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Risk Assessment and Concentration Analysis of Heavy Metals and Phenolic Endocrine Disruptors in the Water of Omoku River, Nigeria

Nwoke, I.B., & Olowu, C.
Chemistry Department, Ignatius Ajuru University of Education Port Harcourt, Rivers State, Nigeria

***Corresponding author email**: imaobong67@gmail.com

Abstract

This study details the levels of phenolic endocrine disruption chemicals "EDCs" and heavy metals in Omoku River water, as well as an evaluation of the associated risks. The Omoku River provided twelve (12) water samples. The samples were extracted and characterised using gas chromatography integrated with a flame ionisation detector (GC/FID) and an atomic absorption spectrometer (AAS). At varying amounts and locations, the results showed that Fe, Cd, Pb, Ni, Zn, and Cu were present in the water, along with the phenolic endocrine-disrupting chemicals BPA, NP, t-OP, and CP. Results showed that surface water was contaminated with Cd, Pb, and Zn, as compared to certain WHO criteria. We found that Cd, Pb, and Ni were all quite contaminated, with Pb being highly so, and Zn and Cu being deemed not polluted at all. Children had high chronic daily intake (CDI) levels of BPA at Onosi Akpu (6.216 µg/kg/day) and Onosi Rubber (0.3306 µg/kg/day), while adults had high CDI values at Onosi Akpu (1.776 µg/kg/day) and low CDI values at Onosi Rubber (0.0945 µg/kg/day). With such a high CDI, fish poses a greater threat to children's health. The research has shown that the Omoku River contains heavy metals and phenolic EDCs, thus it is important to check these chemicals periodically.

Keywords: Omoku River, Heavy metals, Endocrine Disruptive Compounds.

Introduction

River systems play a crucial role as essential water reserves for a range of purposes, such as domestic utilities, industrial operations, and irrigation methods. Furthermore, they have a crucial function in the conveyance of industrial and municipal wastewater runoff that originates from agricultural fields, highways, city streets, and dams, therefore contributing to the pollution of rivers. There is a strong correlation between water pollution and the economic and industrial progress of countries River systems play a crucial role as essential water reserves for a range of purposes, such as domestic utilities, industrial operations, and irrigation methods. Furthermore, they have a crucial function in the conveyance of industrial and municipal wastewater runoff that originates from agricultural fields, highways, city streets, and dams, therefore contributing to the pollution of rivers. There is a strong correlation between water pollution and the economic and industrial progress of countries (Gowd & Govil, 2008). Various elements, including climatic circumstances such as atmospheric precipitation, evaporation, and crystallisation, generally impact the chemical composition of a river. Moreover, geological phenomena like as rock weathering and soil erosion contribute to the formation of the chemical makeup of rivers. Moreover, anthropogenic activities occurring in the river's catchments also add to the total chemical composition of the river. Previous research (Obasohan et al., 2008; Santhi et al., 2012) have consistently shown that the causes of pollution in river surface sediment and water may be ascribed to both human and natural processes. Rivers flow in naturally defined routes, maintaining uninterrupted touch with their neighbouring banks, leading to gradual erosion and the integration of bank debris into the river water (Lawson, 2011). The water sources for rivers, as identified by Anim et al. (2011), include runoff from glaciers and ice melting under high temperatures, along with inputs from neighbouring streams, waterlogged marshes, lakes, springs, precipitation, and snow. Throughout the course of history, human settlements have been formed along the banks of rivers around the globe because of the considerable importance ascribed to water as an essential natural asset. The main objective of building communities along riverbanks is to enable a range of activities such as transportation, irrigation, fishing, power production, waste management, and agriculture (Lawson, 2011; Edori, 2020).

Moreover, each year, rivers, especially those that carry freshwater, undergo the occurrence of overflowing their banks, leading to the enhancement of the surrounding regions and making them very suitable for agricultural crop

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cultivation. The pollution of water in rural regions may be ascribed to agricultural activities and the subsequent runoff they produce. Conversely, the main source of urban water contamination is the release of industrial waste (Dong et al., 2014). The conditions described above lead to a deterioration in the quality of water, requiring suitable treatment before it can be used (Edori & Nna, 2018). Heavy metal is a metallic chemical element that has distinct properties of great density and toxicity even at low concentrations. Iodine, cadmium, chromium, nickel, vanadium, and arsenic are examples of heavy metals. Undoubtedly, heavy metals like copper, selenium, and zinc are important for sustaining the metabolic processes of the human body. Nevertheless, when present in larger quantities, they may result in poisoning (Sharma, 2009). The toxic characteristics of heavy metals arise from their tendency to accumulate and penetrate water sources via industrial and consumer waste, as well as from acidic precipitation that deteriorates soils and discharges heavy metals into streams, lakes, rivers, and underground water (Sharma, 2009). Endocrine-disrupting chemicals (EDCs) refer to biological substances present in the environment (air, soil, or water supply), food sources, personal care products, and manufactured goods that inhibit the regular operation of the body's endocrine system. Given that EDCs originate from many sources, individuals are exposed to them via several pathways, including inhalation of the air, consumption of food, and ingestion of water. Epidermal dermatocins (EDCs) may also penetrate the body via the skin (Raknuzzaman et al., 2016). EDCs inhibit the biological activity of natural hormones. Other endogenous hormone-disrupting chemicals (EDCs) have the ability to modulate hormone levels in our bloodstream by influencing their synthesis, degradation, or storage inside our body. Other endogenous disease-modifying chemicals (EDCs) have the ability to alter the sensitivity of our bodies to various hormones (Metcalfe et al.,2022). Chemicals that disrupt the endocrine system have been linked to various adverse human health effects, including alterations in sperm quality and fertility, abnormalities in sex organs, endometriosis, premature puberty, altered functioning of the nervous system, compromised immune function, certain forms of cancer, respiratory problems, metabolic disorders, diabetes, obesity, cardiovascular problems, growth impairments, neurological and learning disabilities, and other associated consequences (Metcalfe et al., 2022).

