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Occurrence, Distribution and Contamination Levels of Heavy Metals and Phenolic Endocrine-Disrupting Chemicals in Water, Sediment, and Oreochromis niloticus (TILAPIA) in Bonny River, Nigeria

 Nwoke, I. B¹, Boma, M²

1,2. Department of Chemistry Ignatius Ajuru University of Education Rumuolemini, Port Harcourt. Rivers State, Nigeria

 *Correspondence: imaobong67@gmail.com

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Abstract: This study investigated the concentrations of some heavy metals and phenolic endocrine-disrupting chemicals (EDCs) in surface water, sediment, and biota in the creeks and rivers around Bonny River, Rivers state, Nigeria. Water and sediment samples were collected from four (4) different sampling locations along the river, while the biota (tilapia) was bought from local fishermen along the river banks. The samples were prepared and analyzed for heavy metals using Atomic Absorption Spectrophotometer, and the samples for EDCs were analyzed using Gas chromatograph – Mass Selective detector system (GC/MS). The data obtained were further subjected to index models (Contamination factor and Pollution load index) of heavy metals. The results from the detectable concentrations (mg/l) for heavy metals in water were: Pb (3.23 ± 1.11), Cd (0.05 ± 0.06), Cr (3.67 ± 1.48), Ni (0.14 ± 0.16), As (0.28 ± 0.24), and V (0.01 ± 0.01). Heavy metals concentration (mg/kg) in sediment were: Pb (7.59 ± 3.17), Cd (0.15 ± 0.12), Cr (9.33 ± 3.84), Ni (2.39 ± 1.98), As (0.96 ± 0.83), and V (0.08 ± 0.10). The results from the detectable concentrations (mg/l) for heavy metals in biota were: Pb (1.07 ± 0.00), Cd (0.46 ± 0.12), Cr (1.36 ± 0.20), Ni (0.36 ± 0.06), As (0.38 ± 0.05), and V was below detection limit (BDL < 0.001). The results, on comparison with international and local standards (WHO, NIS, EPA) revealed that all the heavy metals analyzed in water were above the limits, except for V in water. In sediment, all the heavy metals analyzed were below the limits, and in fish, metals Pb and Cd were above the limits, Cr, Ni, and As were below the limits, and V was undetected. The mean concentration ($\mu\text{g/l}$) of EDCs in water was 34.08 ± 22.21 , in sediment was 51.84 ± 33.61 , and in biota recorded 23.98 ± 13.75 . The contamination factor for water shows that there is very high degree of contamination of Pb, Cd, Cr, and As, with moderate degree of contamination for Ni and V. No degree of contamination was seen for sediments, and in biota, moderate degree contamination was seen for Pb and Cr, while low degree of contamination was seen for Cd, Ni, As, and no degree contamination for V. From the findings of this study, it is therefore important that the water should not be consumed until remediation processes are in order.

Keywords: Occurrence, Contamination, Heavy Metals, Phenolic Endocrine-Disrupting Chemicals (Edcs), Water, Sediment

Introduction

Since the early 2000s, the Nigerian manufacturing sector has progressively expanded as a result of economic reforms and industrial policy adjustments [1]. Contamination of river water and surface sediments has become one of the key environmental issues in rapidly urbanizing towns, especially where water quality management and sanitation infrastructure fail to keep pace with population growth and urban expansion [2][3].

Water resources are critical to environmental sustainability, socioeconomic development, and human well-being. However, rapid industrialization, urban expansion, agricultural intensification, and inadequate wastewater management have increasingly compromised aquatic ecosystems worldwide [4]. Among the most pervasive pollutants are heavy metals and endocrine-disrupting chemicals (EDCs), particularly phenolic compounds, which pose significant threats to aquatic life and public health due to their toxicity, persistence, and bioaccumulative properties. Phenolic endocrine-disrupting chemicals have the potential to disrupt hormonal systems in aquatic organisms and pose risks to human health. Field and laboratory studies provide strong evidence that exposure to EDCs can lead to abnormal development, reproductive disruption, and endocrine imbalance in fish and other aquatic species [5].

Heavy metals such as cadmium (Cd), lead (Pb), chromium (Cr), mercury (Hg), and arsenic (As) are naturally occurring elements that become toxic at elevated concentrations. Unlike organic pollutants that degrade over time, heavy metals are non-biodegradable and persist in the environment, accumulating in water, sediments, and aquatic organisms (Alloway, 2013). Similarly, phenolic EDCs—including bisphenol A (BPA), nonylphenol, and related derivatives—enter aquatic systems through industrial effluents, agricultural runoff, and domestic waste streams. These compounds interfere with hormonal regulation in organisms, resulting in reproductive, developmental, and immunological impairments even at low concentrations [5].

The Okrika–Bonny River system in Rivers State forms part of the ecologically sensitive Niger Delta and serves as a critical source of water, fisheries, and livelihoods for surrounding communities. *Oreochromis niloticus* (Nile tilapia) is one of the most economically important fish species in the region and a major protein source for local populations. However, environmental quality in the Okrika–Bonny River has been increasingly threatened by oil and gas exploration, petrochemical discharge, and poor waste management practices [6][7]. These pressures make the river highly vulnerable to contamination by hazardous substances.

Because of their ecological roles and trophic positions, water, sediments, and fish function as reliable indicators of environmental contamination. Sediments act as long-term sinks for heavy metals and phenolic EDCs, while fish accumulate contaminants through direct exposure and food chain transfer, posing potential risks to human consumers [8].

Previous studies in the Niger Delta have documented elevated concentrations of heavy metals and organic pollutants in aquatic environments [9][10]. However, there remains a significant gap in integrated risk assessments that simultaneously evaluate contamination in water, sediment, and biota while linking pollutant levels to ecological and human health outcomes. A comprehensive risk assessment is therefore necessary to quantify contaminant burdens, determine potential adverse effects, and inform effective management strategies to protect environmental and public health [11].

This study therefore aims to assess the occurrence, distribution, and contamination levels of selected heavy metals and phenolic endocrine-disrupting chemicals in water, sediment, and *Oreochromis niloticus* from the Okrika–Bonny River., this research will provide evidence-based insight into the environmental status of the river system and support sustainable water resource management.

Study Area

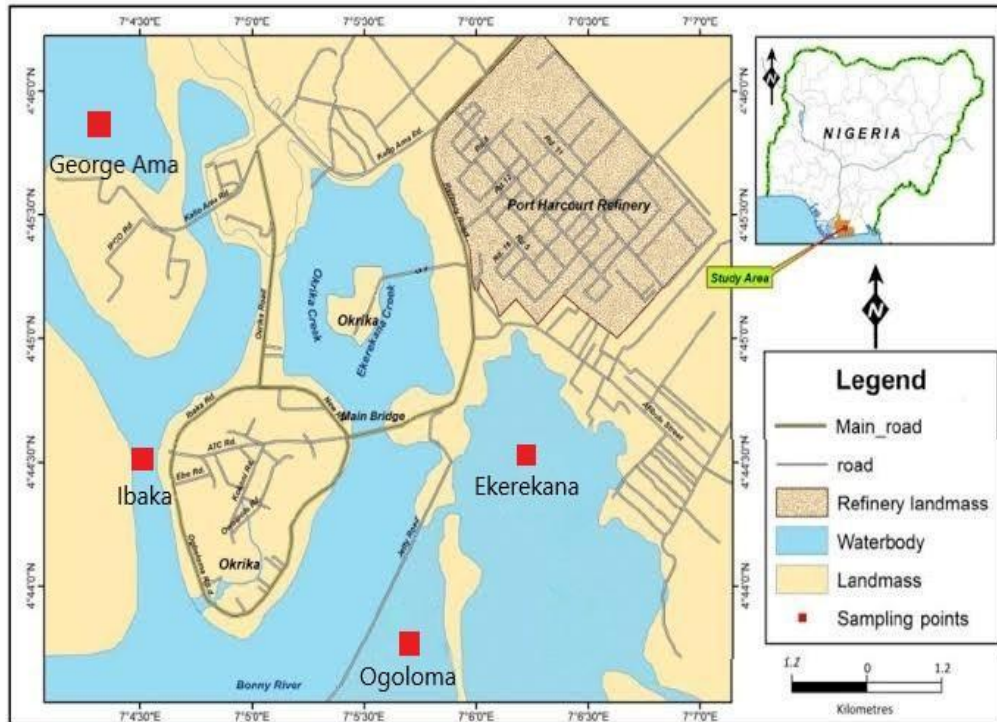


Figure 1. Map of Bonny River showing Sampling Locations.

