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QUANTIFICATION OF TRACE METALS IN WATER AND FISH (*Pelmatolapia mariae*) FROM QUA IBOE RIVER TRIBUTARY, AKWA IBOM STATE, NIGERIA.

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ABSTRACT

The concentrations of five trace metals (Zn, Ni, Mn, Cr, Pb) were quantified in water and fish from July 2013 to September 2013 (wet season) and from November 2013 to January 2014 (dry season) for seasonal variability and health risk assessment. The results of the study showed that mean levels of five trace metals under study showed significant levels at $p = 0.05$ and 0.01 and most metals exhibited higher levels in the wet season than in dry season. The results also revealed that manganese (0.557µg/g) and (5.353 µg/l) were respectively higher in fish and water samples compared to other metals. The mean concentrations of trace metals in water and fish followed the same trend Mn > Zn > Ni > Cr > Pb. However the concentrations of trace metals under study in fish and water were below the maximum acceptable limits provided by World Health Organization (WHO) and United States Environmental Protection Agency (US EPA). Further analysis of the fish pollution status using Bioaccumulation Factor (BAF) revealed that Ni (1.000) had the highest BAF while Zn (0.0029) recorded the lowest BAF. An assessment of health risk due to consumption of fish and water (ingestion/dermal) was undertaken using Hazard Quotient (HQ) and Hazard Index (HI) for both adult and children residing in the study area. HQ for each element was found to range from (1.75E-07 to 6.90E-03) for adults and (5.72E-08 to 1.16E-02) for children from consumption of fish and water (ingestion/dermal). HQ was generally low and within safe limits. Similarly, the HI calculated was less than unity (HI<1), indicating non-potential health risk associated with the consumption of fish and water (ingestion/dermal) from the tributary.

INTRODUCTION

In many developed countries, contamination of surface water and sediments by metals have been a problem due to man's activities and natural processes, which has led to gradual deterioration of the environment. In recent years, serious concern has been voiced about the rapid deteriorating state of fresh water bodies with respect to trace metal pollution. Fresh Water comprises about 3% of the total water on earth and humans use only 0.01% of this fresh water available (Desta *et al.*, 2012) and even this small portion of fresh water is under stress due to lithogenic and anthropogenic sources, particularly from rapid population growth, urbanization and unsustainable consumption of water in industrial and agricultural activities. The tributary is located very close to an abandoned battery industry and must have been receiving wastes particularly trace metals from this source. Also agriculture is the dominant land use in this region and large amount of agrochemicals have been applied to the farming area surrounding the tributary which eventually drains into the river by means of erosion and runoff or storm water which subsequently pollute the river.

Fish is widely consumed because of its protein content, low saturated fat and also contain omega – 3 fatty acids that help to reduce the risk of certain cancers and cardiovascular diseases. Among aquatic species, fishes are the inhabitants that cannot escape from the detrimental effects of metal pollution. This is because water carries the metals in solution or suspension and fish have to extract oxygen from water by passing the water over their gills (Adenirola *et al.*, 2011).

The aim of this study was to determine the concentrations of selected trace metals (Zn, Ni, Mn, Cr, Pb) in drinking water of the tributary and evaluate the health risk associated with human exposure to these trace metals via oral ingestion and absorption through the skin. The results obtained from this study would provide information for background levels of metals in fish and water from Adahaeyop water course, a tributary of Qua Iboe River in Essien Udim Local Government Area of Akwa Ibom State, Nigeria.

MATERIALS AND METHODS

Study Area

The study was carried out in Adahaeyop water course, a tributary of Qua Iboe River, Akwa Ibom State located on longitude $7^0 40^1 8^{11}$ E and latitude $5^0 8^1 47^{11}$N in South – South, Nigeria (Fig.1). The tributary is situated downhill which makes it highly available for surface run-off from the abandoned battery wastes, domestic wastes, open dumps site wastes and agrochemical wastes from agricultural farmlands, hospital wastes and wastes from automobile repair workshops located along the roads . The inhabitants of the area enjoy two distinct seasons viz. wet and dry seasons. While the wet season sometime begins in March and ends in September or October, with the peak in July, the dry season sometime start in October or November and end in February. Most of the inhabitants of this community depend on the tributary for their domestic water needs, recreation, fishing, washing of vehicles and sand mining.

