Original Research Article

Ecological risk assessments of heavy metal contamination in water, sediment and biota of Otamiri and Imo Rivers, Nigeria

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ABSTRACT

Heavy metals pollution of the environment is a serious concern because of the hazardous effects they pose to human health, ecosystems and other biological receptors. The aim of this study was to assess the ecological risk of exposure to heavy metals and physicochemical parameters around Otamiri and Imo rivers in Etche and Oyibo Local Government Areas of Rivers State. Water, sediment, arrow head plant *(Sagittaria latifolia*) and christmas bush Plant (*Ceratopetalum gummiferum),* tilapia fish samples (*Oreochromis niloticus*) and cat fish (*Clarias gariepinus*) were collected at different points from five sample stations for wet and dry seasons. These samples were analyzed quantitatively to assess the levels of contamination in the samples using the ecological risk assessment models associated with exposure to these contaminants. The results of the heavy metal analysis show that the Estimated Daily Intake (EDI) for biota samples ranged from 0.000 – 1.254 mg/kg/day while water ranged from 0.000 - 0.322 mg/kg/day. The target hazard quotient (THQ) ranged from 0.000 – 69.228 for both biota and river water samples for Otamiri and Imo rivers The hazard index values indicated significant public health risk with values of 1.42 was recorded for Tilapia and 33.14 for Christmas bush plant. Cancer risk due to heavy metals exposure had a peak value of 1.04 $x10^{-1}$ for wet season. The bioaccumulation of the metals showed that the pollution load index values ranged from 2.467- 5.822 in wet season and 9.708 – 99.853 in dry season. The presence of these heavy metals above threshold values suggest that the aquatic life that inhabit such rivers risk bioaccumulation which may affect the human population that depends on Otamiri/Imo rivers for fishing, drinking or irrigation. These poses a danger if bioaccumulation was to take place over a long period of time.

Keywords: Ecological risks, Heavy metal, Bioaccumulation, Aquatic plants, fishes, sediment, Rivers.

Introduction

Most water pollutants originate from human activity, while a small percentage of them have their sources in natural activities such as volcanic eruptions. Human activities in urban areas render surface waters including streams, river, lagoons, etc. ~~and~~ ground water bodies susceptible to contamination from organic pollutants such as heavy metals, industrial chemicals, sewage discharged from sources like urban runoffs, industrial activities, subsurface infiltration, or atmosphere precipitation effluents, sewage treatment plants, chemical fishing activities, leachate from decomposing refuse dumps, agricultural fertilizer applications (Nwankwoala and Ekpewerechi, 2017). Once pollutants are introduced into receiving surface water and groundwater bodies via discharge processes, they are transported within the water cycle. Of more serious concern is the fact that heavy metals can cause serious health effects with different symptoms depending on the nature and quality of the metal ingested (Nwankwoala and Ekpewerechi, 2017). Most of these organic pollutants bind to cellular proteins and DNA resulting in biochemical disruptions and cell damage leading to mutations, developmental malformations, tumors, and cancer in humans (Ramesh *et al*., 2011). Lipmann, (2009). Some other pollutants come primarily from occupational hazards on workers exposed to mixtures of Polycyclic aromatic hydrocarbons (PAHs) such as benz[*a*]anthracene, benzo[*b*]fluoranthene, indeno[1,2,3-cd]pyrene, benzo[*k*]fluoranthene, dibenzo[*a,e*]pyrene which are known to cause increased risk skin, lung, bladder and gastrointestinal cancers. Cancer Index (2019) show that ingestion of these contaminants can increase current cancers burden in Nigeria with 102,100 people diagnosed yearly while about 71,600 dying from cancer yearly.

The impact of anthropogenic activities on Otamiri and Imo Rivers as a result of the increasing rate of urbanization and other industrial activities because of the closeness of the vicinity and linkage to Trans-Amadi industrial layout shows that Otamiri River is a major tributary that receives effluents from the activities and operations of companies operating within the flanks of the rivers in Rivers State. Worrisome is the fact that water from these rivers serves as a source of water distributed for public consumption and domestic uses. These rivers are vulnerable to surface water pollution because effluents from industries, municipal wastes, agricultural and urban run-off are discharged into it thereby deteriorating the water quality (Ogbonna *et al.,* 2021). Heavy metals and polycyclic aromatic hydrocarbons (PAHs) come from industrial and urban activities. As pollutants, these compounds are toxic and many are identified

as carcinogenic, mutagenic and teratogenic. They stress the ecosystem, lowering its resilience so that the health of the ecosystem is weakened and becomes less productive, causing increased mortality of aquatic life and poor water quality. Eventually the compounds enter the food web as pollutants through the filter-feeders such as bivalves and worms which then bioaccumulate, threatening the health of those higher up in the food web – a major concern for people who eat seafoods as a major diet.

Other human impacts affecting water resources include Oil spills through accidental discharges from ships at sea, ballast water from ships, reclaiming land by drainage, building bridges (structures such as sea walls, bridges, drains, jetties, marinas, levy banks, rock walls and breakwaters can all affect the passage of water and can change the conditions), sand extraction for construction aggregates, rubbish/ocean dumping (litter on beaches or rivers and floating in the salt and fresh water pollutes) contribute grossly to water pollution These impacts on estuaries contribute to the reduction of habitats for estuarine animals and plants and spoil recreational activity and the beauty of our estuarine coastline. They also jeopardize the role estuaries play in maintaining the health of coastal waters, including the marine organisms within them, which affects the fishing industry. Industries like fishing and oyster farming can impact the water quality and also the movement of water in such rivers. Over-fishing and habitat loss reduces the amount of fish in the ocean and disrupts the food chain.