The study area is in Bonny River and creeks around Okrika Local Government Area of Rivers State, Nigeria, a widespread river body which lies in the north bank of the Bonny River, about 35 miles (56 km) upstream from the Bight of Benin in the eastern Niger Delta region of Nigeria. It is a riverine and intertidal wetland which is linked to a maze of rivers and winding creeks, within which are stretches of marshy land having mangrove trees which comprises of tangled roots as the vegetation. The river is used as a major transportation route for people, various goods and services to different communities and areas, due to its easy accessibility and transport system. It is a typical estuarine tidal water zone characterized by various species of fishes, crabs, and periwinkles.

The river is characterized by activities such as fishing which is a major livelihood of residents, where fishermen from neighbouring and interconnected communities access the river for fishing purposes and these fish are sold at local markets and other nearby villages. Other activities such as boat repair are also done on the river, where petroleum diesel is emptied into the river during the cleaning and repair process, and also paints used for coating the metals used for the boat are leaked into the river body. The area is also home to a range of metal scrap companies where metals are collected, assembled, and then carefully selected to be melted and sold, or recycled for boat making, where some of these metals are left in the water over a period of time that induces rusting and decomposition of metals in the water.

The river also receives domestic waste from the dumping of refuse and sewage from households within the area. The area, like most parts of the Niger Delta has suffered extensive degradation due to oil exploration and exploitation as the oil industry has attracted many other industries and economic activities, which has in-turn lead to urban population, leading to a considerable volume of waste production. Indiscriminate direct or indirect discharge of wastes including domestic, refinery, and other kinds of industrial wastes could have great impact on the water quality in the river and its associated creeks.

The river is a recipient of wastewater from the Port Harcourt Refining Company (PHRC) which discharges directly into the river. It is also affected by accidental spillage of petroleum through legal or illegal oil bunker activities due to the river's importance as a transport route between rural and urban areas in the state. These various activities may lead to contamination from organic waste, metals,

petroleum, etc. which can affect aquatic and terrestrial life. Many urban and industrial wastes are rich in trace toxic elements [12].

Methodology

A random composite sampling method was used for this research, as it was aimed at getting an average concentration of the heavy metals and EDCs over sampling locations across the Bonny River. The samples were collected from four (4) different locations and made into composite samples. The samples for heavy metals were run in triplicates and the mean calculated. The samples for EDCs were run in triplicates and the mean calculated.

Sample collection

Sampling was carried out from four (4) designated locations in the Bonny River and creeks around Okrika, in which a boat was used to navigate the river to the various sampling stations. Sediment samples were collected at low tides at over a depth of 60cm deep to account for the toxic zone where aerobic respiration takes place and therefore, ease of chemical flow from the sediment to the water column. This was done by grab method using composite sampling method at three (3) points at each location to be able to determine seasonal variations and contaminant concentrations. The samples for heavy metals and phenolic EDCs were put in polythene bags previously washed in dilute hydrochloric acid (HCl).

Water samples were collected at low tides using amber bottles at the four (4) sampling locations using composite sampling method at three (3) points at each location to get an overall overview sample of each location, to represent the whole river. The sample bottles were washed with acetone to remove unwanted chemicals that may be in the bottles, rinsed three times with deionized water, and then rinsed again with the sample water at the collection locations before samples were collected. The samples for heavy metals were acidified to a pH of less than three (3) for preservation of target compounds by adding 1ml of concentrated HNO_3 per 250ml of the water sample.

The water samples for endocrine disrupting chemicals (EDCs) were acidified to a pH of less than or equal to two (≤ 2) to avoid degradation of the target compounds, while 1.0g of sodium azide was added to the sediment samples for EDCs to inhibit microbial growth, fix the organic matter, and slow down any possible decay [13].

The biota (tilapia) were bought from fishermen along the sampling locations. The biota, sediment and water samples were placed in a cooler with ice packs and immediately transported to the laboratory for analysis. Sample containers were labelled properly to reflect date, time of sampling and locations of various samples.

Sample Preparation and Analysis

Preparation of Standards

Standard solutions for lead (Pb), chromium (Cr), cadmium (Cd), nickel (Ni), arsenic (As) and vanadium (V) were prepared using zinc nitrate, cadmium chloride, chromium nitrate, nickel (II) nitrate, lead nitrate salts, arsenic trioxide, and vanadium pentoxide, for calibration of the instrument. Stock standards solutions of the metals of interest were prepared by weighing out the appropriate salt of the metal out as calculated in relation to the formula weight, dissolved in 1 dm^3 volumetric flask and made up to mark with deionized water [14]. The working standards of appropriate concentrations were prepared from the stock solutions by diluting appropriate volume with deionized water and made up to mark in 100 cm^3 volumetric flask and used for calibrating the AAS equipment.

For the G.C/MS, individual solutions of surrogates, internal standards, analytes, or mixture of analytes were purchased from commercial suppliers.

Preparation of Water Samples for Heavy Metal Analysis

For water samples, the sample was allowed to cool to room temperature at about 25°C, after which it was agitated and 10ml was taken using a measuring cylinder and then put into a beaker. 10ml Trioxonitrate (v) acid (HNO_3) was added to the conical flask containing the sample (1:1 ratio) to oxidize the sample. 1ml hydrogen tetraoxosulphate (vi) acid (H_2SO_4) was then added to the solution to further oxidize the sample, after which the solution was heated for about 10 minutes using water bath on a hot plate in a fume cupboard and allowed to cool. The solution was then filtered and diluted up to the 50ml

mark. The extracts from the digestion were substantially analyzed using Solar thermo elemental Atomic Absorption Spectrophotometer (Flame AAS: mode: S4 – 71096).

Preparation of Sediment Samples for Heavy Metal Analysis

Wet digestion method: The ration of the acids HNO_3 and HClO_4 used in the digestion were in the ratio of 5:1 [14]. The samples were first air dried, ground and homogenized using a mortar and pestle. Exactly 1.0g of each sample was weighed using analytical balance and placed into beakers. Exactly 20ml of concentrated trioxonitrate (v) acid was added and the solutions were kept for 24 hours, after which it was carefully heated on a hot plate connected to a sun bathe in a fume cupboard and 10ml of concentrated trioxonitrate (v) acid was added at intervals until the release red nitrous oxide (NO_2) stopped. The samples were allowed to cool, after which 2ml of perchloric acid (HClO_4) was added and heated until a clear sample solution was obtained. The samples were allowed to cool, filtered into 100ml volumetric flasks, before making up to the mark with deionized water. Blank sample solutions were also prepared using the same amount of reagents used in the sample digestion under same experimental conditions, but without the sample. The extracts from the digestion were substantially analyzed using Solar thermo elemental Atomic Absorption Spectrophotometer (Flame AAS: mode: S4 – 71096).

Preparation of Water Samples for EDCs

For water samples, liquid-liquid extraction was used. The water was first filtered through glass filters to remove suspended particles. Each cartridge was rinsed with 3ml of methylene chloride (CH_2Cl_2) and allowed to dry after each flush. The cartridges were then rinsed again with 3ml methanol, after which the cartridge packing was not allowed to go dry again. Each cartridge was washed again with 0.05 N of hydrochloric acid (HCl), but before the dilute acid drops below the top edge of the packing, the vacuum was turned off immediately. An additional 3ml of 0.05 hydrochloric acid (HCl) was added to the cartridge before the transfer tube was attached and the vacuum turned on. The inside of the sample bottles was rinsed with 10ml methylene chloride (CH_2Cl_2). At this point, the samples were added slowly and the vacuum was used to pull the solvent through the transfer tube and through the cartridge, collecting the solvent in a collection tube. A known volume of 3ml of methylene chloride (CH_2Cl_2) was then added to the top of the cartridge with disposable pipette, and the solvent pulled through the cartridge at low vacuum, such that the solvent exits the cartridge in dropwise fashion. The solution was then passed through the drying column which was packed with 5 – 7g of anhydrous sodium sulfate (Na_2SO_4) and collected in a clean collection tube, after which the sodium sulfate (Na_2SO_4) was also washed with 2ml methylene chloride (CH_2Cl_2) and collected in the same tube. The extract was then concentrated to approximately 0.9ml in warm (40°C) water bath under a gentle stream of nitrogen (concentration to less than 0.5ml would result in loss of analytes). Methylene chloride (CH_2Cl_2) was added to make the final volume up to 1ml. The extract was then sent to the Gas chromatograph – Mass Selective detector system (GC/MS) for analysis.