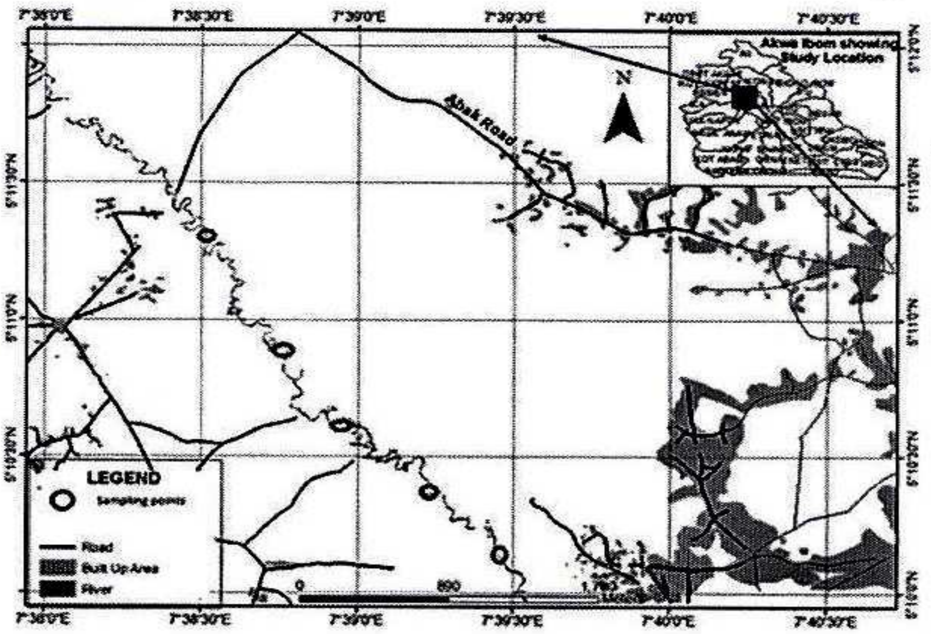

Figure 1: Sampling points at Adahaeyop water course, Essien Udim, L.G.A. in Akwa Ibom State.

Sample Collection, Treatment and Analysis

Water and fish samples were collected from Adahaeyop water course, Essien Udim, Akwa Ibom State, Nigeria. Water samples were randomly taken from five different sampling points along the tributary using pre-cleaned and dried 1L white polythene bottles which were pre-rinsed with the water to be sampled.

Fish sampling was carried out using the locally made fishing traps which were set at dusk and inspected at dawn. Adult fish of similar sizes were selected for the analysis. Sampling was done between July and September (2014) for wet season and November 2014 to January 2015 for dry season. Sixty samples comprising of 30 surface water samples and 30 fish samples were collected throughout the period of study. All the samples collected were transported in cold box to the laboratory for treatment and analysis.

Sample Treatment and Preparation

In the laboratory, five 1L bottles containing water samples for metal determination were acidified with $2cm^3$ concentrated nitric acid to prevent precipitation of metals and growth of algae. Fish samples were washed with de-ionized water to remove slime and ice before they were descaled, gutted and decapitated using stainless steel knife. The fish was filleted on both sides by taking out the muscle tissues which is the most commonly edible part and dried in an oven at a temperature of 105℃ for 12 hours. The dried fish samples were homogenized to powder using porcelain mortar and pestle. About 2g of the was weighed and digested using a mixture of $6\ cm^3$ concentrated nitric acid and $2cm^3$ hydrogen peroxide (3:1) in a digestion flask. The resultant digest was made up to $100cm^3$ with de-ionized water. The digested samples were stored in plastic bottles with plastic lid prior to instrumental analysis.

Determination of Trace Metals

Trace metals in water and fish samples were determined as described by APHA (1985).The digested water and fish samples were quantified for the trace metals Zn, Ni, Mn, Cr, and Pb using UNICAM 939/959 Atomic Absorption Spectrophotometer (AAS).

Bioaccumulation Factor (BAF)

The bioaccumulation of five trace metals in water and fish samples was quantified with a bioaccumulation factor (BAF) which is the ratio of the concentration of metals in fish to the concentration of metals in water. (Chiou, 2002).

$$BAF = \frac{\text{Concentration of trace metals in fish muscles } (\mu g/g)}{\text{Concentration of trace metals in water } (\mu g/l)}$$

Risk Assessment Procedures

Assessment of the Health Risk associated with the consumption of water and fish from the tributary

This was done by making a comparison between environmental status (concentrations of heavy metals in the water and fish) with threshold values which may cause adverse effects in human consumers.

