors like age (El-Moselly *et. al.*, 2014), migratory potential of fish and differential exposure, health conditions etc.

Significant correlation indicates that increased concentration of heavy metals in water results to increase of heavy metals concentration in fish. This shows the relationship between concentrations of heavy metals in two samples.

The EDI and THI obtained in this study was similar to the results obtained by Moslen and Miebaka (2017). who reported lower values for both health risk indices for heavy metals in *Tympanotomous fuscatus*.

5. Conclusion

In conclusion, the heavy metals concentrations obtained in this study were within recommended standards. Heavy metals are of great health concern due to its toxicity and bio-accumulative potential. They move across the food chain and get biomagnified in higher organisms. Several health diseases have been traced and linked to heavy metals accumulation in human organs. Therefore, periodic monitoring of heavy metals and evaluation is required in biota of the study area. Also, anthropogenic activities within aquatic environment should be properly regulated and absolute attention be given to waste management system in order to reduce the contamination of aquatic ecosystem.

Reference

- Asonye, C.C., Okolie, N.P., Okenwa, E.E. and Iwuanyawu, U.G. (2007). Some physicochemical characteristics and Heavy metal profiles of Nigerian Rivers, Streams and Water Ways. *African Journal of Biotechnology* 6 (5) 617-624.
- DPR (2018). Department of petroleum Resources. Environmental Guidelines and standards for the petroleum industry in Nigeria (EGASPIN) Lagos. Third edition, 1-315.
- Ekweozor, I.K.E., Dambo W.B & Daka E.R. (2003). “Zinc and cadmium levels in *Crassostrea*

- gasar from the lower bonny estuary, Nigeria. *Journal of Nigerian environmental Society*, 1(1), 31-40.
- El-Moselhy, K.M., Othman, A.I., El-Azem H. A., & El-Metwally, M.E.A. (2014). Bioaccumulation of heavy metals in some tissues of fish in the Red Sea, Egypt. *Egyptian Journal of Basic and Applied Sciences*. 1(2):97-105.
- FAO/WHO (2013). Joint FAO/WHO food standards programme. Codex Alimentaries commission. Procedural manual. Twenty-first edition. World health Organization/Food and agriculture organization of the United Nations, Rome, Italy.
- FMEnv (2001). Federal ministry of environment. National guidelines and standards for water qualities in Nigeria. *Publication federal ministry of environment*. Lagos, Nigeria. 114p
- IRIS (2013). Reference dose (RfD): Description and use in health risk assessments. Back-ground documents IA. Integrated Risk Information System (IRIS); United States Environmental Protection Agency. Washington, DC.
- Liu, M., Cheng, S.B., Ou, D.N., Hou, L.J., Gao, L., Wang, L.L., Xie, Y.S., Yang, Y. & Xu, S.Y (2007). Characterization, identification of road dust PAHs in central Shanghai areas, China. *Atmospheric Environment*, 41, 8785–8795
- Li, J., Shang, X., Zhao, Z., Tanguay, R. L., Dong, Q & Huang, C (2010). Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Aojiang River waterway in Wenzhou, China. *J Hazard Mater*, 173, 75–81.
- Meybeck, M. and Helmer, R (1996). An Introduction to water quality In: *Water Quality assessments – A guide to use biota, sediments and water in environmental monitoring* 2nd edition, Chapman, (ed). UNESCO/WHO/UNEP. pp. 651.
- Moslen, M., Ekweozor, I.K.E. & Nwoka, N.D. (2017). Assessment of Heavy Metals and Bioaccumulation in Periwinkle (*Tympanotus fuscatus* var. radula (L) Obtained from the Upper Reaches of the Bonny Estuary, Nigeria. *Journal of Heavy Metal Toxicology and Diseases*, 2,3.
- Moslen M.& Miebaka, C.A. (2016). Temporal Variation of Heavy Metal Concentrations in sp obtained from Azuabie Creek in the Upper Bonny Estuary, Nigeria, *Current Studies in Comparative Education, Science and technology*. 3(2) 136-147.
- Nwankwoala, H.O. & Angaya, Y.B. (2017). An evaluation of heavy metals concentration in the choba section of the New Calabar River, Eastern Niger Delta. *Biodiversity international journal*, 1(6),62-68.
- Nwineewii, J.D. & Marcus, A.C. (2015). Polycyclic aromatic hydrocarbon (PAHs) in surface

water and their toxicology effect in some creeks of south east, Rivers State (Niger Delta) Nigeria. *IOSR journal of environment science, Toxicology and food technology (IOSR-JESTF)*, 9(12) 11,27 30.

Ogaga, A.A., Faith, A.M. & Sylvester, C.I. (2018). Impacts of anthropogenic activities on heavy metal levels in surface water of Nun river around Gbarantoru and Tombia towns, Bayelsa state, Nigeria. *Annals of ecology and environmental science*, 2018,2 (2), 1-8

UNESCO Quality assessments – A guide to use biota, sediments and water in environmental monitoring 2nd edition, Chapman, (ed). 651.

USEPA (2000). United States environmental protection agency. Lead compounds. Available via <http://www.epa.gov/ttnatw01/hlthef/lead.html> assessed on august 28th 2018.

USEPA (1993). United State environmental protection Agency. Standard Method for the Examination of Water and Wastewater- US: *American Public Health Association*.

USEPA (2011). United States environmental protection agency. Exposure factors handbook 2011 edition (Final Report) USEPA, Washington, DC EPA/600/R-09/052F.

UNESCO (2003). “Water for People: Water for Life”, UNESCO and Bergahalim Books, Paris, New York.

Wang, X., Wang, F., Chem, B., Sun., H.W., Wen Di, L. & Si Wang, Q. (2012). Comparing the health risk of toxic metals through vegetables consumption between industrial polluted and non-polluted fields in Siaoguan, south China. *Journal of food, agricultural and environment*, 10 (12), 943-48.

World Health Organization (WHO), (1988). IPCS Environmental Health criteria 61 Chromium, WHO, Geneva.2693-2698.

World Health Organization (WHO, 2008). Guideline for Drinking Water Quality Third Edition, Incorporating the first and second Addenda Vol.1 Recommendation – Geneva.