Preparation of Sediment Samples for EDCs

The sediment samples were first ground and homogenized using mortar and pestle in the presence of an anhydrous sulphate. About 5g of the ground sample was weighed using an analytical balance and put into a centrifuge tube spiked with 25ml of a mixture of dichloromethane and hexane in the ratio of 2:1. The tube was ultrasonicated for 15 minutes and then centrifuged at 1500 rpm for 5 minutes. The extraction was repeated with 10ml of the solvent mixture. Both extracts were combined, concentrated to about 2ml and then dried over anhydrous sodium sulphate. The extract was then sent to the Gas chromatograph – Mass Selective detector system (GC/MS) for analysis.

Contamination factor

The Contamination Factor (CF) is a dimensionless factor used to assess the degree of contamination of heavy metals in a particular environmental sample (such as soil, sediment, or water). It is commonly used in environmental studies to quantify the extent of pollution by heavy metals. CF was used to determine the levels of water, sediment and biota contamination by heavy metals.

Table 1.1. Intervals of Contamination Factor.

Degree	Contamination Factor
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Low degree	CF < 1
No contamination	CF = 1
Moderate degree	CF ≤ 3
Considerable degree	CF > 3/4
Very high degree	CF ≥ 6

$$\text{Contamination factor (CF)} = \frac{C_s}{C_b} \tag{1}$$

Where Cs is the concentration of the heavy metal in the sample, and Cb = background or reference concentration of the heavy metal from known standards.

Pollution load index (PLI)

The Pollution Load Index (PLI) is a numerical indicator used in environmental science to assess the overall pollution status of a given area or region. It is a composite index that takes into account multiple pollutants and their concentrations. The Pollution Load Index is particularly useful in evaluating the cumulative impact of various pollutants on the environment. The PLI was determined as the nth root of the product of nCFs, as calculated based on the formula by Ranjani et al. (2021).

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times \dots \times CFn} \tag{2}$$

Where n is the number of variables, and CF are the calculated contamination factors for each target metal in the river.

PLI = 0 indicates environmental quality is within standard limits and there is only baseline level of contaminants, and PLI > 1 indicates that the area is polluted. The higher the PLI, the higher the degree of pollution.

The PLI evaluated the overall toxicity status of the samples.

Results

Table 1. Mean Concentration of Heavy Metals in Water of Bonny River.

Parameter	Station 1	Station 2	Station 3	Station 4	Mean ± SD
Lead (Pb)	2.12 ± 0.63	2.43 ± 0.32	4.28 ± 1.06	4.08 ± 0.93	3.23 ± 1.11
Cadmium (Cd)	0.03 ± 0.03	0.01 ± 0.01	0.02 ± 0.01	0.13 ± 0.04	0.05 ± 0.06
Chromium (Cr)	2.13 ± 0.99	3.53 ± 0.78	3.35 ± 2.16	5.68 ± 1.38	3.67 ± 1.48
Nickel (Ni)	0.03 ± 0.02	0.06 ± 0.03	0.10 ± 0.05	0.38 ± 0.32	0.14 ± 0.16
Arsenic (As)	0.04 ± 0.01	0.13 ± 0.06	0.42 ± 0.28	0.54 ± 0.30	0.28 ± 0.24
Vanadium (V)	0.01 ± 0.01	0.00 ± 0.00	0.01 ± 0.01	0.03 ± 0.02	0.01 ± 0.01

Table 2. Mean Concentration of Heavy Metals in Sediment of Bonny River.

Parameter	Station 1	Station 2	Station 3	Station 4	Mean ± SD
Lead (Pb)	4.38 ± 0.40	6.50 ± 0.62	7.57 ± 1.22	11.91 ± 1.39	7.59 ± 3.17
Cadmium (Cd)	0.07 ± 0.08	0.07 ± 0.01	0.14 ± 0.03	0.32 ± 0.14	0.15 ± 0.12
Chromium (Cr)	6.04 ± 1.71	7.45 ± 3.11	9.02 ± 1.74	14.79 ± 2.69	9.33 ± 3.84
Nickel (Ni)	0.32 ± 0.12	1.10 ± 0.71	3.76 ± 0.78	4.37 ± 1.23	2.39 ± 1.98
Arsenic (As)	0.11 ± 0.02	0.63 ± 0.43	1.03 ± 0.24	2.08 ± 0.68	0.96 ± 0.83
Vanadium (V)	0.01 ± 0.01	0.02 ± 0.01	0.05 ± 0.04	0.22 ± 0.02	0.08 ± 0.10

Table 3. Mean Concentration of Heavy Metals in Biota of Bonny River.

Parameter	Fish 1	Fish 2	Mean \pm SD
Lead (Pb)	1.07 \pm 0.71	1.07 \pm 0.57	1.07 \pm 0.00
Cadmium (Cd)	0.37 \pm 0.01	0.54 \pm 0.01	0.46 \pm 0.12
Chromium (Cr)	1.22 \pm 0.63	1.50 \pm 1.52	1.36 \pm 0.20
Nickel (Ni)	0.32 \pm 0.01	0.40 \pm 0.03	0.36 \pm 0.06
Arsenic (As)	0.34 \pm 0.01	0.41 \pm 0.01	0.38 \pm 0.05
Vanadium (V)	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00

Table 4. Mean Concentration of EDCs in Water of Bonny River.

Parameter	Station 1	Station 2	Station 3	Station 4	Mean \pm SD
Phenol	3.83 \pm 0.02	1.63 \pm 0.01	4.41 \pm 0.03	2.73 \pm 0.02	3.15 \pm 1.23
2-Chlorophenol	1.34 \pm 0.01	8.28 \pm 0.01	2.22 \pm 0.04	1.51 \pm 0.02	3.34 \pm 2.32
4-Chlorophenol	0.94 \pm 0.01	2.22 \pm 0.03	5.15 \pm 0.02	0.75 \pm 0.02	2.26 \pm 2.03
2-Methylphenol	1.56 \pm 0.03	0.33 \pm 0.01	0.51 \pm 0.02	1.42 \pm 0.01	0.95 \pm 0.62
4-Methylphenol	3.44 \pm 0.02	1.81 \pm 0.01	2.12 \pm 0.01	3.91 \pm 0.01	2.82 \pm 1.02
2-Nitrophenol	1.41 \pm 0.01	2.43 \pm 0.01	1.50 \pm 0.01	1.15 \pm 0.03	1.62 \pm 0.56
3-Nitrophenol	2.91 \pm 0.02	1.63 \pm 0.02	4.17 \pm 0.01	6.82 \pm 0.01	3.88 \pm 2.22
4-Nitrophenol	1.19 \pm 0.02	4.92 \pm 0.02	8.21 \pm 0.02	1.40 \pm 0.01	3.93 \pm 3.33
2,3-Dichlorophenol	1.91 \pm 0.03	6.53 \pm 0.01	4.51 \pm 0.02	1.53 \pm 0.02	3.62 \pm 2.35
2,4-Dichlorophenol	3.62 \pm 0.02	3.72 \pm 0.02	1.47 \pm 0.02	3.62 \pm 0.02	3.11 \pm 1.09
2,5-Dichlorophenol	0.44 \pm 0.03	2.01 \pm 0.03	0.82 \pm 0.01	0.17 \pm 0.02	0.86 \pm 0.81
3,4-Dichlorophenol	1.31 \pm 0.02	2.18 \pm 0.01	7.26 \pm 0.06	1.44 \pm 0.02	3.05 \pm 2.84
3,5-Dichlorophenol	0.54 \pm 0.03	2.51 \pm 0.02	1.34 \pm 0.02	1.54 \pm 0.03	1.48 \pm 0.81
Total	23.72 \pm 0.24	40.20 \pm 0.17	43.68 \pm 0.28	27.98 \pm 0.21	34.08 \pm 22.21

Table 5. Mean Concentrations of EDCs in Sediment of Bonny River.