In order to assess human health risk of any chemical contaminant, a complete risk assessment procedure, which involved a four-step process was involved: The first step was achieved by measuring the concentrations of trace metals in surface water and fish. The second step which was the exposure assessment for the inhabitant of the area was estimated for Adult and Child and examined through ingestion (water and fish) and dermal routes based on the US EPA risk assessment methodology. Exposure assessments were evaluated for these two pathways because they are the most significant routes of exposure to these contaminants. In the light of the two pathways discussed above, the exposure assessment was calculated using some mathematical models such as:

Exposure Doses for Water

$$EXP_{ingestion} = \frac{CW \times IR \times EF \times ED}{BW \times AT}$$

$$EXP_{dermal} = \frac{CW \times SA \times Kp \times ET \times ED \times CF}{BW \times AT}$$

where $EXP_{ingestion}$ is the exposure dose through ingestion of water (µg/kg/day), EXP_{dermal} is the exposure dose through dermal absorption (µg/kg/day), CW is concentration of trace metals in water (µg/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 exposure skin area (cm^3); ET is exposure time (h/day), CF is the conversion factor (l/cm^3) and KP is the dermal permeability coefficient.

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 the equation

$$EXP_{fish} = \frac{CF \times IR \times FI \times EF \times ED}{BW \times AT}$$

Where CF is the contaminant's concentration in fish tissue (mg/kg), IR is the mean ingestion rate, EF is the exposure frequency (365 day/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/g).

Dose – response which is the third process was based on the existing toxicity information that is being developed for different chemical pollutants (US EPA,2009).

The final step, which is 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 contaminant from each exposure route (ingestion and dermal) with the reference dose was carried out using the equation below (Naveedullah *et al.*, 2014)

$$HQ_{ingestion} = \frac{EXP_{ingestion}}{RfD_{ingestion}}$$

$$HQ_{dermal} = \frac{EXP_{dermal}}{RfD_{dermal}}$$

Where HQ ingestion is the hazard Quotient through ingestion and HQ_{dermal} is the hazard Quotient via dermal contact, $RfD_{ingestion}$ is the oral reference dose ingestion and RfD_{dermal} is the dermal reference dose (µg/kg/d) (Wu, Zhao and Jia,2009). Hazard quotients (HQ) for fish consumption were determined by expressing it as the ratio of intake of fish to the oral reference dose (RfD) of the metal of concern according to the equation (Li and Zhang, 2010).

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

Hazard Index (HI) was introduced to evaluate the total potential for non-carcinogenic effects posed by more than one pathway, the sum of the HQs from all applicable pathway equations. HI>1 shows a potential for adverse effect on human health (Naveedullah *et al.*, 2014).

$$HI_{ingestion/dermal} = \sum HQ_{ingestion/dermal}$$

In the absence of a health criteria in Nigeria all the parameters for exposure assessment (ingestion and dermal) of metals in water samples used in this study for the studied trace metals were provided by Wu *et al.*(2009), Naveedullah *et al.*(2014) and US EPA (2014).

Statistical Analysis

Statistical package for social sciences (SPSS) version 20 was used to analyse the data.. Relationship between mean concentrations of water and fish from the tributary for wet and dry seasons were investigated using the Pearsons correlation coefficient, r, at P = 0.05 and 0.01 significant levels. All tests were two- tailed.

RESULTS

Levels of Trace Metals in Fish and Water

The Distribution of the studied trace metals levels (mean ± SD) in water and fish samples from the tributary with comparison with national and international standards are given in Tables 1 and 2. The levels of the trace metals Zn, Ni, Mn, Cr, Pb have shown significant temporal variability in both seasons.

