



Risk Assessment of Toxic Heavy Metals Concentration of Fish and Drinking Water in Nsukka Metropolis, South East, Nigeria

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HIGHLIGHTS:

- Fish and drinking water in Nsukka Metropolis were contaminated with Toxic Heavy Metals except Pb in water.
- Hg in roasted fish and Cd in both tap and plastic bottled water were in high concentrations exceeding the Maximum Permissible Limit.
- No carcinogenic risk was revealed for Toxic Heavy Metals via the consumption of contaminated fish unlike for Cd and As in drinking water.

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Acronyms and abbreviations

AAS=Atomic Absorption Spectrophotometer
CR=Cancer Risk
EDI=Estimated Daily Intake
HI=Hazard Index
MPL=Maximum Permissible Limit
PTDI=Provisional Tolerable Daily Intake
THMs=Toxic Heavy Metals
THQ=Target Hazard Quotient

ABSTRACT

Background: Toxic Heavy Metals (THMs) threaten food safety and result in human poisonings. It seems to be few studies on THMs contamination in food chain in developing countries. Current investigation determine the concentration and health risk of arsenic (As), cadmium (Cd), lead (Pb), as well as mercury (Hg) in fish and water at Nsukka, Metropolis, Enugu state, Nigeria.

Methods: Forty eight samples; 24 (catfish and tilapia) fish and 24 (borehole, sachet, and bottled) water were randomly collected from two major markets and districts in Nsukka Metropolis and were evaluated for THMs using Atomic Absorption Spectrophotometer. The Estimated Daily Intake, Target Hazard Quotient, Hazard Index, and Cancer Risk (CR) were assessed as well.

Results: THMs analysis showed that As, Cd, and Hg were at 100% and Pb being at 16% in all the fish samples while 12.5% of fish of exceeded the Hg Maximum Permissible Limit (MPL) of 0.050 mg/kg, that not statistically significant ($p>0.05$). On the other hand, based on the analysis of all water samples, Hg and As were detected at 100% rate, Cd at 58.3% while Pb was not identified. The values above the MPL appeared to be 9 (37.5%), 2 (8.3%), and 3 (12.5%) for Hg, As, and Cd, respectively in water while not statistically significant ($p>0.05$). The mean value of Hg (0.06425 mg/kg) in roasted fish as well as Cd (0.0065 and 0.0105) mg/ml in tap and bottled water respectively surpassed the MPL although not statistically significant ($p>0.05$). The Estimated Daily Intake of THMs except Cd in fish were proved to be within the Provisional Tolerable Daily Intake in contrast with As and Cd in water. CR is present both in children and adults with CR value >1 .

Conclusion: The finding of THMs in fish and water above the MPL is regarded as potential health risk for the consumers of such contaminated water and fish in the investigation scope.

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Introduction

Toxic Heavy Metals (THMs) including arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) proved to be noxious to plants and animals even in very low quantities (Sankhla et al., 2020; Sonone et al., 2021). They are produced naturally, however could be released into the environment through industrial activities including metal smelting, burning of fuels, alloy processing, and mining (Lo et al., 2012). THMs can contaminate water, soil, and vegetation through surface runoff as well as agricultural and industrial effluents (Baby et al., 2010; Smitha et al., 2007). Their non-degradable nature promotes bio accumulation and environmental persistence, and they are easily deposited in human tissues through diet and water (Sonone et al., 2021). Continuous exposure to THMs through diet and contaminated water sources could engender a number of adverse health effects including cancer (Aloke et al., 2019; Sonone et al., 2021). This should cause concern for the developing countries due to population growth, increasing water scarcity, urbanization, and also climate change (WHO and Unicef, 2013), particularly among the fishing communities where fish comprise a chief portion of human diet (Ihedioha et al., 2016; Yakubu, 2016). Meanwhile, approximately 30% of the human population has been reported to be dependent on untreated water for drinking and distinct domestic purposes worldwide (European Environment Agency and WHO Regional Office for Europe, 2002). Therefore, the high risk of THMs exposure to over 200 million individuals and the associated public health and economic consequences globally (Naujokas et al., 2013; Rajeshkumar et al., 2018).