Parameter	Station 1	Station 2	Station 3	Station 4	Mean \pm SD
Phenol	4.59 \pm 0.12	3.53 \pm 0.03	3.83 \pm 0.02	6.43 \pm 0.03	4.60 \pm 1.30
2-Chlorophenol	2.55 \pm 0.32	1.81 \pm 0.03	4.61 \pm 0.02	1.71 \pm 0.02	2.67 \pm 1.35
4-Chlorophenol	10.79 \pm 0.05	7.86 \pm 0.03	15.15 \pm 0.02	2.53 \pm 0.02	9.08 \pm 5.30
2-Methylphenol	3.92 \pm 0.01	9.33 \pm 0.02	3.52 \pm 0.02	8.75 \pm 0.01	6.38 \pm 3.09
4-Methylphenol	5.93 \pm 0.02	1.52 \pm 0.02	4.46 \pm 0.02	1.15 \pm 0.02	3.26 \pm 2.31
2-Nitrophenol	1.86 \pm 0.02	18.83 \pm 0.01	1.31 \pm 0.01	3.83 \pm 0.01	6.46 \pm 8.32
3-Nitrophenol	2.23 \pm 0.03	1.18 \pm 0.01	2.53 \pm 0.02	1.65 \pm 0.02	1.90 \pm 0.60
4-Nitrophenol	1.63 \pm 0.02	4.28 \pm 1.34	1.84 \pm 0.02	3.72 \pm 0.01	2.87 \pm 1.33
2,3-Dichlorophenol	1.22 \pm 0.02	4.46 \pm 2.36	1.60 \pm 0.01	4.52 \pm 0.02	2.95 \pm 1.79
2,4-Dichlorophenol	1.82 \pm 0.01	2.46 \pm 0.99	1.44 \pm 0.03	2.63 \pm 0.01	2.09 \pm 0.55
2,5-Dichlorophenol	6.93 \pm 0.01	2.42 \pm 1.25	0.92 \pm 0.02	3.45 \pm 0.01	3.43 \pm 2.56
3,4-Dichlorophenol	1.72 \pm 0.02	1.30 \pm 0.02	7.25 \pm 0.01	8.14 \pm 0.04	4.60 \pm 3.59
3,5-Dichlorophenol	0.86 \pm 0.03	3.84 \pm 0.02	0.88 \pm 0.02	0.65 \pm 0.02	1.56 \pm 1/53
Total	46.05 \pm 0.66	62.81 \pm 6.11	49.34 \pm 0.20	49.17 \pm 0.23	51.84 \pm 33.61

Table 6. Mean Concentrations of EDCs in Biota of Bonny River.

Parameter	Fish 1	Fish 2	Mean ± SD
Phenol	1.55 ± 0.12	0.77 ± 0.05	1.16 ± 0.55
2-Chlorophenol	2.76 ± 0.07	1.52 ± 0.02	2.14 ± 0.88
4-Chlorophenol	0.11 ± 0.02	2.15 ± 0.02	1.13 ± 1.44
2-Methylphenol	2.93 ± 0.02	1.82 ± 0.03	2.38 ± 0.78
4-Methylphenol	2.33 ± 0.02	3.44 ± 0.01	2.88 ± 0.78
2-Nitrophenol	0.49 ± 0.01	3.94 ± 0.03	2.22 ± 2.44
3-Nitrophenol	0.23 ± 0.03	1.16 ± 0.02	0.70 ± 0.66
4-Nitrophenol	4.18 ± 0.01	2.24 ± 0.01	3.21 ± 1.37
2,3-Dichlorophenol	2.13 ± 0.02	0.35 ± 0.01	1.24 ± 1.26
2,4-Dichlorophenol	1.95 ± 0.01	4.12 ± 0.01	3.03 ± 1.53
2,5-Dichlorophenol	0.62 ± 0.02	0.90 ± 0.02	0.76 ± 0.20
3,4-Dichlorophenol	1.10 ± 0.03	0.65 ± 0.02	0.88 ± 0.32
3,5-Dichlorophenol	3.34 ± 0.02	1.17 ± 0.02	2.26 ± 1.53
Total	23.73 ± 0.37	24.23 ± 0.25	23.98 ± 13.75

Table 7. Contamination Factor and Pollution Load Index of Heavy Metals in Water of Bonny River

Parameter	Station 1	Station 2	Station 3	Station 4
Lead (Pb)	212.00	243.00	428.00	408.00
Cadmium (Cd)	10.00	3.33	6.67	43.33
Chromium (Cr)	42.60	70.60	67.00	113.60
Nickel (Ni)	0.43	0.86	1.43	5.43
Arsenic (As)	4.00	13.00	42.00	54.00
Vanadium (V)	0.50	0.00	0.50	1.50
PLI	6.53	9.28	13.38	30.98

Table 8. Contamination Factor and Pollution Load Index of Heavy Metals in Sediment of Bonny River

Parameter	Station 1	Station 2	Station 3	Station 4
Lead (Pb)	0.01	0.02	0.02	0.03
Cadmium (Cd)	0.00	0.00	0.00	0.00
Chromium (Cr)	0.06	0.07	0.09	0.15
Nickel (Ni)	0.01	0.03	0.11	0.12
Arsenic (As)	0.00	0.00	0.00	0.01
Vanadium (V)	0.00	0.00	0.00	0.00
PLI	0.13	0.19	0.24	0.13

Table 9. Contamination Factor and Pollution Load Index of Heavy Metals in Fish of Bonny River.

Parameter	Station 1	Station 2
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Lead (Pb)	2.14	2.14
Cadmium (Cd)	7.40	10.80
Chromium (Cr)	0.61	0.75
Nickel (Ni)	0.53	0.67
Arsenic (As)	0.68	0.82
Vanadium (V)	0.00	0.00
PLI	0.33	0.49

Discussion

Mean Levels of Heavy Metals in Water of Bonny River

The mean levels of Pb in the river ranged between 2.12 ± 0.63 to 4.28 ± 1.06 mg/l across all stations and the overall mean was 3.23 ± 1.11 mg/l. The highest value of Pb was discovered in station 3 (4.28 ± 1.06 mg/l) and the lowest was discovered in station 1 (2.12 ± 0.63 mg/l). The mean concentration of Pb found in all stations were discovered to be above WHO and NIS recommended limits of 0.01 mg/l. This may be attributed to smelting and drainage from both active and inactive bunkering operations, burning of coal from the activities of oil companies, and welding operations in the area. These operations emit polluted chemicals into the atmosphere which in-turn interact with the water. Pb has no beneficial or nutritional effect in the body, hence it becomes a matter of urgency when Pb is released into the atmosphere in high concentrations as it has been well documented that Pb causes adverse effects on human health [15]. In light of the toxic nature of Pb, a number of international agencies have issued advisory standards for or enforceable regulations for Pb levels in different media. Protecting children from exposure to Pb is imperative to promote long-term good health as no safe blood Pb level in children has been identified [16]. Low levels of Pb in the blood of children can result in anemia, hearing problems, slowed growth, lowered IQ, and behavior and learning problems [17].

The gastrointestinal tract can readily absorb lead. The bones, kidneys, and liver absorb between 70 and 90% of the lead that is ingested (Tokahoglu et al., 2007) and decreases some of the functions of the liver membrane's permeability as well as the brain's cells (Matoso & Cadore, 2012). Pb is also harmful to adults and exposure to Pb can cause cardiovascular effects, increased blood pressure, decreased kidney function, reproductive issues in both men and women [17]. Mean levels of Zn recorded in this study were high compared to the result recorded by Marcus et al. in Okrika (0.0059 mg/l) and this can be attributed to the continuous industrial activities whose emissions react with the river [12]. Results from this study were higher in comparison to a study by Dibofori-Orji et al. in Woji Creek where the level of Pb ranged from 0.229 ± 0.333 mg/l to 1.534 ± 0.103 mg/l [18].