However, this fragile ecosystem has been degraded seriously because of environmental changes such as global climate change and environmental pollution (Ogbonna *et al.,* 2021). Among various pollutants, heavy metals with persistence, non-biodegradation, toxicity and bioavailability pose a major threat to rivers biodiversity and human health. Unfortunately, the fragile ecosystem of Otamiri and Imo Rivers are increasingly being threatened by these anthropogenic activities. Therefore, the aim of this study was to assess the Ecological risks associated with contamination of heavy metals in water resources as well as its impact on the biota of the ecosystems. Ecological risk assessment focuses on evaluating the impacts of human activities on ecological systems and the services they provide. Ecological risk assessment has its roots in estimating exposure and risk or hazard from chemicals in the environment, with range of stressors facing ecological receptors (McIntosh and Pontius, 2017).

Materials and Methods

Description of Study Area

The Imo River is one of the major rivers in the Southern part of Nigeria. It originates in the vicinity of Okigwe and takes a Southerly course until it is joined by the Otamiri River which flows from the neighborhood of Owerri. It then proceeds eastward meandering close to Akwete from where it moves towards the Imo tidal basin as a smooth straight river. Imo River is considered as part of Niger Delta River basin. It is a deep freshwater river which cuts across Imo State, Abia State and Rivers State. The river flows through coastal plain, alluvium and mangrove swamp and empties into the Atlantic Ocean through the Opobo creek at the Bight of Benin (Akoma, 2008). The study area lies within the Etche and Oyibo LGA axis of Otamiri and Imo River in Rivers State. The dimension of the study area is approximately 94665.46 km^2 as shown in Figure 1.

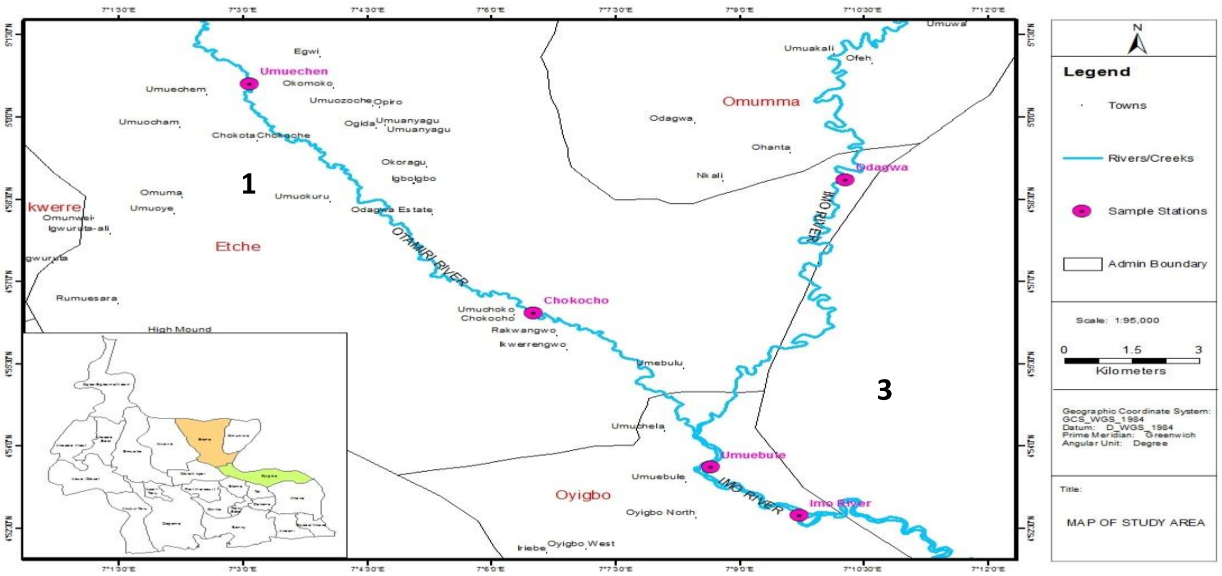

Figure 1: Map of the study area showing Sampling Stations.
Source: NDDC GIS laboratory.

Table 1: Description of sampling stations

S/N	Sampling Stations	Location	Coordinates		Type of Sample
			Latitude	Longitude	
1	Station 1	Otamiri River at Umuechem Etche LGA, Rivers State	5° 0' 38.1'' N	7° 3' 22.7'' E	Water, Sediment
2	Station 2	Otamiri River at Chokocho Etche LGA, Rivers State.	4° 59' 37.0'' N	7° 3' 22.7'' E	Water, Sediment, Biota
3	Station 3	Imo River at Odagwa Etche LGA, Rivers State.	4° 58' 54.1'' N	7° 10' 16.7'' E	Water, Sediment, Biota
4	Station 4	Imo River at Umuebulu Oyibo LGA, Rivers State.	4° 53' 37.0'' N	7° 8' 36.8'' E	Water, Sediment
5	Station 5	Imo River at Imo Gate, Oyibo LGA, Rivers State.	4° 53' 16.3'' N	7° 8' 42.1'' E	Water, Sediment

Sampling Technique

The purposive sampling frame was adopted in this study. Five sampling stations were established along the Imo River and its adjoining tributary along Otamiri River covering a distance of approximately five kilometers. Notably, samples were collected for both wet and dry seasons in this study. The description of the sampling stations using the coordinates is shown in Table 1.

Sample Collection and Preparation

Water, sediment and biota (fish and plant) samples were collected from Otamiri and Imo rivers during the wet and dry seasons. Selection of organisms was based on the different niches in which they normally thrive within the river ecosystem. The fish samples were identified by a fishery expert and a hydrobiologist and eventually assigned an aquarium number. The biota (fish and plants) samples, collected in this study consisted of two species namely, tilapia and catfish while the arrow head plant *(Sagittaria latifolia)* and christmas bush plant (*Ceratopetalum gummiferum)* were the plants collected from the sampling stations.