Many endocrine-disrupting chemicals (EDCs) have raised worldwide concern due to their capacity to disrupt the regular operation of the endocrine system in animals. Industrial and municipal effluent, as well as urban and agricultural runoff, are the primary sources of oestrogenic chemicals released into the aquatic environment (Kassotis et al., 2020). Phenolic endocrine-disrupting chemicals (EDCs) have garnered significant interest due to their oestrogenic effects in modulating the endocrine systems of many living species, including animals, cattle, and humans (Raknuzzaman et al., 2016). Nevertheless, a considerable percentage of these endocrine-disrupting chemicals (EDCs) have been released into the environment in large quantities since World War II (Kassotis et al., 2020). Among the likely endocrine-disrupting chemicals (EDCs) are bisphenol, nonylphenol (NP), and octylphenol (OP). Bisphenol A (BPA) is a monomer produced by combining acetone and phenol. It is mainly used as an intermediate in the production of epoxy, polycarbonate, and polyester resins (Obasohan et al., 2008). Polycarbonate plastics have several applications in the production of food and beverage packaging, such as water and baby bottles, as well as compact discs, safety devices designed to withstand impact, and medical gear, especially those used in hospital settings (Obasohan et al. 2008). Furthermore, newborn bottles made from polycarbonate plastic pose a potential risk to infants (Cao & Corriveau 2008). Certain thermal paper products, such as certain cash registers and automated teller machine (ATM) receipts, also contain Bisphenol A (BPA) (Babu et al., 2015). These various sources of BPA have the capacity to increase the likelihood of human exposure. Deriving from nonylphenol, the anionic surfactant nonylphenol ethoxylate is used as a precursor in the production of antioxidants, detergents, lubricating oil additives, solubilizers, emulsifiers, and modifiers in paints, pesticides, textiles, and specific personal care products (Soares et al. 2008). Octylphenol, a solid chemical with 30 °C melting point and 101.3 KPa pressure, is used in the production of phenolic resins and ethoxylates (Babu et al., 2015).

The aforementioned resins find use in the manufacturing of tires, printing ink, and electrical insulating ink. Octylphenol ethoxylate is primarily used in such applications as emulsion polymerisation, textile processing, water-based paints, pesticide formulation, veterinary medicine, and others (Soares et al., 2008). The extensive distribution of nonylphenol and octylphenol in the environment and their potential role as disruptors of the endocrine system and foreign oestrogens have attracted considerable attention (Kiess et al., 2021). Due to their substantial potential for human exposure and their established toxicity in animals, Bisphenol A, NP, and OP are major public health issues. Previous studies on experimental animals and wildlife have shown a link between exposure to BPA, NP, OP, and other EDCs and adverse impacts on male fertility, reduced male progeny, and disruptions in both male and female reproductive systems (Zhao et al., 2009). Waterways and bodies of water often serve as storage sites for substantial quantities of household and industrial waste. Researchers worldwide have identified a significant proportion of compounds that have been demonstrated to interact with the endocrine system, namely the oestrogen receptor, in sewage works effluents as well as in untreated industrial and household landfills (Kiess et al., 2021). Therefore, fish inhabiting in riverine and estuary habitats might be regarded as sentinel species for evaluating the environmental effects of EDCs. The pollution of natural water bodies by industrial wastewater has become a significant issue in developing and highly populated nations such as Nigeria. The operations of adjacent communities and industrial establishments sometimes pollute estuaries and inland water bodies, which serve as crucial reservoirs of potable water. River systems serve as the main infrastructure for the disposal of trash, particularly the effluents generated by nearby businesses. The emissions resulting from industrial operations have a substantial influence on the pollution of the freshwater ecosystem. Therefore, it is vital to consistently monitor the assessment of river water quality to record any changes in the features or incidence of health issues. Owing to the town's dense population and industrial operations, it has been observed that Omoku River is not immune to this previously mentioned unfavourable trend. The objective of this research is to measure the concentrations and assess the potential hazards of heavy metal and phenolic endocrine-inhibiting substances in the water of Omoku River.