Numerous studies have reported THMs contamination of drinking water in various countries including China and Malaysia where chemical purification techniques, pipeline corrosion, as well as elemental leaching from (water) distribution/storage pipes have been incriminated (Saha et al., 2017; WHO and Unicef, 2013). The reports of THMs contamination in drinking water in Thailand (Chowdhury et al., 2016) and India (Bajwa et al., 2017) has been linked to pipeline corrosion and subpar domestic water treatment, pharmaceutical, paint, pesticide, and fertilizer industries. Additionally, the growing reports of THMs concentration in various food and water sources has caused the international authorities suggest a Maximum Permissible Limit (MPL) value; a benchmark for heavy metals in edible products for safety and consumer's protection (Njoga et al., 2021; Pipoyan et al., 2023). The report of 42.1% of THMs contamination above the recommended MPL in the Bangladesh's drinking water samples compared to low values below the same level as reported in countries like Germany and USA could be associated with the level of environmental pollution among other factors available in the study areas (EPA, 2012; WHO and Unicef, 2013).

The cumulative effect of THMs on consumption above the tolerant limit via food chain could result in hypertension, nephrotoxicity, endothelial cells damage, impaired renal function, liver damage, diminished cognitive function, congenital, and impaired reproductive capacity, neurological impairment, brain damage, fragile bones, kidney, and lung damage as well as cancers (De Mattia et al., 2004; Tchounwou et al., 2012; U.S. Department of Health and Human Services and USDA, 2015; WHO, 2003). In Japan, the reason of Itai-Itai disease, a very unusual and painful disease, has been traced to chronic Cd poisoning among consumers of contaminated fish. Even consumption of methyl mercury contaminated fish has resulted in countless death among the fishing community (Kessler, 2013; Lo et al., 2012). Pb poisoning and child death in Zamfara state in Nigeria's northern region have also been caused by illegal mining activities (Lo et al., 2012). A report on THM contamination of processed goat carcasses intended for human consumption in Nsukka, in the country's eastern region, was published a few years ago (Njoga et al., 2021). Furthermore, the country is vulnerable to population growth and urbanization which challenge both water and food safety supply chain (EPA, 2012; WHO and Unicef, 2013). This study sought to ascertain the THMs concentration and health risks associated with fish and drinking water in Nsukka Metropolis, South East, Nigeria.

Materials and methods

Quality assurance and control

All reagents and chemicals utilized in the analysis were of analytical grade and were pre-tested for probable heavy metal contamination. Before use, all of the glassware and plastics were soaked overnight in 10% nitric acid and rinsed twice with distilled water. The used instruments were all calibrated and standardized with standard solutions prepared from commercially available chemicals. All analytical work and the preparation of working solutions involved the use of distilled water.

Study area

The study was conducted in the ever-growing Metropolis of Nsukka urban in Enugu state, South East Nigeria. It is located at latitudes 6°51'N to 6°53'N and longitudes 7°23'E to 7°34'E, with the growing population beyond 1.26 million (NGIA, 2008; Nwankwo et al., 2021). It bears a tropical climate that supports livestock production including fish farming. The communities in the Metropolis receive fish from two significant fish markets. Additionally, the borehole continues to be the main water source, supplemented by rain storage, especially during the

rainy season. Moreover, the quality of water from boreholes being transported by tankers to various homes and the levels of water treatment prior to distribution/supply fail to be generally ascertained.

Survey layout and sampling approach

A cluster sampling method was used for a cross-sectional study. A total of 48 samples, 24 each for fish (catfish and tilapia) and water (borehole, bottled, and sachet), were randomly chosen and purchased at the fish markets and water distribution points/companies, respectively in the study area. According to the availability of fund. All samples were collected and analyzed between April and July, 2021. For each samples, 5 g of the fish tissues and 100 ml of water samples were aseptically collected in sterile containers placing in a clean thermo flask, kept cold, and transported to the laboratory for further THMs analysis using Atomic Absorption Spectrophotometer (AAS; AA-7,000 Shimadzu, Kyoto, Japan).