The mean levels of Cd in the river ranged between 0.01 ± 0.01 to 0.13 ± 0.04 mg/l across all stations and the overall mean was 0.05 ± 0.06 mg/l. The highest value of Cd was discovered in station 4 (0.13 ± 0.04 mg/l) and the lowest was discovered in station 2 (0.01 ± 0.01 mg/l). The mean concentration of Cd found in all stations was discovered to be above WHO and NIS recommended limits of 0.003 mg/l. Cd is a by-product of zinc-production and is one of the utmost toxic elements known to man as it is efficiently reserved in the body once it enters the body, where it accumulates throughout life [19]. Dumping of wastes and phosphate fertilizers are routes through which Cd enters into the environment [20]. It is not essential for biological systems, hence has no benefit to the ecosystem at large, and multiple toxic effects have been recorded. Cd is highly toxic to humans and animals at very low concentrations. Cd has been linked to having carcinogenic properties. Exposure to Cd has been linked to lung cancer as well as cancers of the prostate, kidney, liver, hematopoietic system, pancreas, testicles, and stomach [21]. Industrial activities, waste treatment plants, unsafe use, handling and disposal of Ni-Cd batteries, anthropogenic activities, as well as some agricultural fertilizers are sources of Cd in rivers [19]. The concentration of Cr in this study was higher when compared to a study by Abdel where the concentrations of heavy metals were determined in Lake Manzala, Egypt (0.0034 mg/l)

The mean levels of Cr in the river ranged between 2.13 ± 0.99 to 5.68 ± 1.38 mg/l across all stations and the overall mean was 3.67 ± 1.48 mg/l. The highest value of Cd was discovered in station 4 (5.68 ± 1.38 mg/l) and the lowest was discovered in station 1 (2.13 ± 0.99 mg/l). The mean concentration

of Cr found in all stations was discovered to be above WHO and NIS recommended limits of 0.05 mg/l, which can be due to the indiscriminate discharge of untreated and contaminated solid wastes products, emissions from chemical plants, industrial activities, incineration and oil and construction activities going on in the sampling area. Cr is an important element in human health and well-being [22]. It is involved in various metabolic processes, particularly in enhancing insulin sensitivity and glucose regulation. Cr is commonly used in rubber manufacturing, and leather and tanning industries. Excess exposure to Cr can lead to the accumulation of this trace element in the human body which can cause adverse and toxic health effects [22]. Cr(III) is necessary in the human body as it plays an important role in glucose, protein, and fat metabolism, however, Cr(VI) form poses human health effects, most likely through chronic and acute inhalation exposures, leading to respiratory and other health problems [23]. High levels of exposure to Cr can cause liver and kidney damage, skin ulcers, and also damage the central nervous system [24]. The mean concentrations of Cr in groundwater in Ogun state were lower (0.016 mg/l) when compared with results from this study [25].

The mean levels of Ni in the river ranged between 0.03 ± 0.02 to 0.38 ± 0.32 mg/l across all stations and the overall mean was 0.14 ± 0.16 mg/l. The highest value of Ni was discovered in station 4 (0.38 ± 0.32 mg/l) and the lowest was discovered in station 1 (0.03 ± 0.02 mg/l). The mean concentration of Cr found in all stations was discovered to be above WHO and NIS recommended limits of 0.07 mg/l. Ni occurs naturally in soils and volcanic rocks [26]. It plays an important role in the synthesis of red blood cells. Anthropogenic activities, particularly mining and industrial processes contribute to the release of Ni into the environment [27]. Ni is a versatile transition metal known for its various industrial applications such as the manufacture of stainless steel, automobile and aircraft parts, batteries, electroplating, coins, and is also used particularly for the making of Ni-Cd batteries industrially [28]. Human exposure to Ni occurs through various means such as inhalation of airborne Ni particles in work settings, ingesting Ni contaminated food and water, and having direct contact with Ni containing products [26].

Exposure to high concentrations of Ni can lead to allergic contact dermatitis for sensitive people, and this can manifest in the shape of skin rashes, redness and itching [29]. Chronic exposure to elevated concentrations of nickel, particularly in work environments such as nickel mining and processing, may result in respiratory complications, which may elevate the risk of lung cancer [30]. The concentrations of Ni in this study were found to be higher than the concentrations of Ni in water in Lake Manzala, Egypt (0.04 mg/l), and lower than the concentration in groundwater in Ogun state (0.084 mg/l) [25][31].

The mean levels of As in the river ranged between 0.04 ± 0.01 to 0.54 ± 0.30 mg/l across all stations and the overall mean was 0.28 ± 0.24 mg/l. The highest value of As was discovered in station 4 (0.54 ± 0.30 mg/l) and the lowest was discovered in station 1 (0.04 ± 0.01 mg/l). The mean concentration of As found in all stations was discovered to be above WHO and NIS recommended limits of 0.01 mg/l. As is not beneficial to humans and is in fact a toxic substance. While As is naturally occurring and found in some foods and water sources, it is not considered essential for human health [32]. As is naturally present in the Earth's crust and can seep into groundwater, particularly in areas where arsenic concentrations in geological formations are high [33]. Anthropogenic activities, including mining, industrial activities, and the use of As-based pesticides contribute to the release of As into the environment [34]. Extensive exposure to As, mainly through potable water and food, can lead to a range of health hazards such as respiratory issues, cardiovascular diseases, and it is also carcinogenic and nature and can lead to certain cancers including lung, skin, and bladder cancers [32]. Exposure to arsenic, especially during infancy, can have negative effects on neurological development and potentially cause intellectual deficiencies and behavioral issues in children [35]. When compared with a study by Nduka et al., the concentrations of Ni were lower than the concentrations in Enugu, Nigeria (0.081 mg/l) [36].

The mean levels of V in the water ranged between 0.01 ± 0.01 to 0.03 ± 0.02 mg/l across all stations and the overall mean was 0.01 ± 0.01 mg/l. The highest value of V was discovered in station 4 (0.03 ± 0.02 mg/l) and the lowest was discovered in stations 2 where V was not detected. The mean concentrations of V found in all stations in water of Bonny River was discovered to be below the EPA

maximum permissible limits of 0.021 mg/l. V is a chemical element used in various industrial applications, but it can have adverse effects on human health and the environment in high concentrations. V is released to the environment through a variety of industrial activities such as fossil fuel combustion, and steel and alloy production [37]. It is also a naturally occurring element, present in the earth's crust and can leach into surface and groundwaters. V compounds such as vanadyl sulfate and bis(maltolato)oxovanadium(IV) have been studied for their potential to improve insulin sensitivity and glucose metabolism. This has led to research exploring their use as insulin-enhancing agents in the treatment of type 2 diabetes [38]. High concentration of V can be toxic to human health, such as acute V toxicity which can result in gastrointestinal distress, while extensive exposure can lead to more intense health issues including respiratory distress, impaired functioning of the kidneys and livers, and nervous system breakdown [39].

Mean Levels of Heavy Metals in Sediment of Bonny River

The result of the analysis of sediment samples revealed that the levels of Pb in the sediment ranged from 4.38 ± 0.40 to 11.91 ± 1.39 mg/kg across all stations, and the overall mean was 7.59 ± 3.17 mg/kg. The highest value of Pb was discovered in station 4 (11.91 ± 1.39 mg/kg) and the lowest was discovered in station 1 (4.38 ± 0.40 mg/kg). The EPA defines a soil lead (Pb) hazard as when the total lead equal or exceeds 400 mg/kg, therefore, the mean concentrations of Pb found in all stations were discovered to be below the EPA recommended standards. The concentrations of Pb in this study were found to be higher than the concentrations of sediments in Abonnema shoreline ($<0.001 - 0.0526$ mg/kg) [40].

The mean levels of Cd in the river ranged between 0.07 ± 0.08 to 0.32 ± 0.14 mg/kg across all stations and the overall mean was 0.15 ± 0.12 mg/kg. The highest value of Cd was discovered in station 4 (0.32 ± 0.14 mg/kg) and the lowest was discovered in station 2 (0.07 ± 0.08 mg/kg). The mean concentrations of Cd found in all stations was discovered to be below EPA recommended limit of 85 mg/kg in soil samples. This could be attributed to low emissions by industries within the environment. The concentration of Pb is lower when compared to values recorded by Nwineewii et al. in New Calabar River (0.089 ± 0.12) [41].