The fish and plant samples were preserved in a dark bottle away from sunlight to guard against sunlight induced photo-degradation. Samples were preserved at -4^{0}C using an ice pack. Sediment samples were collected from the top 10-cm layer of the river bed. Sediment samples were air-dried for 14 days to reduce moisture and sieved using 2mm sieve. The sieved samples were mashed to powder and stored in the refrigerator until analysis.

Water samples were collected in transparent and brown glass bottles prewashed with detergent, rinsed with water and acetone (99.9%) and dried before sample collection. Samples were taken from 0.1 m below the water surface and transported directly to the laboratory. All samples were sent to laboratory and biota samples stored in refrigerator at -4^{0}C until the analysis.

Physicochemical characteristics

The physico-chemical parameters of the water sample namely, pH, temperature, turbidity, conductivity, total dissolved solids, total suspended solids, total alkalinity, biological oxygen demand, chemical oxygen demand, dissolved oxygen, total organic carbon, sulphate, nitrate, phosphate, salinity, chlorine, bromine, and conductivity were all determined in this study using standard procedures as listed below:

~~i.~~ The conductivity was determined using conductivity meter (model SM 3030)

ii. Turbidity was determined using turbidity meter (model - SGZ – 200BS). Dissolved oxygen was determined using dissolved oxygen meter (model DO 5509)

iii. Salinity was determined by salinity meter (HI98203)

iv. The pH was determined using pocket series waterproof digital pH meter.

v. Conductivity was measured using an electrical conductivity meter (EC meter) from Mettler Toledo, TDS tester (model TDS SCAN 30 manufactured by ASBL).

vi. Chlorine and bromine were determined using a 3-way pool and SPA test kit

vii. Temperature was determined using a Liquid Crystal Thermometer

viii. The BOD meter OxiDirect was used in determining the biochemical oxygen demand.

Heavy metal Determination

The EPA vigorous digestion method described by Ekeanyanwu *et al* (2010) was adopted. For the water sample, 10ml of concentrated HNO_3 was added to 100ml of each of the representative water samples in a Pyrex beaker. The samples were boiled slowly and then evaporated on a hot plate to the lowest possible volume (20ml). The beakers were allowed to cool and another 5ml of concentrated HNO_3 was added and heated until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by the addition of 5ml of HCl solution (1:1 v/v). The solutions were then warmed and 5ml of 5M NaOH was added, then filtered. The filtrates were transferred to 100ml volumetric flasks and diluted to the mark with distilled water. These solutions were then used for the elemental analysis using atomic absorption spectrophotometer (UNICAM 929 AAS).

Heavy metals (Pb, Cd, Ni, V, Cr), and metalloid (As) in both the sediment and biota was determined using Solar Thermo Elemental Flame Absorption Spectrometer (S4 710). To accurately determine the presence of the heavy metals of interest, sediment and biota samples were air dried to reduce moisture and 9 ml of 65% concentrated HNO_3 and 3ml perchloric acid was used to digest 5g of each biota and sediment samples. The solution was then transferred to a hot plate at 110°C for 5 hours. Afterwards, the samples were introduced into an oven under a temperature that was gradually increased in 100°C every 60 minutes until the desired final temperature of 450°C was reached eighteen hours later; white ashes were obtained. Following this, samples were left to cool. The white ashes were then dissolved with 1.5% HNO_3 (5ml) and a final volume of 25ml was made by adding deionized water. The resulting solution was filtered using a Whatman filter paper (number 42) fitted into a Bucher funnel into a beaker before it was transferred into a tightly sealed plastic container.

Heavy Metal Risk Assessment Method

Significant carcinogenic and non-carcinogenic human health risk associated with heavy metals (Cd, Hg and Pb) exposure from samples was determined using estimated daily intakes (EDI), target hazard quotient (THQ), hazard index (HI) and Carcinogenic risk.

Estimated Daily Intakes (EDI) of Metals

The daily intake of metals depends on the metal concentration in samples, the daily food consumption rate and the body weight. The estimated daily intake (EDI) of metals is a concept introduced to take into account these factors. The EDI was calculated based on the following formula by Singh *et al* (2010).

$$\mathrm{EDI} = \frac{\mathrm{Cmetal\ x\ Dfood\ intake}}{BWaverage}$$

Where *C* is the metal concentration in food in mg/kg, *D* is the daily intake of food in kg person^{-1}, and BW is average body weights for children (4 to 9 years old), adolescents (10 to 19 years old), male adults (20 to 65 years old) are 24kg, 54.5kg, 70.0kg, respectively (Falco *et al.,* 2003).

Target Hazard Quotient (THQ)

Non-carcinogenic risk estimation of heavy metals consumption was determined using THQ values and Hazard Index Values. THQ is a ratio of the determined dose of a pollutant to a reference level considered harmful. THQ values were determined based on the following formula by Singh *et al* (2010).

$$\mathrm{THQ} = \frac{\mathrm{Efr} \times \mathrm{ED} \times \mathrm{FIR} \times C}{\mathrm{RfDo} \times \mathrm{Baverage\ wt} \times \mathrm{ATn} \times 10 - 3}$$

where Efr is exposure frequency assumed to be 365 days year^{-1}, ED is exposure duration in 56 years equivalent to an average lifetime, FIR is average daily consumption in kg person^{-1}day^{-1}, (0.116 g/day, 0.109 g/day and 0.097 g/day for adults, adolescents and children respectively (Ihedioha *et al.*, 2014), *C* is concentration of metal in food sample in mg/kg, RfDo is reference dose in mg/kg day^{-1}, and ATn is average exposure time for non-carcinogens in days. Reference doses of 0.003, 0.001, 1.5, 0.0371, 0.0035, 0.0016, 0.03 and 0.007 mg/kg/day for As, Cd, Cr, Cu, Pb, Hg, Zn and Fe respectively were used (Kamunda *et al.*, 2016)

Ecological Risk Assessment

The determination of ecological Risk was determined using two different models namely; Bioaccumulation factor and pollution load index.