Sample preparation for digestion

The frozen fish samples were allowed to thaw at room temperature (25-30 °C) and all the fish samples were oven-dried (Carbolite Gero, Pennsylvania, PA, USA) to constant weight at 70 °C and granulated with mortar and piston (Changsha Jinto Co., Hunan, China). Afterwards, these samples and water samples were digested (Njoga et al., 2021).

AAS analysis

Wet digestion of samples and subsequent analysis with Agilent FS240AA. AAS were accomplished based on standards EN 13804:2013 and EN 13805:2014 (CEN, 2013, 2014). In summary, 5 g of each sample was weighed and transferred into a digestion flask (Global spec., New York, NY, USA) containing 20 ml of the concentrated acid mixture of HNO₃ and HCl (Sigma-Aldrich Corp., Missouri, MO, USA) in the ratio of 1:3. A clear solution was obtained by heating the mixture to 80 °C in a fume-cupboard. It was diluted to 50 ml utilizing distilled water. Water sample was rigorously mixed by shaking, and 50 ml of it transferred into a glass beaker of 250 ml volume, to which 5 ml of conc. Nitric acid was added and heated to boil for 30 min, adequately filtered. The sample was aspirated into an oxidizing air-acetylene flame. The sensitivity for 1% absorption was observed, as the aqueous sample was aspirated. Each solution was analyzed for the presence of As, Cd, Pb, and Hg using Flame Atomic Absorption Spectrophotometer (FAAS) (AA-7,000 Shimadzu, Kyoto, Japan; ROM 1.01) at wavelengths of 193.7, 228.8, 253.7, and 217.3, respectively as described by Njoga et al. (2021) and the obtained values compared

with their respective MPL (Table 1).

Operational Parameters

The fish and water samples were quantitatively analyzed for the THMs using the calibration curve technique while the qualitative and quantitative precision of the spectrophotometer was determined via metal recovery test (MRT) as previously defined (Njoga et al., 2021). The Limits of Detections (LODs) were quantified as the concentration corresponding to three times the Standard Deviation (SD) of blanks, while the Limits of Quantifications (LOQs) were computed as 10 times the SD of reagent blanks (Table 2).

Health risk assessment

The multifarious health effects accompanied with the consumption of THMs in both fish and water were investigated based on the following: (a) Estimated Daily Intake (EDI), (b) Target Hazard Quotient (THQ), (c) Hazard Index (HI), and (d) Cancer Risk (CR). Each of these health risk assessment parameters is succinctly illustrated below:

-EDI

The EDI of As, Cd, Hg, and Pb in the consumed fish and water specific to the study area have been considered following the equation:

$$\text{EDI} = \frac{C \times \text{QDC}}{\text{BW}}$$

as modified by the United States Environmental Protection Agency (EPA, 2020). C seems to be the mean concentration of the specific THM in the fish (mg/kg) or water (mg/ml) and BW is the average body weight (kg). The quantity of daily consumed (QDC) fish (0.25 kg) or water (2,250 ml) as determined by survey of 48 randomly selected fish and water sellers and buyers at selling/buying points of the fish markets and water distribution companies in the study area. The average BW of children ≤18 years and adults >18 years were supposed to be 30 and 60 kg, respectively (EPA, 2020). The Provisional Tolerable Daily Intake (PTDI), of the respective THMs which are the quantities of the toxic heavy metals being consumed on a daily basis with no lifetime health risk was compared with the computed EDI values (WHO, 2017).

-THQ

The THQ was presumed to indicate the non-carcinogenic health risks of consuming fish and water contaminated by respective THMs. This status has been estimated following the equation (Eq. 2)

$$\text{THQ} = \frac{[(C \times \text{Ed} \times \text{Ef} \times \text{QDC}) / (\text{RfD} \times \text{BW} \times \text{Et})]}{10^{-3}}$$

as described by EPA (2020).