Table 1: Mean levels of trace metals in water compared with International Guidelines

Metals	Wet Season µg/L	Dry Season µg/L	Permissible Limits	
			WHO (2008) µg/l	USEPA (2011) µg/l
Zn	2.34±0.08	1.867±0.07	5000	5000
Range	1.23-3.17	1.28-2.86		
Ni	0.023±0.15	0.030±0.04	70	1000
Range	0.01-0.03	0.01-0.05		
Mn	5.353±0.08	4.650±0.09	200	50
Range	3.76-6.45	3.45-6.01		
Cr	0.040±0.04	0.037±0.05	50	100
Range	0.02-0.07	0.01- 0.06		
Pb	0.023±0.05	0.027±0.16	10	15
Range	0.01-0.05	ND- 0.05		

Table 2: Mean levels of trace metals in fish compared with International Guideline

Metals	Wet Season µg/L	Dry Season µg/L	Permissible Limits	
			IAEA (2003) µg/l	FEPA (2003) µg/l
Zn	0.070±0.08	0.243±0.06	67.1	75
Range	0.03- 0.13	0.14- 0.43		
Ni	0.015±0.04	0.030±0.03	0.6	0.6
Range	ND-0.02	ND- 0.05		
Mn	0.227±0.07	0.557±0.16	3.52	0.5
Range	0.08- 0.53	0.27- 3.36		
Cr	0.013±0.13	0.020±-0.03	0.73	0.15
Range	ND-0.02	ND- 0.03		
Pb	0.023± 0.03	0.023±0.029	0.12	0.2
Range	ND- 0.03	ND- 0.03		

In both seasons, manganese was found to be the most prominent trace metal in water with the highest mean level of 5.35µg/l for wet and 4.65µg/l for dry season followed by zinc (2.34µg/l) for wet and 1.867µg/l for dry. However, the lowest level was found for nickel and lead (0.023µg/l) for each of the metals. In general, the mean levels of the trace metals in the water samples were observed to be higher during wet season than dry season, which may be attributed to the seasonal variations in the inflow of water into the tributary..

Results for levels of trace metals in water were compared with WHO and USEPA as presented in Tables 1 and 2. The levels of Zn, Ni, Mn, Cr and Pb recorded in the tributary were lower than the maximum acceptable limits in drinking water recommended by US EPA (2011).

On the other hand, the mean levels of trace metals in fish samples investigated were found to be higher in dry season compared with wet season, (Table 2) with manganese having the highest concentrations in both seasons (0.557µg/g) for dry and 0.227µg/g for wet compared with other metals. The high level of trace metals in fish samples during dry season can be attributed to increase in temperature of the surrounding water which leads to high activity by fish and hence increase their feeding habits. Also increase in temperature will lead to high rate of evaporation thereby resulting in low water level in the tributary, hence the high increase in the concentration of the metals in the water body. The domination in manganese in both fish and water samples compared to other metals studied could be attributed to improper disposal of wastes such as domestic, agrochemical as well as leaching from the abandoned paint industry.

Comparing the trace metal levels in water and fish of the present study with those of other studies in Nigeria and other countries, it is found that levels of trace metals in the water of the tributary are higher than that reported for Lagos Lagoon, Nigeria (Aderinola *et al*., 2011), but lower than that reported for Siling water shed, China and Tekeze River Dam Ethiopia, (Naveedullah *et al*., 2014 Desta *et al;* 2012). However, the concentration levels of the studied metals in fish from this work are lower than those reported for Tekeze River Dam, Ethiopia (Desta *et al*., 2012).

Correlation Analysis

Correlation study was also carried out in order to find out the viable relationships among trace metals in water and fish samples for both seasons as shown in Table 3. During wet season, The Pearson's correlation matrix reveals positive significant relationships between metals in fish and water. There are strong positive correlations between lead and zinc (r = 0.999) and chromium and nickel (r = 0.999) at P = 0.05 level. Lead also showed a strong relationship with chromium (r = 0.998) at P = 0.01 level.

Negative correlations were observed between metals in water alone and fish alone as presented in Table 3. In water alone, chromium correlated negatively with nickel, lead and zinc at p = 0.05 level while in fish alone, lead correlated negatively with chromium.