The mean levels of Cr in the river ranged between 6.04 ± 1.71 to 14.79 ± 2.69 mg/kg across all stations and the overall mean was 9.33 ± 3.84 mg/kg. The highest value of Cr was discovered in station 4 (14.79 ± 2.69 mg/kg) and the lowest was discovered in station 1 (6.04 ± 1.71 mg/kg). The mean concentrations of Cd found in all stations was discovered to be below EPA recommended limit of 100 mg/kg in soil samples which could be attributed to low emissions and discharge of untreated waste products containing Cr contaminants. Cr enters into the environment through natural and anthropogenic activities such as agricultural runoff, industrial discharges, burning of fossil fuels, volcanic activities, municipal wastewaters, etc. [22]. The concentrations of Cr in this study were found to be lower than the concentrations in sediments of the Northern Persian Gulf (72.9 mg/kg) [42].

The mean levels of Ni in the river ranged between 0.32 ± 0.12 to 4.37 ± 1.23 mg/kg across all stations and the overall mean was 2.39 ± 1.98 mg/kg. The highest value of Ni was discovered in station 4 (4.37 ± 1.23 mg/kg) and the lowest was discovered in station 1 (0.32 ± 0.12 mg/kg). The mean concentrations of Ni found in all stations was discovered to be below WHO recommended limit of 35 mg/kg which could be attributed to low anthropogenic activities in the area and reduced industrial emissions. The mean concentration of Ni recorded for this study were found to be lower than the values recorded by Nwineewii & Nna in Eleme creeks, Rivers state [43].

The mean levels of Arsenic (As) in the river ranged between 0.11 ± 0.02 to 2.08 ± 0.68 mg/kg across all stations and the overall mean was 0.96 ± 0.83 mg/kg. The highest value of Ni was discovered in station 4 (2.08 ± 0.68 mg/kg) and the lowest was discovered in station 1 (0.11 ± 0.02 mg/kg). The mean concentrations of Ni found in all stations was discovered to be below EPA recommended limit of 20 - 230 mg/kg. The concentration of Ni in this study was lower when compared to the concentration of Ni in offshore surface sediments of the Northern Persian Gulf (59.8 mg/kg) [42]

The mean levels of V in the river ranged between 0.01 ± 0.01 to 0.22 ± 0.02 mg/kg across all stations and the overall mean was 0.08 ± 0.10 mg/kg. The highest value of V was discovered in station 4 (0.22 ± 0.02 mg/kg) and the lowest was discovered in station 1 (0.01 ± 0.01 mg/kg). The mean

concentrations of V found in all stations was discovered to be below EPA maximum permissible limit of 1 - 150 mg/kg for soil standards. Results from this study were found to be higher than the concentration of V in Kalabari Creeks where V were below detection limits (BDL < 0.001) [44].

Mean Levels of Heavy Metals in Biota of Bonny River

The result of the analysis of fish samples revealed that the levels of Pb in the fish ranged from 1.07 ± 0.57 to 1.07 ± 0.71 mg/kg, and the overall mean was 1.07 ± 0.00 mg/kg. The highest value of Pb discovered was 1.07 ± 0.71 mg/kg and the lowest discovered was 1.07 ± 0.57 mg/kg. The WHO defines a lead (Pb) hazard in fish as when the total lead equal of exceeds 0.5 mg/kg, therefore, the mean concentrations of Pb found in fish were discovered to be above the WHO maximum permissible limit. This may be due to the use of lead pipes in oil exploitation, and also high emissions from industries around the river. The concentration of Pb was higher in comparison to a study by Mshana in Lake Rukwa, Tanzania in all three fish species studied [45].

The mean levels of Cd in the river ranged between 0.37 ± 0.01 to 0.54 ± 0.01 mg/kg and the overall mean was 0.46 ± 0.12 mg/kg. The highest value of Cd was discovered to be 0.54 ± 0.01 mg/kg and the lowest was discovered to be 0.37 ± 0.01 mg/kg. The mean concentrations of Cd found in all stations was discovered to be above WHO maximum permissible limit of 0.05 mg/kg in aquatic organisms. The concentration of Pb in Bonny River is lower when compared to values recorded by Bolawa & Gbenle in tilapia fish in Makoko and Carter Bridge rivers (1.13 ± 0.08 and 4.49 ± 0.05 mg/kg) [46].

The mean levels of Cr in the river ranged between 1.22 ± 0.63 to 1.50 ± 1.52 mg/kg and the overall mean was 2.49 ± 0.08 mg/kg. The highest value of Cr was discovered to be 1.50 ± 1.52 mg/kg and the lowest was discovered to be 1.36 ± 0.20 mg/kg. The mean concentrations of Cd found in all stations was discovered to be below WHO maximum permissible limit of 2.0 mg/kg in aquatic organisms. The concentration of Cr in Bonny River is higher when compared to values recorded by Bolawa & Gbenle in tilapia fish in Makoko and Carter Bridge rivers (0.11 ± 0.01 and 0.04 ± 0.05 mg/kg) [46].

The mean levels of Ni in the river ranged between 0.32 ± 0.01 to 0.40 ± 0.03 mg/kg and the overall mean was 0.36 ± 0.06 mg/kg. The highest value of Ni was discovered to be 0.40 ± 0.03 mg/kg and the lowest was discovered to be 0.32 ± 0.01 mg/kg. The mean concentrations of Ni found in all stations was discovered to be below WHO maximum permissible limit of 0.6 mg/kg in aquatic organisms. The concentration of Ni in Bonny River was similar when compared to values recorded by Hashim et al. in which the concentrations of Ni in Kelantan River, Malaysia was within WHO permissible limits [47].

The mean levels of As in the river ranged between 0.34 ± 0.01 to 0.41 ± 0.01 mg/kg and the overall mean was 0.38 ± 0.05 mg/kg. The highest value of As was discovered to be 0.41 ± 0.01 mg/kg and the lowest was discovered to be 0.34 ± 0.01 mg/kg. The mean concentrations of As found in all stations was discovered to be below the WHO maximum permissible limit of 2.0 mg/kg in aquatic organisms. The concentration of As is lower when compared to values recorded by Uhegbu et al. in Warri, Delta state (0.046 ± 0.01 to 0.083 ± 0.05) [48][49][50][51][52].

The heavy metal vanadium (V) was not discovered in fish in Bonny River. The levels were below detection limits (BDL)[53][54][55][56].

Concentrations of EDCs in Water of Bonny River

The concentrations of the detected endocrine disrupting chemicals (EDCs) in surface water of Bonny River at various sampling locations are shown in tables 4.4. In terms of individuality, all the compounds analysed were detected in various quantities at all stations. At station 1, 13 EDCs were analysed, they include; Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol with mean concentrations 3.83 ± 0.02 , 1.34 ± 0.01 , 0.94 ± 0.01 , 1.56 ± 0.03 , 3.44 ± 0.02 , 1.41 ± 0.01 , 2.91 ± 0.02 , 1.19 ± 0.02 , 1.91 ± 0.03 , 3.62 ± 0.02 , 0.44 ± 0.03 , 1.31 ± 0.02 , and 0.54 ± 0.03 µg/l for station 1. The highest concentration discovered at station 1 was phenol (3.83 ± 0.02 µg/l) and the lowest concentration was found to be 3,5-Dichlorophenol (0.54 ± 0.03 µg/l).

At station 2, the concentrations discovered were 1.63 ± 0.01 , 8.28 ± 0.01 , 2.22 ± 0.03 , 0.33 ± 0.01 , 1.81 ± 0.01 , 2.43 ± 0.01 , 1.63 ± 0.02 , 4.92 ± 0.02 , 6.53 ± 0.01 , 3.72 ± 0.02 , 2.01 ± 0.03 , 2.18 ± 0.01 , and 2.51 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 2 was 2-Chlorophenol (8.28 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 2-Methylphenol (0.33 ± 0.01 $\mu\text{g/l}$).

At station 3, the concentrations discovered were 4.41 ± 0.03 , 2.22 ± 0.04 , 5.15 ± 0.02 , 0.51 ± 0.02 , 2.12 ± 0.01 , 1.50 ± 0.01 , 4.17 ± 0.01 , 8.21 ± 0.02 , 4.51 ± 0.02 , 1.47 ± 0.02 , 0.82 ± 0.01 , 7.26 ± 0.06 , and 1.34 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 3 was 4-Nitrophenol (8.21 ± 0.02 $\mu\text{g/l}$) and the lowest concentration was found to be 2-Methylphenol (0.51 ± 0.02 $\mu\text{g/l}$).