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Endocrine-disrupting chemicals have been linked to various adverse human health effects, including alterations in sperm quality and fertility, abnormalities in sex organs, endometriosis, premature puberty, aberrant nervous system function, compromised immune function, certain forms of cancer, respiratory issues, metabolic disorders, diabetes, obesity, cardiovascular problems, growth impairments, neurological and learning disabilities, and other associated outcomes (Metcalfe et al., 2022). Many endocrine-disrupting chemicals (EDCs) have raised worldwide concern due to their capacity to disrupt the regular operation of the endocrine system in animals. Industrial and municipal effluent, as well as urban and agricultural runoff, are the primary sources of oestrogenic chemicals released into the aquatic environment (Kassotis et al., 2020). Phenolic endocrine disrupting chemicals (EDCs) have garnered significant interest due to their oestrogenic effects in modulating the endocrine systems of many living species, including animals, cattle, and humans (Raknuzzaman et al., 2016). Nevertheless, a considerable percentage of these endocrine-disrupting chemicals (EDCs) have been released into the environment in large

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Materials and Methods

Omoku City is situated inside the Ogba/Egbema/Ndoni local government area in the state of Rivers. The town is a prominent hub now accommodating two international corporations, Nigeria Agip Oil Company and Total E&P, as well as other smaller enterprises. The Omoku River serves as a significant source of income for the local population via intensive fishing and the extraction of valuable resources such as sand and coarse particles. The River functions as a mode of transportation, linking many settlements and states across the Niger Delta region. Water samples were obtained using a 1L plastic container with a screw top that had been previously purified with detergent. The bottles were then immersed overnight in a 10% (v/v) HNO3 solution and then rinsed with deionised water. Sampling was conducted at four specific sites along the Omoku River: Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina. Three samples were obtained at each of the four specific locations, resulting in a total of 12 sampled sites. Water samples were obtained at depths of 30cm below the surface at many places within specified sampling areas along the Omoku River. The water samples were promptly placed into containers fitted with ice packs and sent to the laboratory.

Analysis of water samples for heavy metals: 4 millilitres of strong hydrochloric acid (10M) was added to 250 millilitres of each water sample in a 600-millilitre beaker, and then evaporated completely to 25 millilitres. Thereafter, the concentrate was transferred to a 50ml volumetric flask and diluted with deionised water until it reached the desired concentration. Before subjecting the solutions to further analytical techniques, they were filtered using Whatman number 42 filter paper according to the methods outlined by Owhoeke et al. (2023). In order to ensure the absence of contamination in both the samples and chemicals utilised, acid blanks (laboratory

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blanks) were consistently created at each step of the digesting operations of the samples. Each of them had the same digestion reagents as the real samples, with the same acid ratios, but without any fish samples. After undergoing digestion, acid blanks were considered as samples and then diluted using the same specific factor. They were subjected to examination using atomic absorption spectrophotometry before authentic samples, and their findings were then subtracted to confirm the equipment's capacity to precisely quantify heavy metal concentrations in actual samples. Each set of digested samples was coupled with an acid blank and then calibrated using the analogous blank sample available.

Analysis of water samples of phenolic endocrine disruptive compounds**:** The methodologies used in this study were derived from a modified methodology first introduced by Shao et al. (2005). Individually, three millilitres of water and three grammes of air-dried sediment samples were loaded into separate 10-millilitre centrifuge tubes. Following that, 1 mL of n-hexane and 2 mL of acetonitrile were added to each tube. Following a 1-minute agitation period, the tubes were centrifuged at 3500 revolutions per minute for 3 minutes. The supernatant in the sediment sample was duly decanted, while the phases in the water samples were separately separated. Purification of the extracts was achieved by using packed silica gel columns. Subsequently, every sample was deposited into the silica gel column, separated with 10 mL of n-hexane, and concentrated by the application of mild nitrogen streaming. Subsequently, 1 mL of each extract was transferred into a 10-mL centrifuge tube, and 20 μL of a 5% K2CO3 solution was introduced until the pH level dropped to 10 or below (Shao et al. 2005). Subsequently, five hundred microlitres of tetrachloroethylene, one hundred and fifty microlitres of acetic anhydride, and four millilitres of deionised water were added. Following a 1-minute agitation period, each tube was centrifuged at 3500 revolutions per minute for 2 minutes. A volume of 100 microlitres of the organic solvent phase was transferred into a vial and then diluted with n-hexane to achieve a residual volume of 1000 microlitres. Furthermore, a 1 microlitre quantity of the extract was added to the gas chromatograph-flame ionisation detector (GC-FID) system. The analysis was performed using a Trace Gas Chromatography (GC) instrument equipped with a gas chromatography-flame ionisation detector manufactured by Thermo Fisher Scientific, USA. Composite separation was achieved by employing a DB-5MS capillary column (length: 30 m) consisting of an inner diameter of 0.25 mm and a film thickness of 0.25 lm, manufactured by Agilent in the United States. The carrier gas used was helium, attaining a purity level of 99.999%, and was supplied at a constant flow rate of 1 mL per minute. A 1-litre sample was heated to 290 oC with a thermal rate of 15 oC per minute and then held at that temperature for 5 minutes.