Table 3: Correlation between mean concentration of trace metals in fish and water in Adahaeyop during wet season

	W Zn	W Ni	WMn	W Cr	W Pb	F Zn	F Ni	F Mn	F Cr	FPb
W Zn	1									
W Ni	.973	1								
W Mn	.993	.993	1							
W Cr	.969	0.999**	.991	1						
W Pb	0.999**	.974	.994	.971	1					
F Zn	.821	.666	.750	.655	.817	1				
F Ni	.977	.901	.947	.895	.976	.924	1			
FMn	.520	.704	.615	.715	.526	-.060	.327	1		
F Cr	.577	.751	.667	.761	.583	.009	.391	.998*	1	
F Pb	.968	.883	.933	.875	.966	.939	.999*	.288	.353	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed). W = Water , F= Fish

Table 4: Correlation between mean levels of trace metals in fish and water in Adahaeyop during dry season

	W Zn	W Ni	W Mn	W Cr	W Pb	F Zn	F Ni	F Mn	F Cr	F Pb
W Zn	1									
W Ni	.707	1								
W Mn	.997*	.756	1							
W Cr	.754	.068	.705	1						
W Pb	-.984	-.820	-.994	-.626	1					
F Zn	.518	-.238	.456	.953	-.360	1				
F Ni	.633	-.100	.576	.986	-.487	.990	1			
F Mn	-.308	-.891	-.376	.393	.471	.654	.541	1		
F Cr	.705	-.004	.652	.997*	-.569	.972	.995	.458	1	
F Pb	.529	-.227	.466	.956	-.371	1.000**	.992	.645	.975	1

*. Correlation is significant at the 0.05 level (2-tailed). F = fish
**Correlation is significant at the 0.01 level (2-tailed) W = water

The Pearson's correlation matrix reveals positive significant relationships (p = 0.05, p = 0.01) between metals in fish and water during dry season as presented in Table 5.

There is an association between manganese in fish and zinc in water (r = 0.997) at p = 0.05 level, also chromium in fish shows strong positive correlation with chromium in water (r = 0.997**) at P = 0.01 level. Similarly, lead and zinc (r = 0.999**) shows strong correlation at P = 0.01 level. However, lead in water correlated negatively with zinc and manganese at p = 0.05 level.

Bioaccumulation of Trace Metals in Fish

The bioaccumulation of the studied trace metals was determined using bioaccumulation factor (BAF). The BAF of trace metals calculated for muscle tissues are shown in Table 5.

Table 5: Bioaccumulation Factor (BAF) for Different Metals from Water to Fish (Mean)

Parameter	Metals	BAF WET(X)	BAF DRY (X)
	Zn	**0.029**	**0.130**
Fish / water	**Ni**	**0.652**	**1.000**
	Mn	0.042	0.119
	Cr	0.325	0.541
	Pb	0.869	0.852

From the trace metals (Zn, Ni, Mn, Cr and Pb) studied, the highest BAF was recorded by Nickel (1.000) while Zn recorded the least BAF of 0.029. It was observed from this study that BAFs were higher in dry season compared to wet season, (Table 5). The high BAF in dry season is attributed to higher water temperature at this period. Higher temperatures can result in higher activity in fish. This tends to lower oxygen affinity of the blood, increase the rate of seeding and thus increase the rate of pollutant accumulation. The BAF values among the studied metals showed the order Pb> Ni > Cr >Mn> Zn for wet season and Ni>Pb> Cr > Zn >Mn for dry season. From our observation, there was no distinct relationship between trace metals in fish and water in which they survive. This is because trace metals accumulation in fish organism depends on the ability of the organism to digest the metals and the concentration of the metal in the surrounding biota may not be directly or solely derived from water but from living or dead, suspended particles and from sediment.

The result from this study is similar to Ololade et al. (2008), who reported low levels of BAF values for Mn (0.09) and Zn (0.77) in *Tilapia zilli* from Ondo Coastal region. Comparing this work with other works, BAFs of the studied metals were found to be low compared with previous works from Nigerian Rivers. Okoye *et al.* (1991), reported a high BAF of 604 for Manganese and 284 for lead in *Tilapia guineensis* in Lagos Lagoon. Similarly Obodo (2002) working on the lower reaches of River Niger at Onitsha reported BAF of 300 and 220 for Mn and Pb respectively in *Synodontis membranaceus.* The low BAF recorded in this study compared to other works is attributed to the fact that fish muscles was used for the investigation since it is the part most likely to be consumed by humans.