C refers to the mean concentration of the heavy metal (mg/kg); Ed pertains to the exposure duration in a lifetime (70 years); Ef relates to the exposure frequency in days (365 days); QDC refers to the quantity of fish (g) or water (ml) consumed. In addition, the RfD involve the oral reference dose of the metals at 3.5×10^{-3} , 1.0×10^{-3} , 3×10^{-3} , and 1×10^{-4} mg/kg/day for Pb, Cd, As, and Hg, respectively (EPA, 2020; Wu et al., 2023). The RfD value for methyl mercury was calculated since Hg is presented in methylated form (Živković et al., 2019). The BW demonstrates the body weight (60 kg for an average adult), the lifetime exposure is introduced by the Et (365days \times 70years). It is extensively perceived in case the THQ value is <1 , it is considered very little or no non-carcinogenic health risk. Furthermore, while the THQ value is >1 , it is regarded a non-carcinogenic adverse health effects risk on drinking or eating THMs through contaminated fish or water.

-HI

The HI which appears to be the summary of the individual THQs of the THMs examined in the water and fish was calculated as following equation (Eq. 3):

$$HI = THQ_{As} + THQ_{Cd} + THQ_{Pb} + THQ_{Hg}$$

When the HI value is considered ≥ 1 , it reflects non-carcinogenic adverse health, but in case being <1 , it reflects little or no non-carcinogenic effect.

-CR

The potential CRs associated with life time exposure to carcinogens is presented by the CR. This has been calculated using the formula (Eq. 4) (Naseri et al., 2021; Njoga et al., 2021):

$$CR = CSF \times EDI$$

The available Cancer Slope Factor (CSF) value ($\mu\text{g}/\text{kg}/\text{day}$) of 1.5, 0.008, and 0.38 for As, Pb, and Cd, respectively as adopted from EPA screening levels were used in the calculation (EPA, 2021; Saha et al., 2017). A risk level of 1×10^{-6} was considered as excess cancer risk, indicating 1 per 1,000,000 chance of getting cancer via consumption of drinking water or fish containing THMs, estimated in $\mu\text{g}/\text{L}$ for 70 years.

Data analysis

With one sample student test, the mean concentrations

values of THMs in water and fishes sources and the known permissible limits were compared. The data have been displayed in terms of mean values \pm standard error of mean (SEM). *p*-values less than 0.05 were considered significant. All analyses were accomplished using the SPSS, version 20.

Results

Cd, and Hg were examined in all the fish samples at 100% rate, Pb which appeared to be at 16% while 3 (12.5%) values of Hg in fish exceeded the MPL of 0.050 mg/kg although it failed to be statistically significant (*p*>0.05). The concentrations' ranges were (0.000-0.038, 0.000-0.030, 0.000-0.069, and 0.000-0.0028) mg/kg for As, Cd, Hg, and Pb, respectively.

On the other hand, based on the analysis THMs of water samples, Hg and As were detected at 100% rate, Cd at 58.3% while Pb was not detected. The ranges of concentrations were (0.000-0.039, 0.000-0.012, and 0.000-0.002) mg/ml for As, Cd, and Hg, respectively. The values above the MPL were 9 (37.5%), 2 (8.3%), and 3 (12.5%) for Hg, As, and Cd, respectively in water though not statistically significant (*p*>0.05).

Furthermore, the mean value of Hg (0.06425 mg/kg) in roasted fish and Cd (0.0065 and 0.0105) mg/ml in tap water and bottled water, respectively, also exceeded the MPL although they were not statistically significant (*p*>0.05) (Tables 3 and 4).

The EDI for As through the consumption of locally produced fish was at the level of the PTDI of (0.003 mg/kg/day) in children while Cd intake with imported frozen fish were above the PTDI in both children and adult despite the intake in case of roasted fish was also above the PTDI in children. However, no CR of THM was found in fish consumption as all the CR values were <1 (Table 5).

In addition, As was unveiled to be higher than the PTDI value when drinking water from different tested sources, resulting in increased CR, which was not significantly higher in children than in adults (*p*>0.05). The Cd value was also higher than the PTDI for tap water and plastic bottled water consumption, but not for CR (Table 6).

Using the HI, no THMs cancer risk was observed through fish consumption, while a very high risk was found for water consumption in both adult and children where HI>1 (Table 7).