Determination of Bioaccumulation Factor (BAF)

The bioaccumulation factor (BAF) is determined using the formula below

$$BAF = \frac{\text{Conc of metal in plants collected}}{\text{Conc of analyzed metal in soil (mg/kg)}}$$

BAF value greater than 1 indicates high accumulation potential of the biota (Mendil *et al*., 2005).

Pollution Load Index (PLI)

Pollution Load Index PLI using the Tomlinson's approach (Tomlinson *et al.,* 1980). The PLI represents how much a metal concentration exceeds average and normal background levels. It also provides a summation of the overall heavy metal toxicity found in an examined sample. The control samples were taken to represent natural background. The summation of the BAF gives the PLI (Adamo *et al*., 2005).

This was achieved using Equations (7);

$$PLI = (BAF_1 \times BAF_2 \times BAF_3 \times\text{---}\times\text{----}\ BAF_n)^{1/n}$$

where,

BAF: Bioaccumulation factor, n = number of metals = 7;

C_{sample}: Mean metal concentrate in the plants;

$C_{background}$: Mean metal concentration in the soil/background/substrate.

RESULTS

Physico-Chemical Analysis of Water Samples

The physico-chemical characteristics of the water samples is presented in Table 2. pH is one of the vital environmental characteristics that decides the survival, metabolism, physiology and growth of aquatic organisms. The pH values range of water sample across the stations was between 5.56 and 5.80 as compared to the WHO limit of 6.5-8.5. The pH showed significant variations across the sample stations at p-value < 0.05. The pH is not less than 4 (<4) hence is suitable for aquatic life. Notably, Odagwa had the highest pH value of 5.80 while Umuechem and Umuebulu 5.56. Electrical Conductivity which is a measure of the total ionic composition of the water samples had mean values of 73.00 µS/cm and 113.50µS/cm, which were below the WHO permissible limit of 500 µS/cm. There were remarkable variations in the electrical conductivities of water in the sample stations. Imo Gate 92.50µS/cm < Umuechem, 73.00µS/cm < Chokocho, 94.50µS/cm < Umuebulu, 104.50µS/cm < Odagwa 113.50µS/cm. Odagwa had the highest conductivity value of 113.50µS/cm while Umuechem had 73 µS/cm. Statistical test a p-value < 0.05 showed that there was a significant difference.

Turbidity gives an expression of the scattering and absorption of light through water. Turbidity level is increased by the presence of clay, silt, fine organic and inorganic matter, soluble coloured organic compounds, plankton and other microscopic organisms. Turbidity values for water samples was recorded as 3.00 NTU to 27.50 NTU

The Total Dissolved Solids (TDS) value of 62.50mg/l was obtained from Odagwa while Umuechem had39.00mg/l as against the permissible limit of 500mg/l Total Suspended Solids (TSS) is the dry-weight of suspended particles that are not dissolved in a water sample that can be trapped by a filter and analyzed. Table 3 and figure 2 TSS values for water samples across stations ranged from 2.00mg/l to 37.00mg/l. Umuechem and Chokocho had 6.50mg/l and 2.00mg/l respectively, while Odagwa, Umuebulu and Imo Gate Stations had 37.00mg/l; 31.50mg/l and 30.50mg/l respectivelyBiochemical Oxygen Demand (BOD_5) BOD is a measure of the amount of oxygen that bacteria will require to decompose organic matter under aerobic condition. The values for BOD ranged from 2.31 mg/l to 2.76 mg/l. Chemical Oxygen Demand (COD) is a measure of the total quantity of oxygen required to oxidize all organic material into carbon IV oxide (CO_2) and water. The water samples had 4.56mg/l and 5.12mg/l.

Table 2: Physico-chemical Characteristics of Surface water

Parameters	Sampling Stations					WHO Limits	P- value
	Chokocho	**Odagwa**	**Imo River**	**Umuechem**	**Umuebulu**		
pH	5.71±0.23	5.80±0.22	5.70±0.50	5.56±0.69	5.56±0.55	6.5-8.5	0.000
Temperature (**°C)**	23.35±3.61	24.25±2.90	24.25±2.33	25.55±0.78	25.40±0.57	26.5-32	0.033
EC (**µS/cm)**	94.50±19.09	113.50±17.68	92.50±23.33	73.00±12.73	104.50±14.85	500	0.000
TDS (mg/l)	52.00±7.07	62.50±6.36	49.00±12.73	39.00±5.66	56.50±6.36	500	0.000
Turbidity (NTU)	3.00±2.83	31.00±11.31	27.50±9.19	6.50±2.12	26.00±11.31	5	0.269
TSS (mg/l)	2.00±1.41	37.00±31.11	30.50±28.99	6.50±2.12	31.50±27.58	25	0.000
BOD (mg/l)	2.46±0.51	2.43±0.32	2.76±0.20	2.40±0.13	2.31±0.29	4	0.002
COD (mg/l)	5.12±0.13	4.78±0.18	4.56±0.08	5.00±0.01	4.73±0.17	120	0.000

Keys: EC- **Electrical Conductivity*, TDS-* Total Dissolved Solids (mg/l), TSS- Total Suspended Solids, BOD-Biological Oxygen Demand, and COD-Chemical Oxygen Demand**
Note: *Values represents mean±SD*