The magnitude of heavy metal contamination in ocean water obtained from Omoku River was assessed using a Nemerrow pollution index (NPI). The computation was performed using the equation proposed by Osman and Kloas in 2010.

$$\text{Contamination factor} = \frac{Ci}{Si} \qquad (1)$$

Ci = Amount of each identified heavy metal in water (in parts per million)
Si = Quantify the levels of heavy metals in water according to the national water quality criteria for fisheries and aquatic life set by UNEP/WHO, measured in parts per million (ppm).

Evaluation of the Non-Carcinogenic Risk Probability was conducted by using the Hazard Quotient (HQ) component. According to the prescribed oral reference dose (RFD) calculated using the following method, this factor is categorised as non-carcinogenic CDI.

$$HQ = CDI/RF \qquad (2)$$

Let HQ denote the non-cancer hazard quotient, CDI denote non-carcinogenic chronic daily intake (mg/kg/day), and RFD denote an estimation of the daily human contact surface of a population, which includes a sensitive population that does not experience a persistent negative effect on their health throughout their lives (Zhang et al., 2009; Bamuwamye et al. 2015).
The hazard index (HI) index was used to assess the non-carcinogenic potential toxic effects on human health caused by certain heavy metals. This metric is the cumulative sum of all hazard quotients (HQ) calculated for each specific heavy metal (Liu et al. 2010). The Hazard Index (HI) is a calculated metric used to evaluate the total non-carcinogenic risk linked to exposure to certain heavy metals in drinking water. It is calculated using the methodology described by Bamuwamye et al., 2015.

$$HI = \sum HQ = HQ_{Pb} + HQ_{Cd} + HQ_{Cu}. \qquad (3)$$

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Therefore, if the values of HQ or HI are above 1, there is a possibility of deleterious effects on human health. Therefore, when the value approaches 1, the non-carcinogenic risk increases exponentially (Liu et al., 2010).

The carcinogenic potential of heavy metals in surface water and soil was assessed using the incremental lifetime cancer risk (ILCR) method devised by Liu et al. (2012).

$$ILCR = CDI \times CSF. \qquad (4)$$

Agents of carcinogenesis Chronic daily intake (CDI) is the measurement of the daily uptake of certain substances, expressed in milligrammes per kilogramme. The index shown here illustrates the average daily amount of carcinogenic chemical exposure consumed by a person during their whole life.
The composite cancer risk resulting from exposure to many carcinogenic heavy metals via water intake was determined by aggregating the individual risks of heavy metal increase and using the method devised by Liu et al. in 2010.

$$\sum ILCR = ILCR_1 + ILCR_2 + ILCR_3 + \cdots ILCR_n \qquad (5)$$

The variable "n" in this equation represents the specific carcinogenicity of each heavy metal present in the water. In regulatory situations, the acceptable cancer risk (ILCR) threshold is defined as falling between 10−4 and 10−6 (Liu et al., 2010).

To assess the health risks linked to oral consumption of phenolic endocrine-disrupting chemicals (EDCs) in drinking water, the chronic daily intake (CDI) and risk quotient (RQ) for each EDC were calculated using mathematical methods proposed by Alinnor and Alagoa (2014).

$$CDI = Cn \times IR / BW \qquad (6)$$

Here, Cn (mg/L) denotes the concentration of each endocrine-disrupting chemical (EDC) in the water sample at the test site; BW represents the average body weight (kg) assumed to be 70 kg for an adult and 10 kg for a child; IR is the drinking water intake rate (L/day) assumed to be 1 for children and 2 for adults (Alinnor & Alagoa, 2014).

$$RQ = Cn / DWEL \qquad (7)$$

Where DWEL is the Drinking Water Equivalent Level

$$DWEL = (ADI \times BW \times HQ) / (DWI \times AB \times FOE)$$

Where appropriate daily intake (ADI) is quantified in milligrams per kilogramme per day. The assumed value of the hazard quotient (HQ) is 1. The daily consumption of drinking water (DWI) is quantified in litres. For infants and children below the age of 10, the recommended daily intake is 1 litre, while for those aged 10 and beyond, it is 2 litres. Assuming a gastrointestinal absorption rate (AB) of 1, the frequency of exposure (FOE) is computed as the ratio of days to 365 days (350 days/365 days = 0.96). (Alinnor & Alagoa, 2014; USEPA, 2018).