Table 1: Maximum Permissible Limit (MPL) of Toxic Heavy Metals (THMs) in fish and water according to International Standards

Toxic Heavy Metals	MPL (mg/kg) in fish (CEN, 2003)	MPL (mg/ml) in water (EPA, 2021)
Cadmium (Cd)	0.050	0.005
Lead (Pb)	0.300	0.050
Arsenic (As)	0.100	0.050
Mercury (Hg)	0.500	0.002

Table 2: Operational parameters used for quantification of Toxic Heavy Metals (THMs) in fish and water in Nsukka Metropolis, South East, Nigeria

Parameters	Arsenic (As)	Cadmium (Cd)	Lead (Pb)	Mercury (Hg)
Wavelength (nm)	193.7	228.8	283.3	258
Slit width (nm)	0.7	0.7	0.7	0.7
LOD (mg/kg)	0.0005	0.0001	0.0001	0.0001
LOQ (mg/kg)	0.002	0.001	0.001	0.001
Metal recovery range (%)	98-101.4	98.2-101.5	97-100.9	81-100

LOD=Limit of Detection; LOQ=Limit of Quantification

Table 3: Mean concentration of Toxic Heavy Metals (THMs) (mg/kg) in fish in Nsukka Metropolis, South East, Nigeria

Fish source	Mean Concentration \pm SEM				t-value	p-value
	Mercury (Hg)	Arsenic (As)	Lead (Pb)	Cadmium (Cd)		
Locally produced fresh catfish	0.0155 \pm 0.01	0.0325 \pm 0.02	ND	0.007 \pm 0.01		
Imported frozen tilapia	0.0105 \pm 0.01	0.036 \pm 0.02	0.026 \pm 0.02	0.028 \pm 0.02		
Roasted tilapia	0.06425\pm0.01	0.0285 \pm 0.01	ND	0.0165 \pm 0.01	1.117	0.3456
Max p. Units	0.050	0.1	0.30	0.50		

Values in bold >MPL (Maximum Permissible Limit); ND=No Detection

Table 4: Mean concentrations of Toxic Heavy Metals (THMs) (mg/ml) in drinking water in Nsukka Metropolis, South East, Nigeria

Water source	Mean Concentration \pm SEM				t-value	p-value
	Mercury (Hg)	Arsenic (As)	Lead (Pb)	Cadmium (Cd)		
Tap water	0.002 \pm 0.01	0.029 \pm 0.02	ND	0.0065\pm0.01	1.44	0.2452
Plastic bottled water	0.002 \pm 0.01	0.009 \pm 0.01	ND	0.0105\pm0.01	0.9073	0.2452
Sachet water	ND	0.016 \pm 0.01	ND	ND		
Max p. Units	0.002	0.05	0.05	0.005		

Values in bold >MPL (Maximum Permissible Limit); ND=No Detection

Table 5: Estimated Daily Intake (EDI) and Cancer Risk (CR) of Toxic Heavy Metals (THMs) in children and adult via consumed fish in Nsukka Metropolis, South East, Nigeria

THMs	Sources	EDI		CR	
		Children	Adult	Children	Adult
Mercury (Hg)	Local fresh catfish	0.0013 \pm 0.01	0.0006 \pm 0.01		
	Imported frozen tilapia	0.0009 \pm 0.01	0.0004 \pm 0.01		
	Roasted tilapia	0.0535 \pm 0.02	0.0268 \pm 0.01		
Arsenic (As)	Locally p. fresh catfish	0.0027 \pm 0.02	0.0014 \pm 0.01	0.0041 \pm 0.01	0.0402 \pm 0.01
	Imported frozen tilapia	0.0001 \pm 0.01	0.0000	0.0002 \pm 0.01	0.0000
	Roasted tilapia	0.0024 \pm 0.02	0.0012 \pm 0.01	0.0036 \pm 0.02	0.0018 \pm 0.01
Cadmium (Cd)	Local fresh catfish	0.0006 \pm 0.01	0.0003 \pm 0.01	0.0002 \pm 0.01	0.0001 \pm 0.01
	Imported frozen tilapia	0.0023 \pm 0.01*	0.0012 \pm 0.01*	0.0009 \pm 0.01	0.0005 \pm 0.01
	Roasted tilapia	0.0014 \pm 0.01	0.0007 \pm 0.01	0.0005 \pm 0.01	0.0003 \pm 0.01
Lead (Pb)	Local fresh catfish	NA	NA	NA	NA
	Imported frozen tilapia	0.0022 \pm 0.01	0.0011 \pm 0.01	0.0000	0.0000
	Roasted tilapia	NA	NA	NA	NA

* EDI values that exceeded the World Health Organization (WHO)'s Provisional Tolerable Daily Intake (PTDI); The PTDI for As=0.003, Cd=0.001, Pb=0.002 mg/kg/day, Hg=1.3 μ g/kg/day. Note: Cancer Slope Factor (CSF) for Hg was not provided hence not included in the calculation for CR.