Heavy Metal concentrations in Surface Water

Table 3 shows the mean concentration of heavy metals (Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Zinc and Iron) in water across the sample stations. The concentration of Arsenicin water from the sample stations was below detectable limits (BDL). From the Umuechem station, the Cd mean value was 0.34 mg/kg while Chokocho, had 0.29mg/kg, Odagwa 0.30mg/kg, Umuebulu 0.32mg/kg and Imo Gate 0.23mg/kg. Umuechem had for Copper 0.02mg/kg, Odagwa 0.05 mg/kg, Chokocho 0.04mg/kg, Umuebulu 0.05mg/kg while Imo Gate 0.02mg/kg.Umuechem, Chokocho, Odagwa and Umuebulu had same Pb value of 0.12mg/kg respectively while Imo Gate had 0.52mg/kg. Hg in water was absent below detectable limit. Umuechem recorded for Zn0.24 mg/kg, Chokocho0.23mg/kg, Odagwa

0.22mg/kg and Umuebulu 0.17 mg/kg while Imo Gate had 0.18 mg/kg. It differed significantly at p-value <0.05.The value of Fe at Umuechem was 4.68mg/kg, while Chokocho 3.39mg/kg and Odagwa had0.94mg/kg, also Umuebulu station had 1.40 mg/kg while Imo Gate recorded 1.12mg/kg.

Table 3: Heavy metal and Nutrient concentrations in Surface Water

Parameters (mg/kg)	Sampling Stations					WHO Limits	P-value
	Chokocho	Odagwa	Imo River	Umuechem	Umuebulu		
Arsenic	BDL	BDL	BDL	BDL	BDL	0.01	-
Cadmium	0.29±0.22	0.30±0.21	0.23±0.15	0.32±0.19	0.34±0.16	0.003	0.003
Chromium	BDL	BDL	BDL	BDL	BDL	0.05	0.695
Copper	0.05±0.04	0.04±0.02	0.02±0.01	0.02±0.01	0.05±0.04	2	0.002
Lead	0.12±0.17	0.12±0.17	0.52±0.73	0.12±0.17	0.12±0.17	0.01	0.180
Mercury	BDL	BDL	BDL	BDL	BDL	0.001	-
Zinc	0.23±0.10	0.22±0.05	0.18±0.04	0.24±0.09	0.17±0.07	3	0.000
Iron	0.39±0.02	0.94±0.97	1.12±0.21	4.68±4.89	1.40±0.98	0.3	0.152
Calcium	5.06±0.84	4.88±1.44	3.78±0.79	2.69±0.80	4.49±0.68	200	0.000
Magnesium	1.08±0.08	1.06±0.04	1.13±0.08	1.11±0.13	1.36±0.20	50	0.000
Sodium	0.57±0.61	1.17±0.08	1.46±0.19	1.07±0.07	1.26±0.07	200	0.000
Potassium	1.71±0.81	0.21±0.10	0.82±0.23	1.23±0.15	0.36±0.15	NIL	0.132
Chloride	15.03±13.68	19.36±21.55	15.24±13.39	12.38±10.50	18.13±18.63	250	0.000
Nitrate	2.45±1.51	2.31±1.12	2.24±0.74	1.82±0.93	2.33±1.03	50	0.000
Sulphate	2.05±0.35	6.36±5.01	6.12±4.53	3.00±2.91	6.04±5.14	200	0.000
Ammonia	0.28±0.06	0.59±0.19	0.57±0.12	0.48±0.16	0.66±0.13	1.5	0.004
Phosphate	0.12±0.02	0.17±0.06	0.17±0.04	0.10±0.04	0.19±0.04	0.1	0.127
Hardness	13.00±4.24	16.00±11.31	13.00±4.24	8.00±5.66	15.00±7.07	200	0.000

Heavy Metal concentration in Fishes and Plants

Table 4 show the concentration of heavy metals in Tilapia and Catfish samples. concentration of Cadmium ranged from 0.32 to 0.42 mg/kg in Tilapia fish, Lead ranged from 0.2mg/kg in Tilapia fish to 0.9 mg/kg in Catfish, Zinc recorded 0.32 mg/kg (Catfish) to 0.54 mg/kg (Tilapia) and Iron ranged from 0.88 mg/kg in Catfish to 1.56 mg/kg in Tilapia fish while Table 5 shows heavy metal concentrations in two plant species namely arrow head plant *(Sagittaria latifolia*) and christmas bush lant (*Ceratopetalum gummiferum)*. Generally, it was observed that all heavy metals analysed except Iron was significantly high in christmas bush plant (*Ceratopetalum gummiferum)* compared to *Sagittaria latifolia.*

Table 4: Heavy metals in fishes

Parameters	Tilapia	Catfish	WHO Limit	P-value
Arsenic	BDL	BDL	1.4	-
Cadmium	0.42±0.03	0.32±0.09	0.05	0.176
Chromium	BDL	BDL	1	-
Copper	0.49±0.63	0.04±0.02	3	0.111
Lead	0.2±0.01	0.9±1.18	0.5	0.67
Mercury	BDL	BDL	0.5	-
Zinc	0.54±0.14	0.32±0.10	30	0.013**
Iron	1.56±1.13	0.88±0.40	100	0.013**

Note: *Values represents mean±SD; BDL represents Below Detectable Limit; *** Significant