EVALUATION OF HUMAN EXPOSURE TO TRACE METALS

Estimated Exposure levels to Trace Metals through Water ingestion, Dermal absorption and fish ingestion

Manganese (0.150) recorded the highest exposure level through oral ingestion ($EXP_{INGESTION}$) while nickel (0.01) Cr (0.01) and Pb (0.01) recorded the least exposure levels for adult. The same trend was observed in a child. The exposure level of a child to manganese (0.249) was the highest whereas nickel and lead recorded the least exposure levels of 0.001 (Table 6). The estimated exposure levels through oral ingestion followed the trend Mn > Zn > Cr = Ni = Pb for adult and Mn > Zn > Cr > Ni = Pb for child. Nickel was seen to record the highest exposure level by dermal absorption through contact with water in both adult (9.504 E-07) and child (1.517 E-06) while Chromium (1.144 E-08) for adult and (1.826 E-08) for child were the least exposure levels through dermal contact with water for adult and child (Table 6). The estimated exposure levels through dermal absorption through contact with water was observed in the order Ni > Mn > Zn > Pb > Cr for both adult and child. In the estimated exposure to trace metals through fish ingestion (EXP_{FISH}), Manganese was seen to record the highest exposure level of 1.128 E-04 and 4.706 E-04 in both adult and child respectively while chromium 4.890 E-06 and 2.065 E-05 had the least exposure levels for both adult and child respectively (Table 6). The estimated exposure levels to trace metals through fish ingestion were observed in the order Mn > Zn > Pb > Ni > Cr for adult and Mn > Zn > Ni > Pb > Cr for child.

Table 6: Estimated Exposure to Metals through Water, Fish and Dermal contact from the tributary

Metal	EXP_{dermal} Adult	Child	EXP_{Water} Adult	Child	EXP_{Fish} Adult	Child
Zn	1.852E-07	2.955E-07	0.063	0.015	**4.516E-05**	1.907E-04
Ni	9.504E-07	1.517E-06	0.001	0.001	6.616E-06	2.794E-05
Mn	7.336E-07	1.171E-06	0.150	0.249	1.128E-04	4.701E-04
Cr	1.44 E-08	1.826E-08	0.001	0.002	4.890E-06	2.065E-05
Pb	1.467E-08	2.340E-08	0.001	0.001	6.329E-06	2.672E-05

EXP_{water}= Exposure for water, EXP_{fish}= Exposure for fish EXP_{dermal} = Exposure for dermal contact

The values for the estimated toxic risk by oral ingestion of water (HQ_W) was observed in this order Mn > Pb > Cr > Zn > N i> for both adult and child. The results of the calculated toxic risk (HQ_S) for exposure pathways (HQ_W, HQ_D, HQ_F) are presented in Tables 7. From the results, manganese 6.25 E-03 and 1.04 E-02 was seen to have the highest HQ in water for both adult and child while nickel with the same value (5.00 E-05) for both adult and child was the lowest. Similarly, it was observed from the calculated HQ_D that nickel recorded the highest hazard quotient values of 1.19 E-06 and 1.90 E-06 for adult and child respectively while zinc recorded the least calculated HQ_D value of 3.09 E-09 and 4.93 E-09 for adult and child respectively (Table 7). Also, the estimated toxic risk to trace metals exposure by fish ingestion (HQ_F) had manganese with the highest HQ values of 4.70 E-06 and 1.98 E-05 for adult and child respectively while zinc had the least toxic non-values of 1.51 E-07 and 6.36 E-07 for adult and child respectively (Table 7).

Table 7: Summary of the Estimated Hazard Index (HI) to Trace Metals Exposure Due to Water Ingestion, Dermal Absorption and Fish Ingestion.

	Adult				Child			
Metals	HQ_W	HQ_D	HQ_F	HI	HQ_W	HQ_D	HQ_f	HI
Zn	2.10E-04	3.09E-09	1.51E-07	2.10E-04	3.50E-04	4.93E-09	6.36E-07	3.51E-4
NI	5.00E-05	1.19E-06	3.31E-7	5.15E-05	5.00E-05	1.90E-06	1.40E-06	15.33E-5
Mn	6.25E-05	1.64E-07	4.70E-06	6.26E-03	1.04E-02	1.22E-06	1.98E-05	5.33E-05
Cr	3.33E-04	1.53E-07	1.63E-06	3.35E-04	6.67E-04	2.43E-07	6.88E-06	6.74E-04
Pb	7.14E-04	3.49E-08	4.42E-06	7.18E-04	7.14E-04	5.57E-08	1.91E-05	7.33E-04
HI	7.56E-03	2.12E-06	1.12E-05		1.22E-02	3.42E-06	4.78E-05	