NA=Not Applicable

** CR value $>1=CR$

Table 6: Estimated Daily Intake (EDI) and Cancer Risk (CR) of Toxic Heavy Metals (THMs) in children and adult via drinking water in Nsukka Metropolis, South East, Nigeria

THMs	Sources	EDI		CR	
		Children	Adult	Children	Adult
Mercury (Hg)	Tap water	0.75±0.02	0.375±0.01		
	Plastic bottled water	0.75±0.02	0.375±0.01		
	Sachet water	NA	NA		
Arsenic (As)	Tap water	2.175±0.02*	1.0875±0.01*	3.2625±0.01**	1.6313±0.01**
	Plastic bottled water	0.675±0.02*	0.3375±0.01*	1.0125±0.01**	0.5063±0.02
	Sachet water	1.200±0.01*	0.6000±0.01*	1.8000±0.01**	0.9000±0.02
Cadmium (Cd)	Tap water	0.4875±0.01*	0.2438±0.01*	0.1853±0.01	0.0926±0.01
	Plastic bottled water	0.7875±0.01*	0.3938±0.02*	0.2993±0.01	0.1496±0.01
	Sachet water	NA	NA		
Lead (Pb)	Tap water	NA	NA		
	Plastic bottled water	NA	NA		
	Sachet water	NA	NA		

* EDI values that exceeded the World Health Organization (WHO)'s Provisional Tolerable Daily Intake (PTDI). The PTDI for As=0.003, Cd=0.001, Pb=0.002, and Hg=1.3 mg/ml/day

** CR value >1=CR; NA=Not Applicable

Table 7: Target Hazard Quotient (THQ) and Hazard Index (HI) of Toxic Heavy Metals (THMs) in children and adult via consumed fish and drinking water in Nsukka Metropolis, South East, Nigeria

Sources	THQ								HI	
	Mercury (Hg)		Arsenic (As)		Lead (Pb)		Cadmium (Cd)			
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Fish	0.012	0.02	0.001	0.002	0.0003	0.006	0.002	0.004	0.015	0.032
Water	0	0	0.666	0.019	0.274	0.549	1.904	3.862	2.844	4.43

THQ or HI <1 indicates no or very little non-carcinogenic health risk

Discussion

The study has demonstrated that the fish and drinking water were contaminated with THMs in a high concentration above the WHO's recommended limit and this status could be a reflection of the environmental pollution and resultant contamination of food and water sources in the study area. This poses a public health concern due to the exposure risks and the associated detrimental health consequences including kidney damage, reproductive disorders, and cancer among the long time consumers of such contaminated fish and water (Huseen and Mohammed, 2019). The detection of THMs in fish samples, particularly Hg (0.000-0.069) mg/kg in roasted Tilapia exceeding the MPL has further highlighted the risk of the long time exposure through fish diet especially among children and the elderly that have preference for fish diet. Lower values of THMs as illustrated in the locally produced fish compared to those of imported/frozen and the roasted fish especially for Pb and Hg could indicate higher contamination rate in some importing countries where the THMs in industrial wastes including used batteries, petrol additives, cable sheathing, and ammunitions transported into the water bodies, therefore their bio accumulation in fishes compared to less industrialized areas such as the study area (Varsha, 2013). The obtained result was in agreement with the high THMs contamination of fish and sea food in the industrialized countries including Bosnia and Herzegovina that

consequently 100% detection rates for Hg and Cd as well as 82% for Pb in fish reported (Djedjibegovic et al., 2020). The similarities in the works could be associated with identical fish types; domestically farmed fish, and imported fish as deployed in this study. This condition implies that humans are at the risk of THMs intoxication through ingestion of contaminated fish and other sea food regardless of the industrial status of the country of origin since THMs can be transported to water bodies and persist in the environments over a long time (Saikat et al., 2022).