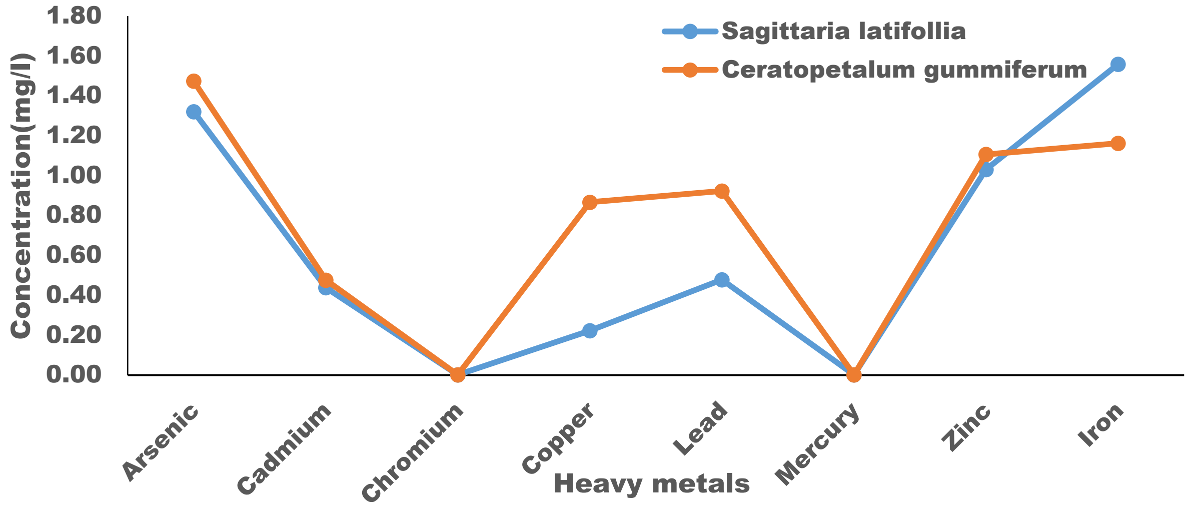

Figure 2: Heavy metal mean concentrations in plants

Target Hazard Quotient and Hazard Index of Heavy Metals

The Target Hazard Quotient **(**THQ) and Hazard Index (HI) from the heavy metals in water and biota for both seasons are shown in Tables 5 and 6. Table 5 shows the seasonal variation in the target hazard quotient and hazard index of heavy metals in surface water in dry season. Chromium and Mercury recorded zero concentrations in the biota (plants and fishes) sampled. The target hazard quotient and hazard index of heavy metals in surface water for Cadmium ranged from 0.81 to 0.89mg/kg in the plants and 0.42 to 0.72mg/kg in the fishes; Copper 0.02 to 0.07 mg/kg in the plants and 0.04 mg/kg only recorded for Tilapia fish. Lead ranged from 0.36 to 0.78mg/kg in plants and 0.09 to 0.82mg/kg in the fishes while Zinc had 0.01mg/kg in the plants and was absent in the fishes. Table 6 shows the seasonal variation in the target hazard quotient and hazard index of heavy metals in surface water in wet season. Arsenic, Chromium and Mercury, Copper and Zinc recorded zero values in the all samples in the study. Concentration target hazard quotient and hazard index of heavy metals in surface water for Cadmium ranged from 0.65 to 0.66mg/kg in plants and 0.65 to 0.68 mg/kg in the fishes.

Table 5: Seasonal Variation in the Target Hazard Quotient and Hazard Index of Heavy Metals in Biota for Dry Season

Metals	Arrow Head Plant (*Sagittaria latifolia*)	*Christmas Bush Plant (Ceratopetalum gummiferum)*	Tilapia (*Oreochromis niloticus*)	Cat Fish (*Clarias gariepinus*)
As	7.54	9.24	0.00	0.00
Cd	0.81	0.89	0.72	0.42
Cr	0.00	0.00	0.00	0.00
Cu	0.02	0.07	0.04	0.00
Pb	0.36	0.78	0.09	0.82
Hg	0.00	0.00	0.00	0.00
Zn	0.01	0.01	0.00	0.00
Fe	0.42	0.37	0.56	0.28
HI	9.15	11.36	1.42	1.53

Table 6: Seasonal Variation in the Target Hazard Quotient and Hazard Index of Heavy metals in Biota for Wet Season

Metals	Arrow Head Plant (*Sagittaria latifolia*)	*Christmas Bush Plant (Ceratopetalum gummiferum)*	Tilapia (*Oreochromis niloticus*)	Cat Fish (*Clarias gariepinus*)
As	0.00	0.00	7.05	7.05
Cd	0.66	0.65	0.65	0.68
Cr	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00
Pb	0.09	0.03	0.09	0.09
Hg	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00
Fe	0.18	0.14	0.32	0.19

HI	0.93	0.83	8.12	8.02

DISCUSSION

The safety of water and biota regarding contaminants such as heavy metals is a major concern due to their deleterious impacts on human health. More attention is gained when these contaminants are found in drinking water which is most frequently consumed by the most vulnerable population. Heavy metals persist naturally in the environment, however elevated concentrations in the food chain are primarily linked to man-made environmental pollution. Cadmium and Lead are reported as the most toxic heavy metals, while over consumption of some essential mineral elements also can result to poisonous effects (Unak *et al.,* 2007).