HQ_w= Hazard Quotient (water); HQ_D = Hazard Quotient (Dermal Contact); HQ_F = Hazard Quotient (fish)

DISCUSSION

Zinc is an essential element in our diet but too little or too much can be harmful. Zinc is a co-enzyme for over 200 enzymes involved in immunity, new cells growth and acid-base regulation. The results obtained show that the concentration of zinc was the highest in water compared to other samples. Zinc concentration was highest in wet season in water compared to dry season. This could be attributed to excessive run-off during wet season which may have washed wastes laden with zinc from various sources into water bodies. However, none of the samples studied was polluted by zinc since zinc levels did not exceed the recommended value by WHO, USEPA and FEPA

Nickel is considered an essential element for normal growth and reproduction in animals and human beings. However, Ni related health effects such as lung cancer, nausea and immunological effects have been reported (Udosen, 2015). The mean concentration of nickel for both seasons recorded in water and fish were all below the recommended value, (Table 2).

Although manganese is an element of low toxicity, it has considerable biological significance. Udosen (2004) states that manganese is essential for normal development and body functions across the life span of all mammals. Generally the high value of manganese over other metals in water is as a result of improper disposal of wastes such as batteries, domestic and agro-chemicals, as well as leaching from the abandoned battery industry. The levels of manganese in water and fish did not exceed the recommended value..

Chromium is an essential trace nutrient and a vital component of glucose factor but its toxicity damages the liver, lungs and causes organ haemorrhages (Udosen, 2015). This work is comparable to Udoh *et al.*(1999) who reported low level of chromium in water from different aquatic environments in Akwa Ibom State, Nigeria. However, the high value of chromium in fish during dry season can be attributed to increase in the temperature of the surrounding water which leads to high activity by fish hence increase their feeding regime. However, the mean concentration of all the samples did not exceed the recommended limits, (Table 2).

Lead is a toxic metal with no metabolic benefits to humans and aquatic biota. It is the most toxic trace metals in aquatic system (Udosen, 2015). The low level of lead in both water and fish is due to low influx of wastes laden with zinc into the tributary.

Generally, the exposure levels for all the pathways (ingestion and dermal) were higher in children than adults. This is because the body weight of a child is less than that of an adult. Exposure to manganese through oral ingestion was the highest both in adult and child due to high level of Mn in water. The hazard quotient values (HQ_W, HQ_D and HQ_F) of trace metals were found to be less than unity ($HQ < 1$) indicating that all the exposure pathways have little or no health threat. HQ for chromium was the lowest which may be due to its higher oral reference dose. Hazard Index (HI) for adult and child were computed to assess the overall non-carcinogenic risk possesses by the studied trace metals through multiple pathways as a whole. Lee *et al.* (2005) stated that in a situation where there are multiple toxicants and/or multiple exposure pathways, it is important that their possible interactions be considered. This is because the toxic risk due to potential hazardous chemical in the same medium is cumulative.

The HI calculated for both adult and child were less than unity ($HI < I$), an indication that there were no cumulative potentials of adverse health risks in fish and water samples through ingestion or dermal contact with water to the consumer. Similar cases of low HI have been reported by researchers. Li and Zhang (2010) reported low HI for both adult and child from multiple pathways exposure in the upper Han River, China. Udosen *et al.* (2014) reported low HQ and HI values from fish ingestion from Enyong Creek, Itu, Nigeria for both adult and child.

CONCLUSION

From the analyses of the samples, it is concluded that all the metals (Zn, Ni, Mn, Cr, Pb) may have been from natural sources as well as from urban, rural, domestic, solid and agricultural wastes discharged into the tributary. Levels of trace metals in water and fish demonstrated great seasonality with the minimum levels of the trace metals found in dry season and most of the metals having high levels in the wet season due to increase in rainfall resulting in increasing run off into the river during wet season. There were significant positive correlation coefficients among trace metals in water and fish indicating a common source of pollution.

A comparative assessment of the levels of these metals studied with international standards (WHO, USEPA and, IAEA) revealed that all the metals levels were within the maximum permissible limits.

The evaluation of toxic risk (non-carcinogenic risk) using risk assessment models like hazard quotient (HQ) and hazard index (HI) for the studied metals in both adult and child during wet and dry seasons were found to be less than unity, indicating no health risk to consumers of fish and water from the tributary.

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