Cd appears to be a dangerous metallic pollutant associating with chronic renal failure and skeletal damage. Application of phosphate fertilizers (containing 2-200 mg Cd/kg) by farmers in the study area may have resulted in the contamination of water sources via runoff and the ground water that are applied in fish production in the study area, hence the subsequent contamination of locally produced fresh fish in low concentrations of 0.007 mg/kg compared to 0.028 mg/kg in those from the sea. Furthermore, Hg has been reported as the third topmost hazardous substances and its investigation at 0.015-0.065 mg/kg in fish is a concern since exposure at high levels through contaminated fish can cause methylmercury intoxication with resultant inactivation of Na^+/K^+ ATPase and toxic effect on neuronal cells, brain damage, hearing, and speech defects especially in new born and young children (Prakash Bansal, 2020). More attention should be paid to appropriate disposal and treatment of waste as well

as disproportionate use of organic fertilizers in farming and other agrochemicals in the study area. The high contamination rate of Hg in the roasted imported fish above the MPL could be due to the use of saw dust or wood shaving in the roasting/processing of fish as research have displayed that some wood are high in Hg level which are volatile on heating (Yang et al., 2017). Therefore, the inevitable public health consequences among fish farmers and processors with higher risk of the carcinogenic as well as other health defects associated with handling and consumption of roasted fish (Bawuro et al., 2018; Khatri and Tyagi, 2015). According to the reports, women appear to be more at risk due to long hours of exposure to gases and particles from wood smoke on a daily basis because of their occupation as fish processors (Adeyeye and Oyewole, 2016). The high contamination rate of As (0.029-0.036 mg/kg) and (0.009-0.029 mg/ml), in fish and water, respectively in the study area could be the resultant effect of pesticides/herbicides usage in the environment. Since reports have manifested that they are high in As content, their usage in both plant and livestock farming could have led to their leaching into the ground water supplied for drinking or used in local fish production in the study (Semu et al., 2019; Tangahu et al., 2011). Identical (0.015-0.021 mg/ml) and higher (0.091-0.485 mg/ml) values of As have been expressed in drinking water sources in Imo and Ebonyi States of South East Nigeria, respectively (Aloke et al., 2019; Eze et al., 2021). However, much higher value (4.73 mg/ml) had been disclosed in India (Chakraborti et al., 2018). The variations in the reported values could be accompanied with the level of contamination with industrial effluent. Meanwhile, Bhattacharya et al. (2016) in an extensive review had declared tissues and liver damages in human and animals on exposure to low-elevated levels of inorganic As. Even, Smith et al. (2000) had previously depicted that 13 out of 1,000 individuals suffer lung, liver, kidney, or bladder cancer on a daily ingestion 50 μ g/L of As and skin lesions on the uptake of 0.0012 mg/kg/day.

The identical investigation rate of THMs in the water samples as in the fish except for Pb, which failed to be detected in water sample, has manifested that most of the THMs accumulations in fish were from water sources. Furthermore, the 100% detection rate and several values of As, Hg, and Cd in water samples above the MPL should be a source of concern as As has been reported to have resulted in skin damages and respiratory disorders even at a dose of 0.0012 mg/kg/day through dermal contacts and drinking water while long-term exposure to Cd has equally caused chronic renal failure, anemia, hypertension, osteoporosis, as well as cardiovascular diseases (Chowdhury et al., 2016). In current study, the detection of Cd in values (0.0065-0.0105 mg/ml) above the MPL and