Heavy metals are a threat for human health due to their potential damage to human cells and the skeletal system, osteoporosis, kidney failure and lung and blood cancer (Kumar *et al.,* 2007). The routes of entry for these heavy metals are ingestion or inhalation (Mendil, 2006). The toxicity of heavy metals are dependent on a number of factors, the most critical of which are ingestion rate and route, bioavailability, gender, age, excretion rate and the chemical state of the heavy metals (Enb *et al.,* 2009). Among environmental pollutants, heavy metals are of particular concern because they are known for their persistent behaviour in the environment and are harmful, because of their ability to bioaccumulate in the environment causing damage to plants and animal tissues. (Censi *et al*., 2006; Zheng *et al*., 2013). Heavy metals such as Lead (Pb), Cadmium (Cd), Mercury (Hg), Zinc (Zn), and Chromium (Cr), are introduced into the environment from geogenic (weathering) and anthropogenic sources. It is difficult to measure the input of metals in the environment as a result of anthropogenic activities. Concentration of heavy metals in aquatic ecosystem has increased considerably due to the inputs of industrial waste, sewage, runoff and agricultural wastes (Li *et al.,* 2010). In this study, Arsenic, Chromium and Mercury were below detectable limits in the samples across the stations which was far below the permissible limit of 0.01mg/kg by WHO except in Umuechem in Etche and Imo Gate along Oyibo LGAs. The high concentrations of Lead, Cadmium etc recorded in this study can result to exposures of aquatic flora and fauna to unacceptable effects apart from its vital role in carbohydrate metabolism (i.e., glucose tolerance and glycogen synthesis). Among the hazardous heavy metals, Cadmium and Lead recorded values above the WHO permissible limits. However, Sediments are an important sink and long-term store of a variety of pollutants, particularly heavy metals, and may serve as an enriched source of food for benthic organisms in estuarine ecosystems because they are in constant flux with the overlying water column (Bai *et al*., 2010; Deng *et al*., 2010; Ayejuyo *et al.,* 2010). The occurrence of increased concentrations of heavy metals in sediments can be a good indicator of man-induced pollution rather than natural enrichment of the sediment by geological weathering (Adebowale *et al.,* 2008; Wang *et al.,* 2010). However, metals cannot always be fixed by sediments permanently. Some of the sediment-bound metals may be remobilized and released into water as a result of changes in environmental conditions that leads to acidification and reduction/oxidation and impose adverse effects on living organisms (Liu, 2009).

The presence of heavy metals in the two fish species (Tilapia and Catfish) showed that all heavy metals analysed except Lead was higher in Tilapia when compared to Catfish. Cadmium in Tilapia has 0.42mg/kg while the Catfish recorded 0.32mg/kg. Lead concentration in Tilapia fish was 0.2mg/kg while Catfish had 0.9mg/kg. The mean concentration of Zinc in Tilapia was 0.54mg/kg while the Catfish had a mean of 0.32mg/kg. Iron concentration in Tilapia fish was 1.56 mg/kg while Catfish had 0.88mg/kg. The result of heavy metal concentrations recorded in this study are similar to those obtained by Ogbonna and Origbe (2021), who carried out a research on heavy metal concentration of surface water, sediment and fishes impacted by crude oil pollution in Bodo/Bonny River, Nigeria, which revealed that the concentration of metals like Iron, Zinc, Chromium, Copper, Cadmium and Lead in sediment indicating pollution. It also shows that the accumulation of heavy metals is predominant in sediments rather than of water and organisms, which can be linked to the fact that sediments act as an important host for all toxic metals, contaminants and dead organic matter descending from the ecosystem above. Fishes ingest heavy metals from the surrounding waters, planktons, other feeding diets and sediments resulting to their accumulation in reasonable amounts (Olawusi-Peters and Akinola 2017). Metals such as Copper and Zinc are essential for metabolism in fish at low concentrations while some others such as Lead and Cadmium are toxic to living organisms (Virha *et al.,* 2011). When present at high concentrations, these metals impose serious damage to metabolic, physiological and structural systems of organisms in the aquatic environment. These therefore shows the impact of anthropogenic and industrial activities to the concentration of heavy metal. Although, low concentration of heavy metals such as zinc and copper can cause stress in fish which can lead to smaller body weight, thereby reducing their ability to compete for food and habitat. This phenomenon suggests that metal levels in the surrounding biota are very low and are not interfering with the normal metabolic processes of the fishes. This finding showed that fishes can bioaccumulate these metals and therefore may not be safe for human consumption.

Physico-chemical analysis of Surface water samples

Physicochemical properties in water serve as measure of water contamination and are usually evaluated to determine the quality of the water body. Management of water is done to ensure that contaminants that gets into it does not exceed the set or permissible limits, thus, the quality of water is related to the expected use of the water for fishing, recreation, or wild life (Amaku and Akani, 2016). In this study, certain physicochemical parameters such as: pH, Temperature, Electrical Conductivity, Total Dissolved Solids (TDS), Turbidity, Total Suspended Solids (TSS) Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) of the surface water from Otamiri and Imo Rivers in Etche LGA, Rivers State were evaluated.

pH is important in water quality assessment as it influences many biological and chemical processes within a water body (Meregini-Ikechukwu *et al.,* 2020). The results of pH showed that the mean values varied in all the sample stations. The mean pH values recorded in this study were below the acceptable range of 6.5 - 8.5 as prescribed by the regulatory agency (NSDWQ, 2008) and 7.0 to 8.5 by WHO. The pH values recorded ranged from 5.56±0.69 to 5.80±0.22 which were slightly acidic. The pH range for optimum growth of most aquatic bacteria is pH 6.5 and 8.5 (Rheinheimer, 1974), which were in the range of values reported in this study. The variations in pH observed is in consonance with Obunwo and Chukwudi (2015), who reported that variations in pH in surface water were due to the inherent geochemical properties of the formations of chemicals being carried. The pH of water is a property that plays vital role in different biological functions since it has the tendency to impact on the enzymes, hormonal balance, proteins, growth as well as control the metabolism of biota and dissolution of minerals (Yao and Byme, 2001).

Temperature values recorded in the water samples of Otamiri and Imo River in Etche were reasonably warm with consistent temperatures, value within the mesophilic range. The overall mean temperature value for each station was highest in Umuechem and Chokocho station had the least. The range of values were normal for water in the tropics, and are attributed to weather conditions of the study area which is characterized by hot dry season and cold wet season (Akpan *et al.*, 2015). The difference in the water temperature between the stations were expectedly due to the various activities at the sampling stations, but statistically at p-value < 0.05 was obtained when tested against WHO temperature standards, showed a significant difference between the means across the sample stations.