At station 4, the concentrations discovered were 2.73 ± 0.02 , 1.51 ± 0.02 , 0.75 ± 0.02 , 1.42 ± 0.01 , 3.91 ± 0.01 , 1.15 ± 0.03 , 6.82 ± 0.01 , 1.40 ± 0.01 , 1.53 ± 0.02 , 3.62 ± 0.02 , 0.17 ± 0.02 , 1.44 ± 0.02 , and 1.54 ± 0.03 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 4 was 3-Nitrophenol (6.82 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 2,5-Dichlorophenol (0.17 ± 0.02 $\mu\text{g/l}$).

The overall mean concentrations of the 4 stations were calculated to be 3.15 ± 1.23 , 3.34 ± 2.32 , 2.26 ± 2.03 , 0.95 ± 0.62 , 2.82 ± 1.02 , 1.62 ± 0.56 , 3.88 ± 2.22 , 3.93 ± 3.33 , 3.62 ± 2.35 , 3.11 ± 1.09 , 0.86 ± 0.81 , 3.05 ± 2.84 , and 1.48 ± 0.81 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered was 4-Nitrophenol (3.93 ± 3.33 $\mu\text{g/l}$) and the lowest concentration was found to be 2,5-Dichlorophenol (0.86 ± 0.81 $\mu\text{g/l}$).

The presence of these compounds in surface water may be attributed to wastewater from households and industries, as the area is densely polluted with anthropogenic activities and various industrial activities. EDC presence in the Bonny River can also be attributed plastics discharge into rivers from domestic and industrial sources, leaching from landfills, and the plethora of illegal oil bunkering and destruction of stolen crude by burning. The endocrine system, which controls a number of bodily physiological functions like hormone synthesis, development, and reproduction, may be disrupted by EDCs. Hormonal imbalances may result from this disruption [5]. EDCs can also affect reproductive and developmental processes, leading to birth defects, issues with fertility, and irregularities in development. EDCs in water sources have the potential to pollute drinking water supplies and expose humans to these chemicals. Even though concentrations are typically low, prolonged exposure can have negative impacts on health [14]. Exposure to chlorophenols such as 2-Chlorophenol, 4-Chlorophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol were shown to have effects on body weight, the liver, and reproductive functions in animals.

The total content of endocrine disrupting chemicals (EDCs) discovered in water in the stations showed 23.72 ± 0.24 , 40.20 ± 0.17 , 43.68 ± 0.28 , and 27.98 ± 0.21 $\mu\text{g/l}$ for stations 1, 2, 3, and 4 respectively. The overall mean total across the four stations was calculated to be 34.08 ± 22.21 $\mu\text{g/l}$. The total EDCs across the stations show that station 3 had the highest concentration in water, followed by stations 2, 4, and 1. There are no universally established numerical water quality standard for total EDCs in water, however, the concentrations of phenol, 2-Chlorophenol, 2-Methylphenol, 4-Methylphenol, and 2,4-Dichlorophenol are below EPA standards for phenols in drinking water [14]. The summation of all the EDCs in water at the various stations showed that station 3 > station 2 > station 4 > station 1.

Concentrations of EDCs in Sediment of Bonny River

The concentrations of the detected endocrine disrupting chemicals (EDCs) in sediment of Bonny River at various sampling locations are shown in tables 4.5. In terms of individuality, all the compounds analysed were detected in various quantities at all stations. At station 1, 13 EDCs were analysed, they include; Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol with mean concentrations 4.59 ± 0.12 , 2.55 ± 0.32 , 10.79 ± 0.05 , 3.92 ± 0.01 , 5.93 ± 0.02 , 1.86 ± 0.02 , 2.23 ± 0.03 , 1.63 ± 0.02 , 1.22 ± 0.02 , 1.82 ± 0.01 , 6.93 ± 0.01 , 1.72 ± 0.02 , and 0.86 ± 0.03 $\mu\text{g/l}$ respectively. The highest concentration discovered at station 1 was 4-Chlorophenol (10.79 ± 0.05 $\mu\text{g/l}$) and the lowest concentration was found to be 3,5-Dichlorophenol (0.86 ± 0.03 $\mu\text{g/l}$).

At station 2, the concentrations discovered were 3.53 ± 0.03 , 1.81 ± 0.03 , 7.86 ± 0.03 , 9.33 ± 0.02 , 1.52 ± 0.02 , 18.83 ± 0.01 , 1.18 ± 0.01 , 4.28 ± 1.34 , 4.46 ± 2.36 , 2.46 ± 0.99 , 2.42 ± 1.25 , 1.30 ± 0.02 , and 3.84 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 2 was 2-Nitrophenol (18.83 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 3-Nitrophenol (1.18 ± 0.01 $\mu\text{g/l}$).

At station 3, the concentrations discovered were 3.83 ± 0.02 , 4.61 ± 0.02 , 15.15 ± 0.02 , 3.52 ± 0.02 , 4.46 ± 0.02 , 1.31 ± 0.01 , 2.53 ± 0.02 , 1.84 ± 0.02 , 1.60 ± 0.01 , 1.44 ± 0.03 , 0.92 ± 0.02 , 7.25 ± 0.01 , and 0.88 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 3 was 4-Chlorophenol (15.15 ± 0.02 $\mu\text{g/l}$) and the lowest concentration was found to be 3,5-Dichlorophenol (0.88 ± 0.02 $\mu\text{g/l}$).

At station 4, the concentrations discovered were 6.43 ± 0.03 , 1.71 ± 0.02 , 2.53 ± 0.02 , 8.75 ± 0.01 , 1.15 ± 0.02 , 3.83 ± 0.01 , 1.65 ± 0.02 , 3.72 ± 0.01 , 4.52 ± 0.02 , 2.63 ± 0.01 , 3.45 ± 0.01 , 8.14 ± 0.04 , and 0.65 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at station 4 was 2-Methylphenol (8.75 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 3,5-Dichlorophenol (0.65 ± 0.02 $\mu\text{g/l}$).

The overall mean concentrations of the 4 stations were calculated to be 4.60 ± 1.30 , 2.67 ± 1.35 , 9.08 ± 5.30 , 6.38 ± 3.09 , 3.26 ± 2.31 , 6.46 ± 8.32 , 1.90 ± 0.60 , 2.87 ± 1.33 , 2.95 ± 1.79 , 2.09 ± 0.55 , 3.43 ± 2.56 , 4.60 ± 3.59 , and $1.56 \pm 1/53$ $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered was 4-Chlorophenol (9.08 ± 5.30 $\mu\text{g/l}$) and the lowest concentration was found to be 3,5-Dichlorophenol ($1.56 \pm 1/53$ $\mu\text{g/l}$).

EDCs in sediment originate from both natural and anthropogenic sources such as industrial discharges, urban runoff such as those from roads, parking lots, and residential areas as contaminants from everyday products such as household chemicals, pesticides, and personal care products. The presence of these compounds in sediment may be attributed to indiscriminate disposal of untreated or incompletely treated industrial and domestic wastewater effluents. EDCs in sediment have the potential to pollute its surrounding waters, thereby exposing humans to these chemicals. Exposure to chlorophenols such as 2-Chlorophenol, 4-Chlorophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol were shown to have effects on body weight, the liver, and reproductive functions in animals.

The total content of endocrine disrupting chemicals (EDCs) discovered in sediment in the stations showed 46.05 ± 0.66 , 62.81 ± 6.11 , 49.34 ± 0.20 , and 49.17 ± 0.23 $\mu\text{g/l}$ for stations 1, 2, 3, and 4 respectively. The overall mean total across the four stations was calculated to be 51.84 ± 33.61 $\mu\text{g/l}$. The total EDCS across the stations show that station 4 had the highest concentration in water, followed by stations 2, 1, and 3. There are no universally established numerical water quality standard for total

EDCs in water, however, the concentrations of phenol, 2-Chlorophenol, 2-Methylphenol, 4-Methylphenol, and 2,4-Dichlorophenol are above EPA maximum permissible limits for phenols in drinking water [14]. The summation of all the EDCs in water at the various stations showed that station 4 > station 2 > station 3 > station 1 > station 3.