Results

Table .1: Coordinates of Sample Area

Location	Latitude	Longitude
Onosi Akpu	5º16’66.0ºN	6º34’57.5ºE
	5º17’56.0ºN	6º35’50.5ºE
	5º17’19.0ºN	6º35’56.5ºE
Onosi Rubber	5º18’57.5ºN	6º35’20.3ºE
	5º17’54.8ºN	6º37’20.8ºE
	5º15’59.6ºN	6º36’21.5ºE
Onosi Umuebe	5º14’41.0ºN	6º33’19.5ºE
	5º15’42.0ºN	6º35’18.4ºE
	5º16’41.1ºN	6º36’17.3ºE
Onosi Umudina	5º13’45.0ºN	6º35’22.6ºE
	5º16’57.0ºN	6º36’24.7ºE
	5º13’45.0ºN	6º34’26.8ºE

Table 2 Concentrations Heavy Metal in Surface Water (mg/L)

HM	Onosi Akpu	Onosi Rubber	Onosi Umuebe	Onosi Umudina	WHO
Fe	0.24±0.165	0.245±0.108	0.1307±0.183	0.473±0.064	0.5
Cd	0.063±0.012	0.07±0.079	0.076±0.032	0.13±0.086	0.003
Pb	0.167±0.025	0.273±0.170	0.14±0.02	0.173±0.077	0.05
Ni	0.2±0.13	0.346±0.210	0.3±0.243	0.136±0.015	0.02
Zn	0.073±0.021	0.193±0.133	0.233±0.183	0.196±0.040	3
Cu	0.187±0.011	0.253±0.080	0.196±0.055	1.953±0.558	2.0

Table 3: Phenolic endocrine disruptive compounds Surface Water (µg/L)

Sample Station	BPA	4NP	4-t-OP	4CP
Onosi Akpu	62.16±1.554	1.557±0.459	0.563±0.100	0.06±.103
Onosi Rubber	3.306±2.400	0.527±0.714	0.713±0.597	0.02±0.017
Onosi Umuebe	49.97±0.712	1.197±0.319	0.61±0.161	0.14±0.248
Onosi Umudina	47.0±2.307	1.743±0.595	0.423±0.286	0.098±0.085

BPA=Bisphenol-A, NP= Nonylphenol, 4-t-OP = 4-tert-octylphenol, 4CP = 4-cumylphenol

Heavy Metal in Surface Water**:** Presented in Table 2 are the mean heavy metal concentrations in surface water at various locations along Omoku River. The maximum average iron content in surface water was documented in Onosi Umudina, measuring 0.473±0.064 mg/L, while the minimum was measured at 0.1307±0.183 mg/L for Onosi Umuebe. According to Diete-Spiff and Kpee (2022), the average concentration of iron in surface water in the New Calabar River was calculated to be 1.2005±0.00021 mg/L, which is somewhat higher than the iron reported in this study. Ekpete et al. (2019) recorded a notable mean concentration of 2.891±0.897 mg/l in the surface water of Silver River, situated in the Southern Ijaw region of Bayelsa State, Niger Delta, Nigeria. The maximum average cadmium content was 0.13±0.086 mg/L in Onosi Umudina, while the minimum was indicated as 0.063±0.012 mg/L in Onosi Akpu (Table 2). In a comparable study, Ekpete et al. (2019) documented a higher average concentration of 2.414±0.648 mg/l for the surface water in Silver River, Southern Ijaw, Bayelsa State. The findings align with the study conducted by Muhammad et al. (2022), which documented an average concentration of 0.0245 ± 0.31 mg/l in the Kunhar River and its tributaries located in the Kaghan Valley, Northwest Pakistan. The lead content in Onosi Umudina was identified as 0.173±0.077 mg/L, whereas in Onosi Umuebe it was determined to be 0.14±0.02 mg/L. The greatest mean value was observed for Onosi Umudina, while the lowest worth was recorded for the same individual. Kaizer and Osakwe (2010) produced data indicating that the average values for the Ase, Agbarho, Ethiope, Ekakpamre, and Afiesere rivers varied between 0.003 and 0.08 mg/l, respectively. This finding was consistent with the results reported by Vincent-Akpu and Offiong (2015), who documented a concentration of 0.17 mg/l in water from the Qua Iboe River Estuary, Nigeria. The maximum average nickel content was calculated at Onosi Rubber at 0.346±0.210 mg/l, while the lowest was documented at Onosi Umudina at 0.136±0.015 mg/l. Additional concentrations are included in Table 4.1. The zinc study of surface water revealed that Onosi Umuebe had the highest mean zinc content of 0.233±0.183 mg/l, whilst Onosi Akpu had the lowest measured zinc value of 0.073±0.021. The analysis of zinc levels showed that Onosi Umudina had the highest average concentration of 1.953±0.558 mg/l, while Onosi Rubber had the lowest range of 0.253±0.080 mg/l. These results are consistent with the research carried out by Ali et al. (2022) on the distribution of heavy metals in the water of a metropolitan river in a developing country, namely the Bhairab River.

Phenolic endocrine compounds in Surface Water: An analysis of the phenolic endocrine disrupting compounds detected in the surface water of Omoku River is shown in Table 3. An investigation revealed the presence of many phenolic endocrine-disrupting compounds at multiple locations in the Omoku River. Among surface water samples, Onosi Akpu has the highest estimated concentration of BPA at 62.16±1.554 µg/L, while Onosi Rubber has the lowest value at 3.306±2.400 µg/L. Similar elevated concentrations of BPAs were identified in surface water samples collected from different locations. The aforementioned results align with the research conducted by Klecka et al. (2009) on the analysis of bisphenol A in surface water systems in North America and Europe.