Electrical conductivity (EC) in natural waters is the normalized measure of the ability of the water to conduct electricity. Water with EC values between 500 and 1000µs /cm are not usually recommended for human consumption, and such waters are also not suitable for irrigation except for high salt tolerant crops with special techniques of management (Kuyeli *et al.,* 2009). The mean electrical conductivity (EC) values measured in the water sample from the five sampled stations of Otamiri and Imo River were generally low. EC values measured in Odagwa was the highest followed by Umuebulu while Umuechem recorded the least value (73.00 ± 12.73). Akpan *et al* (2015) explained that precipitation, fresh water discharge and low temperature conditions do not favour high concentration of ionized substances in water. Ephraim and Ajayi (2015), considered waters with EC values less than 250µs/cm as excellent waters. Olawusi-Peters(2010) stated that the distribution of fish generally follows environmental quality parameters such as conductivity, which is an index of the total ionic content of water, and indicates the freshness or otherwise of the water. Conductivity values from this study show that the sample stations contains appreciable amount of dissolved ions thus forming a saline barrier for the survival of sensitive organisms. It is important in fish spawning habitat, as many species are sensitive to abrupt changes in the salinity of their environment.

Total Dissolved Solids (TDS) are the inorganic matters and small amounts of organic matter, which are present as solution in water. The TDS values for the five (5) sample stations were below the standard or allowable value of the TDS by WHO. The values found in the water samples were all below the maximum limit of 500mg/l. The highest TDS valueof 62.50mg/l was obtained from Odagwa and the leastTDS values of 39.00mg/l was recorded for Umuechem.

Total suspended solids (TSS) are the dry-weight of suspended particles that are not dissolved, in a water sample that can be trapped by a filter and analyzed. TSS values for the sample stations ranged from 2.00mg/l to 37.00mg/l. Umuechem and Chokocho had mean values of 6.50mg/l and 2.00mg/l respectively, lower than the WHO permissible limit while Odagwa, Umuebulu and Imo Gate Stations had higher values of 37.00mg/l, 31.50mg/l and 30.50mg/l respectively. High concentration of suspended solids can lower water quality by absorbing light hence warmer water and lesser potential of water to hold oxygen necessary for aquatic life.

Biological Oxygen Demand (BOD), is a measure of the biological activities in a water body, which gives an indication of the organic load of water bodies, especially those receiving organic effluent. Biochemical Oxygen Demand (BOD_5) is used as an index to determine the amount of dissolved oxygen required by aerobic biological organisms (microorganisms) to decompose organic materials and also biological activity in the water. Hence high concentrations of BOD is an indication of organic pollution (Ngah *et al.,* 2017). The values for BOD ranged from 2.31 mg/l to 2.76 mg/l..

Chemical Oxygen Demand (COD)is a measure of the total quantity of oxygen required to oxidize all organic material into carbon IV oxide (CO_2) and water. The sampled water had mean value range between 4.56mg/l and 5.12mg/l. All sample stations had mean values below the WHO permissible limit. When subjected to statistical test the values differed significantly at p-value of 0.000

Estimated Daily Intakes of Heavy Metals (EDI)

Heavy metals are considered as one of the most important constituents of food contamination from the environment due to its ability to persist, accumulate, and become toxic to living organism through consumption. Human exposure to heavy metals occurs via various routes such as oral ingestion, dermal contact or inhalation. The degree of toxicity of heavy metals to human health is directly related to their daily intake. The first step in the non-carcinogenic analysis is the computation of the estimated daily intake (EDI) values.

Bioaccumulation Factors and Pollution Load Index

The values obtained for bioaccumulation factor, pollution load index and modified contamination degree respectively in biota (fishes and plants) for both seasons show that the sample stations where moderately polluted by Cadmium, Copper, Lead and Iron, while Zinc pollution was severe in the plants and fish species in the wet season. For dry season the biota from the sample stations were very severely polluted by Cadmium, Lead and Iron while Copper and Zinc excessively polluted the biota. Aquatic organisms have the ability to accumulate heavy metals from various sources including sediments, soil erosion and run off, air depositions of dust and aerosol and discharges of waste water (Asaolu, 1998).

For this reason, monitoring of fish tissue contamination may serve as early warning indicator of contamination or related water quality problems (Kpobari *et al*., 2013). Several studies have indicated that fish and shellfishes are able to accumulate and retain heavy metals from their environment depending upon exposure concentration and duration as well as salinity, temperature, hardness and metabolism of the animals (Karthikeyan *et al*., 2007, Olawusi-Peters *et al.,* 2014a & 2015). Fishes absorb heavy metals into their tissue directly from the water across the surface of the gills and ingestion of sediment particles containing heavy metals as part of their feeding process (Lorenzo *et al*., 2003, Cruz-Rodriguez and Chu, 2003). Also, phytoplankton can take up high levels of heavy metals from contaminated waters and when shrimps consumed planktons containing elevated levels of heavy metals, the heavy metals become concentrated in them (Janssen and Scholz, 1979). Also, their levels of contamination are of great interest as they pose health risk to those humans who consume them

Conclusion

This study has shown clearly that significant risks are inherent in both biota and water samples obtained from the different sample stations. This is attributed to contamination from organic pollutants such as heavy metals, industrial chemicals, sewage discharged from sources like urban runoffs, industrial activities, subsurface infiltration, or atmosphere precipitation effluents, sewage treatment plants, chemical fishing activities, leachate from decomposing refuse dumps, agricultural fertilizer applications. The cancer risk from the present study showed that the highest burden of likely cancer cases was from lead and arsenic. Notably, the cancer risk due to exposure to cadmium was relatively lower in this study. The total cancer risk for both biota and water samples from Umuechem, Chokocho, Odagwa, Umuebulu and Imo gate were all above the recommended safety margin thereby indicating the risk of cancer on the general population and exposed age groups of children and adults.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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