Concentrations of EDCs in Biota of Bonny River

The concentrations of the detected endocrine disrupting chemicals (EDCs) in biota of Bonny River represented as fish 1 and fish 2 are shown in tables 4.6, where 13 phenols were analyzed. They include; Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol. The mean concentrations for fish 1 were 1.55 ± 0.12 , 2.76 ± 0.07 , 0.11 ± 0.02 , 2.93 ± 0.02 , 2.33 ± 0.02 , 0.49 ± 0.01 , 0.23 ± 0.03 , 4.18 ± 0.01 , 2.13 ± 0.02 , 1.95 ± 0.01 , 0.62 ± 0.02 , 1.10 ± 0.03 , and 3.34 ± 0.02 $\mu\text{g/l}$ respectively. The highest concentration discovered for fish 1 was 4-Nitrophenol (4.18 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 4-Chlorophenol (0.11 ± 0.02 $\mu\text{g/l}$).

For fish 2, the concentrations discovered were 0.77 ± 0.05 , 1.52 ± 0.02 , 2.15 ± 0.02 , 1.82 ± 0.03 , 3.44 ± 0.01 , 3.94 ± 0.03 , 1.16 ± 0.02 , 2.24 ± 0.01 , 0.35 ± 0.01 , 4.12 ± 0.01 , 0.90 ± 0.02 , 0.65 ± 0.02 , and 1.17 ± 0.02 $\mu\text{g/l}$ for Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-Methylphenol, 4-Methylphenol, 2-Nitrophenol, 3-Nitrophenol, 4-Nitrophenol, 2,3-Dichlorophenol, 2,4-Dichlorophenol, 2,5-Dichlorophenol, 3,4-Dichlorophenol, and 3,5-Dichlorophenol respectively. The highest concentration discovered at fish 2 was 2,4-Dichlorophenol (4.12 ± 0.01 $\mu\text{g/l}$) and the lowest concentration was found to be 2,3-Dichlorophenol (0.35 ± 0.01 $\mu\text{g/l}$).

The total content of endocrine disrupting chemicals (EDCs) discovered in biota in the stations showed 23.73 ± 0.37 and 24.23 ± 0.25 $\mu\text{g/l}$. The total EDCS across the stations show that the total concentration of EDCs in fish 2 was higher than in fish 1. There are no universally established numerical water quality standard for total EDCs in water, however, the concentrations of phenol were below EPA maximum permissible limits, while 2-Chlorophenol, 2-Methylphenol, 4-Methylphenol, and 2,4-Dichlorophenol are above EPA maximum permissible limits for phenols in drinking water [14].

Fish are a common source of protein for many people. Due to the bioaccumulation of EDCs in fish, regular consumption may lead to human health problems from exposure to these chemicals as they can be transferred to higher trophic levels through the food chain [5]. EDCS can also affect reproductive and developmental processes, leading to birth defects, issues with fertility, and irregularities in development, as well as being carcinogenic. Long-term exposure to contaminated fish could pose risk for certain types of cancer [14].

Contamination Factor of Heavy Metals in Water of Bonny River

The contamination factor was used to ascertain the levels of contamination/pollution due to the concentration of heavy metals present in the water. The WHO and NIS maximum permissible limits were used as the background values for determining the contamination factor (CF) of the water. For Pb, a very high degree of contamination was observed in stations 1, 2, 3, and 4 which recorded 212.00, 243.00, 428.00, and 408.00 respectively. A very high degree of contamination was also recorded for Cd in stations 1, 3, and 4 with 10.00, 6.67, and 43.33 respectively, while station 2 recorded moderate degree of contamination with 3.33. For Cr, very high degree of contamination was observed in stations 1, 2, 3, and 4 which recorded 42.60, 70.60, 67.00, and 113.60 respectively. For Ni, stations 1 and 2 recorded low degree of contamination with 0.43 and 0.86, station 3 recorded moderate degree of contamination with 1.43, and station 4 recorded considerable degree of contamination with 5.43. For As, station 1 recorded considerable level of contamination with 4.00, while stations 2, 3, and 4 recorded very high levels of contamination with 13.00, 42.00, and 54.00 respectively. For V, low degree of contaminations was recorded for stations 1, 2, and 3 with 0.50, 0.00, and 0.50, while station 4 recorded moderate degree of contamination with 1.50. The very high degree of contaminations recorded in this study may be due to the activities of oil bunkering and industrial activities within the area. The PLI calculated indicates that the water of Bonny River is contaminated. The PLI values recorded for stations 1, 2, 3, and 4 were 6.53, 9.28, 13.38, and 30.98 respectively which indicated that the water is polluted.

Contamination Factor of Heavy Metals in Sediment of Bonny River

The contamination factor was used to ascertain the levels of contamination/pollution due to the concentration of heavy metals present in the sediment in Bonny River. The WHO and EPA maximum permissible limits were used as the background values for determining the contamination factor (CF) of the water. For Pb, a low of contamination was observed in stations 1, 2, 3, and 4 which recorded 0.01, 0.02, 0.02, and 0.03 respectively. No degree of contamination was recorded for Cd in stations 1, 2, 3, and 4 with 0.00 recorded across all stations. For Cr, low degree of contamination was recorded for stations 1, 2, 3, and 4 with 0.06, 0.07, 0.09, and 0.15 respectively. For Ni, low degree of contamination was recorded for stations 1, 2, 3, and 4 with 0.01, 0.03, 0.11, and 0.12 recorded respectively. For As, no degree of contamination was recorded for stations 1, 2, and 3 with 0.00 recorded across, while station 4 recorded low degree of contamination with 0.01. For V, no degree of contamination was recorded across all stations 1, 2, 3, and 4. The PLI values recorded for stations 1, 2, 3, and 4 were 0.13, 0.19, 0.24, and 0.13 respectively which indicated that the sediment is not polluted and within standards.

Contamination Factor of Heavy Metals in Biota of Bonny River

The contamination factor was used to ascertain the levels of contamination/pollution due to the concentration of heavy metals present in fish in Bonny River. The WHO and EPA maximum permissible limits were used as the background values for determining the contamination factor (CF) of the water. For Pb, a moderate degree contamination was recorded for the fish 1 and fish 2 with 2.14 calculated for both samples. For Cd, very high degree contamination was recorded for both fish samples at 7.40 and 10.80. For Cr, low degree of contamination was recorded for both samples with 0.61 and 0.75 respectively. For Ni, low degree of contamination was recorded for both samples with 0.53 and 0.67. For As, low degree of contamination was also recorded in both fish 1 and fish 2 samples with 0.68 and 0.82 respectively. For V, no degree of contamination was recorded. The PLI values recorded were 0.33 and 0.49 which indicated that the biota were not polluted and within standards.

Conclusion

This study focused on determining the concentrations of heavy metals and EDCs in the water, sediment and biota in Bonny River at four different sampling locations in the creeks and rivers of Bonny local government area, Rivers state. Results from the analysis revealed that in most of the stations, the concentrations of heavy metals were above WHO, EPA, and NIS maximum permissible limits, while some were others were within the permissible limits. The results from heavy metals show that the concentrations of heavy metals were relatively high, with Pb and Cr being more present. The total EDCs discovered in each station was also high. This indicates that the Bonny River is polluted. This indicates that consumption of water and its products from Bonny River have the ability to cause health hazards to the population if consumed for extended periods.

Recommendations

- i. Due to the high concentration of some heavy metals in the water from Bonny River, adequate and alternate sources of water should be provided for residents around the river to avoid endangering their lives.
- ii. Proper waste disposal methods should be employed and implemented by households and industries within and around the area.
- iii. Awareness should be created to enlighten residents around the river on the potential health impacts of consuming contaminated water and the way forward to help reduce pollution.
- iv. Due to the contamination factor of the heavy metals in water and biota, the government should implement policies to curb various pollution activities such as introducing significant fines for faulters.
- v. Due to high level of EDCs in the Bonny River, proper disposal and recycling habits should be encouraged, as well as waste disposal practices by domestic and industrial sources.

Contributions to Knowledge

- i. This research has contributed to revealing the current level of heavy metal and EDCs in water, sediment and biota of Bonny River in Rivers state.
- ii. From this research, it was discovered that the water from Bonny River and creeks around Okrika is contaminated with heavy metals.

The contamination factor from this study has revealed the levels of heavy metal pollution in water, and biota, indicating contamination.

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