higher in plastic bottle than tap water, has illustrated the likely contribution of plastic containers in Cd contamination of drinking water. This status could be due to leaching from plastic which are more in use than iron in piping of tap water as a result of corrosiveness of iron. Meanwhile, the chemical components of plastic do not usually bound firmly to their polymer cores and are usually released into water particularly under hot environment (Peng et al., 2023). Identical values (0.006-0.018 mg/ml) have been expressed in a water sourced from Njaba river in Imo state, Nigeria (Eze et al., 2021) while lower value (0.002-0.049 mg/ml) had been reported in Ebonyi state, Nigeria (Aloke et al., 2019). Similar high levels of THMs contamination above MPL have also been narrated in other studies including 0.00-0.01, 0.010-2.01, 0.00-0.25, and 0.38-3.04 for Hg, As, Cd, and Pb, respectively, in water sourced from streams ponds/lake and shallow hand dug wells in South East Nigeria (Ekere et al., 2014) as well as 0.038-0.089 and 0.058-0.309 mg/ml in river Niger and Benue confluence, in Kogi state, Nigeria (Yakubu, 2016). The similarities and differences in the reported values could be associated with water sample sources as higher reported values in lakes and rivers compared to tap water in the study. Additionally, the detection of Pb and Cd at 0.00 and 0.0065 mg/ml in the study which were equally less than 0.01 and 0.06 mg/ml for Cd and Pb in water from a lake in Ibadan (Ukachukwu, 2012) could be accompanied with higher industrial activities in Ibadan with the resultant wastes disposal to nearby lakes unlike the study area with less industries and with no lake. The report of higher values (0.02-0.124 and 0.00-1.32 mg/ml) for Cd in drinking water in Egypt and India, respectively, in comparison with 0.00-0.12 mg/ml for Cd in the study area could further be associated with the expected level of environmental contamination in the industrialized countries compared to the study area (Ramachandran et al., 2018; Salman et al., 2019). The lack of Pb detection in water in the study was in agreement with the report that exposure to Pb through water is generally low since the main source of Pb in drinking water is considered old Pb piping and leaching solders which are not in use in the study area. However, the findings disagreed with reports from Iran and Thailand as Pb in drinking water exceeded the MPL level (WHO, 2013, 2017). The similarities and differences could be related to the level of pipeline corrosion with Pb pipes in use (Hadiani et al., 2015; Wongsasuluk et al., 2014).

The exploration of higher rates of THMs in tilapia species in comparison with the catfish in the study could be associated with differences in their sources and dietary habit among other factors; tilapia feeds on plants and debris and could have evaluated more of the THMs through contaminated plants and debris in the locally produced water environment, even more than the catfish

that are known omnivorous in the sea (Yakubu, 2016).

Health risk assessment of current work has revealed the risk of THMs intoxication particularly As and Cd by consumption of fish in children as the EDI were equivalent and above the PTDI values, respectively. However no risk of cancer was related to their consumption in fish as the HI values were <1 . This status was identical to the report of Ihedioha et al. (2016) with a report of low risk among the consumers. On the other hand, identical high values for As above the PTDI values in drinking water with a high carcinogenic risk $HI>1$ for As should be paid a crucial attention since the persistent exposure by drinking water might cause cancer particularly in children as uncovered in the study area. However, the estimated body weight of children and adults in the measurement of the health risk assessment may have influenced the calculated values. Therefore, the level of risk may be less than those measured in the study.

Conclusion

Fish and drinking water in Nsukka Metropolis are contaminated with THMs especially Hg with 12.5% in fish samples and Hg, As, and Cd with 37.5, 8.3, and 12.5%, respectively in water samples above the MPL. The mean value of 0.0642 mg/kg was higher than the MPL level for Hg in roasted tilapia various from the other THMs and fish sources. Likewise, the mean values of 0.0065 and 0.0105 in tap and bottled water, respectively were above the MPL for Cd in water compared to other THMs. This poses a public health concern given the very high risk associated with exposure. Urgent preventive measures against THMs contamination of fish and water including appropriate use of chemicals, adequate water purification, safe fish processing methods cannot be overemphasized.

Author contributions

I.O.N., C.O.A., and C.O.N. designed the study; C.O.N. conducted the research; I.O.N., O.C.N., and C.I. analyzed the data; I.O.N. and C.O.A. supervised the work; I.O.N. wrote the manuscript; C.O.A., O.C.N., and C.I. reviewed the manuscript. All authors read and approved the final manuscript.

Conflicts of interest

All authors declare that there was no conflict of interest regarding the publication of this article.

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