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Similarly, Santhi et al. (2012) documented the presence of bisphenol A in surface water, drinking water, and plasma from Malaysia, as well as an assessment of the exposure resulting from the consumption of drinking water. In each of the aforementioned investigations, the presence and concentration of BPA were judged to be substantially high. A further phenolic endocrine-disrupting chemical detected in the surface water of the Omoku River was identified as 4-nonylphenol (4NP). The analysis showed that Onosi Umuebe had the greatest 4-nitrophenol (4NP) concentration of 1.197±0.319 µg/L, whereas Onosi Rubber had the lowest value of 0.527±0.714 µg/L. An investigation conducted by Araujo et al. (2018) revealed a concentration of 1.20 µg/L of 4-nonylphenol in the surface waters of the Guandu River. Furthermore, the results align with the study conducted by Vargas-Berrones et al. (2020), which documented a greater abundance of 4-nonylphenol in water samples collected from Mexico. Furthermore, the investigation disclosed the existence of OP at every site examined in the Omoku River. The OP content in Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina varied between 0.423±0.286 and 0.713±0.597 µgen per litre. The results presented align with the research conducted by Graca et al. (2016), which explored the historical trends of alkylphenol pollution (specifically 4-tert-octylphenol and 4-nonylphenol) in the Baltic Sea. Similarly, Koniecko et al. (2014) investigated the presence of alkylphenol contamination in the surface sediments of the Gulf of Gdansk in the Baltic Sea.Furthermore, further inquiry revealed the presence of 4CP at the following locations: Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina.The examined locations exhibited a range of 4CP content values from 0.02±0.017 to 0.14±0.248 µg/L, with Onosi Umuebe recording the highest value of 0.14±0.248 µg/L.In a pertinent investigation, Wang et al. (2011) recorded the presence of 4CP and other phenolic compounds that impact the functioning of the endocrine system in the sediment from the aquaculture base of Dianchi Lake. Wang and colleagues (2016) also recorded a substantial fourth convergent pressure (4CP) in the Panlong River, a metropolitan estuary situated in the Yunnan-Guizhou plateau.

Table 4.: Heavy metal contaminated Factor in water

	Onosi Akpu	Onosi Rubber	Onosi Umuebe	Onosi Umudina
Fe	0.48	0.49	0.2614	0.946
Cd	21	23.33	25.33	43.33
Pb	3.34	5.46	2.8	3.46
Ni	10	17.3	15	6.8
Zn	0.0243	0.0643	0.07767	0.06533
Cu	0.0935	0.1265	0.098	0.9765

Table 5: Non-carcinogenic and carcinogenic risk of heavy metals through Water

A	Chronic Daily Intake (CDI)			
Hm	**Onosi Akpu**	**Onosi Rubber**	**Onosi Umuebe**	**Onosi Umudina**
Fe	5.186 E-6	3.394E-6	5.751 E-6	2.011 E-6
Cd	3.771 E-6	2.482E-6	1.0057 E-6	2.703E E-6
Pb	7.857 E-6	5.343 E-6	6.286 E-6	2.42 E-6
Ni	4.086E-6	6.6E-6	7.637 E-6	4.714E10^{-7}
Zn	6.6E-8	4.18E-6	5.751 E-6	1.257 E-6
Cu	3.457 E-6	2.514 E-6	1.729 E-6	1.754E10^{-5}
B	Hazard Quotients of Heavy Metals			
Fe	1.729E-6	1.131E-6	1.917E-6	6.70E-7
Cd	7.542E-7	4.964E-6	2.0114E-6	5.406E-6
Pb	5.612E-7	3.816E-6	4.49E-7	1.729E-6
Ni	2.043E-7	3.30E-8	0.382E-6	2.36E-8
Zn	2.2E-9	1.393E-8	0.019E-6	4.2E-9
Cu	8.6E-9	6.3E-8	4.3E-8	4.4E-7
HI	3.26E-06	1.00E-05	4.82E-06	8.27E-06
C	Cancer Risk of Heavy Metals			
Cd	2.30E-6	1.514E-5	6.135E-6	1.649E-5
Pb	6.679E-6	4.342E-5	5.341E-6	2.057E-5
Ni	3.432E-6	5.54E-6	6.415E-6	3.960E-7
Fe	2.13E-4	1.39E-4	2.35E-4	8.2451E-5
TCR	2.25E-4	2.03E-4	2.53E-4	1.20E-4

Eco-toxicological Risk Assessment of Heavy Metals in the water Samples: To evaluate the levels of pollution and determine the anthropogenic impact of heavy metals in surface water, the contamination factor (CF) was used. Data on the contamination factor of water collected from several locations along the Omoku River is shown in Table 4. The current study produced estimated Nemerrows Pollution Index values for iron (Fe) in Onosi Akpu, Onosi Rubber, and Onosi Umuebe, with Onosi Umudina yielding a value of 0.946. Zhong et al. (2015) classified

NPI values < 0.5 as indicative of no pollution, 0.5–0.7 as suggesting cleanliness, 0.7–1.0 as showing warmth, 1.0–2.0 as indicating pollution, 2.0–3.0 as indicating moderate pollution, and >3.0 as indicating severe pollution. According to these results, the presence of Fe contamination was confirmed to be absent in Onosi Akpu, Onosi Rubber, and Onosi Umuebe. However, the contamination of Onosi Umudina was found to be of a heated nature. Further heavy metals identified as not contaminated in this investigation were zinc (Zn) and copper (Cu). The corresponding sites were Onosi Akpu, Onosi Rubber, and Onosi Umuebe. Observations revealed that the contamination factor of Cd, Pb, and Ni was significantly contaminated. These findings are predicated on the NPI values being over 3.0, with the exception of Pb which is considered highly contaminated due to its NPI value below 3. The contamination factor of water from the river Benue with trace elements in Makurdi was found to be significantly contaminated with Pb and Ni by Akaahan et al. (2015). A similar investigation conducted by Alimor and Alagoa (2014) documented the presence of various contaminants, including Cd and Ni, in Nkisa River.

Health Risk Evaluation of Heavy Metals: Water-based evaluation of the non-carcinogenic and carcinogenic risks associated with heavy metals. Table 5 displays the non-carcinogenic and carcinogenic risks associated with heavy metals when ingested via water exposure. The following table displays the chronic daily intake, hazard quotients, and related cancer risk of heavy metals. The first phase of the non-carcinogenic investigation is calculating the values of chronic daily intake (CDI). Surface water in Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina exhibited significantly reduced daily intake of iron (Fe), cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and copper (Cu) compared to the recommended oral intake. The heavy metal CDI values reported by Maigari et al. (2016) were also small. However, Ekere et al. (2014) observed higher lead CDI values for several heavy metals in surface water. The hazard quotient (HQ) values of the metals at all the examined locations were below 1. The HQ values for adults at all sites were consistently low, indicating that the surface water of the Omoku River is less susceptible to contamination, particularly in rural areas. In their respective studies, Ekere et al. (2014) and Maigari et al. (2016) both documented an HQ value of less than 1 for certain metals examined in the rivers under investigation. The low HQ values observed in this research were attributed to the low CDI values of the metals under investigation. At now, these metals may pose a health hazard to water consumers. However, with prolonged consumption of water in each specific area, people may be exposed to more health risks. Investigation showed that Onosi Rubber has the greatest Hazard Index (HI) of 1.00E-05, while Onosi Akpu has the lowest HI of 3.26E-06. None of the hazard index (HI) values documented in this investigation exceeded 1. The aforementioned conclusion is consistent with the findings documented by Ayantobo et al. (2014), Ekere et al. (2018), and Maigari et al. (2016). The possible long-term health risks are negligible, and the non-carcinogenic toxicological effects are negligible. The objective of this research was to assess the carcinogenic risks (CR) and cumulative carcinogenic risk (TCR) linked to the ingestion of iron (Fe), nickel (Ni), lead (Pb), and cadmium (Cd) via water. The findings of this estimation are shown in Table 5. Within the Onosi Akpu, Onosi Rubber, and Onosi Umuebe communities, the element Fe has the most elevated cancer risk value, above the acceptable threshold of 10-6. It is very probable that the surface will provide a hazard to users. The cancer risk of lead (Pb) and cadmium (Cd) in Onosi Rubber and Onosi Umuebe was determined to exceed the acceptable threshold of 10-6. Therefore, the water in these sample facilities is very probable to be carcinogenic when used for an extended period. The total accumulation of heavy metals fell within the permissible range of conductivity (CR) greater than 10−4, which might pose a long-term risk.

The study undertaken by Bian et al. (2016) unequivocally showed significantly higher levels of CR and TCR over the acceptable limit. Therefore, the researchers concluded that arsenic (As), cadmium (Cd), and iron (Fe) pose cancer risks in the studied area. Khezerlou et al. (2020) conducted an independent study and found that the chemical reactivity (CR) value of arsenic (As) in salad was above the acceptable risk level. Accordingly, they concluded that the ingestion of salad grown in the area raises the probability of cancer among the local people. Furthermore, Gebeyehu and Bayissa (2020) assessed and found that certain vegetables had Total Contaminant Reduction (TCR) values for Arsenic (As), Cadmium (Cd), and Nickel (Ni) that were above the permitted limits. This indicates that exposure to these elements might potentially pose significant cancer risks. Taken together, our results indicate that consuming Rocca, coriander, and parsley grown in agricultural areas in Qatar might elevate the cancer risk in the adult population due to the elevated concentrations of iron (Fe), nickel (Ni), and arsenic (As).

Health risk assessment of the phenolic EDCs in water: The health risk evaluation of phenolic endocrine-disrupting chemicals (EDCs) in water is shown in Table 6. It encompasses pertinent research on the possible hazards of phenolic endocrine-disrupting chemicals (EDCs) for both children and adults who are exposed to water in the Omoku River.

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Table 6: Health risk assessment of the phenolic EDCs in water

	Status	Onosi Akpu	Onosi Rubber	Onosi Umuebe	Onosi Umudina
BPA	Children	6.216	0.3306	4.997	4.7
	Adult	1.776	0.0945	1.428	1.343
4NP	Children	0.1557	0.0527	0.1197	0.1743
	Adult	0.0445	0.0151	0.0342	0.0498
4-t-OP	Children	0.0563	0.0713	0.061	0.0423
	Adult	0.0161	0.0204	0.0174	0.0121
4CP	Children	0.006	0.002	0.014	0.0098
	Adult	0.00171	0.000571	0.004	0.0028

The analysis showed the computed Composite Disease Index (CDI) values for the populations exposed to BPA, 4NP, 4-t-OP, and 4CP at various sampling sites. According to Wasim et al. (2010), the CDI values of BPA were elevated in children, reaching the maximum value of 6.216 µg/kg/day at Onosi Akpu and the lowest value of 0.3306 µg/kg/day at Onosi Rubber. In contrast, the CDI values for adults were high at Onosi Akpu (1.776 µg/kg/day) and low at Onosi Rubber (0.0945 µg/kg/day). The readings fell below the recommended daily intake (mg/kg/day) of BPA at 0.05 mg/kg/day and the Drinking Water Equivalent Levels of 1.823 mg/L and 0.521 mg/L set by EPA's (2018) standards. The analysis revealed the CDI levels of 4NP in the surface water of the Omoku River. The CDI values of 4NP in surface water in Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina were found to be below values recorded by Inam et al. (2019), the minimum recommended daily intake reference dosage of 0.008 mg/kg/day, as well as below the Drinking Water Equivalent Level values of 0.292 mg/L and 0.083 mg/L (EPA, 2018). A comparable investigation conducted by Wasim et al. (2010) reported a CDI-low value of 4 nanoparticles in residential water. The findings indicated the CDI analysis of 4-t-OP in surface water from several sampling sites, including both children and adults. The Carbon Dissolved Ion (CDI) of 4-t-OP, as reported for surface water, fell within the range of 0.0423-0.0713 for children and 0.0121-0.0204 for adults. The present investigation found that the CDI value for children was lower than the values reported by Li et al. (2018) for drinking water in the Suzhou metropolitan area and Cheng et al. (2008) for water in the Yong River of China. The analysis revealed a consistently low range of 4CP for both children and adults in all the regions included in the sample. This is corroborated by the findings of Omoboriowo et al. (2012), who also observed a low 4CP value in water waste in the Yong River.

Conclusion

This research aimed to examine the levels and evaluate the potential hazards associated with heavy metals (Fe, Cd, Pb, Ni, Zn, Cu) and phenolic endocrine disrupting chemicals (BPA, NP, OP, and CP) in water, sediment, and catfish biota populations in Omoku River. Furthermore, we investigated the potential hazards linked to both heavy metals and phenolic endocrine-disrupting chemicals. Sampling was conducted at four separate locations inside Omoku River: Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina. Ferrous, cadmium, lead, nickel, zinc, and copper were identified as the heavy metals present in the Omoku River water. Considerable variations in the concentrations of heavy metals were noted among the many analysed locations. The analysis revealed that the surface water of Omoku River was contaminated with Cd, Pb, and Zn. The phenolic endocrine-disrupting toxins detected in the surface water were BPA, NP, OP, and CP. Surface water samples at Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina detected the presence of BPA, NP, OP, and CP. In contrast, Onosi Akpu lacked CP, Onosi Rubber lacked OP, and Onosi Umuebe lacked both NP and CP. The assessment of the risk associated with the heavy metals (Fe, Cd, Pb, Ni, Zn, Cu) in water indicated that the contamination factor of Cd, Pb, and Ni was substantial, Pb was moderately polluted, and Zn and Cu were classified as uncontaminated. Surface water in Onosi Akpu, Onosi Rubber, Onosi Umuebe, and Onosi Umudina exhibited significantly reduced daily intake of iron (Fe), cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and copper (Cu) compared to the recommended oral intake. High humour (HQ) readings were consistently low for adults at all sites, indicating that the surface water of the Omoku River is less susceptible to contamination, particularly in rural areas. The hazard index (HI) values documented in this investigation were less than 1. The CDI values of BPA were elevated in children, reaching their peak at Onosi Akpu at 6.216 µg/kg/day and their lowest at Onosi Rubber at 0.3306 µg/kg/day. In adults, the CDI values were comparable, with Onosi Akpu at 1.776 µg/kg/day and Onosi Rubber at 0.0945 µg/kg/day. There is an increased likelihood of health hazards for youngstersx.

Recommendations

1. Based on the findings of this study, it is recommended to enforce requirements against the careless discharge of industrial wastes in Omoku River without any previous treatment.

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2. Additionally, regular monitoring of phenolic endocrine disruptive chemicals in Omoku River is recommended, as the study has detected the presence of these substances in the water.

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