**Occurrence of Emerging Contaminants and Heavy Metals in Freshwater and Wastewater Samples from Southwest States in Nigeria**

ABSTRACT

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| The aim of this study was to examine heavy metal, pharmaceuticals, endocrine disruptors and food additive pollutants in some surface water samples from Nigeria.. Samples were collected from Lake 264, Rivers Osun and Ureje from Osun and Ekiti States. Raw effluent, slurry sludge, treated effluent and canal water were collected from Apapa and Festac Town, Lagos State. The concentrations of iron (Fe), lead (Pb), cadmium (Cd), chromium (Cr) zinc (Zn), nickel (Ni) and manganese (Mn), bisphenol A (BPA), phthalates, dioxin, erythromycin, tramadol, paracetamol, diclofenac, diazepam and monosodium glutamate were measured in the samples. The result showed that the concentrations of Cd and Cr in all samples were below the detection limits and the Standard Organisation of Nigeria (SON) permissible limits of 0.03 and 0.05 ppm, respectively. The highest concentrations of Fe (28.33 ppm), Zn (6.50 ppm), Pb (5.00 ppm) and Mn (9.50 ppm) were detected in the slurry sludge. However, Fe (20.00 ppm), Zn (5.00 ppm) and Mn (9.00 ppm) in raw effluent were above the WHO limit of 2.00, 3.00 and 0.04 ppm. The canal water revealed the presence of paracetamol, diazepam, diclofenac, BPA and phthalate esters. In addition, BPA and phthalates were detected in Rivers Osun and Ureje, wastewater, sludge and treated effluents. Human health risk assessment results showed that the chronic daily intake (CDI) values in the slurry sludge and raw effluents were above the reference dose of the metals and found in the order Fe > Mn >Zn>Pb>Ni>Cd>Cr for the children and adult population. Hazard quotients (HQ) and hazard index (HI) values were greater than 1 and may be carcinogenic to humans. This study concludes that pollutants were present in the study location, irrespective of their proximity to industries and recommends further research on emerging contaminants, their human health risks assessment, evaluation and prevention and control of all pollutants. |

*Keywords: phthalates, slurry sludge, bisphenol A, pharmaceuticals, heavy metals*

1. INTRODUCTION

Numerous novel chemical substances, also known as "emerging pollutants" (EPs) or "contaminants of emerging concern", have appeared in the environment because of the fast expansion of human activities in recent decades (Durig et al., 2020). The scientific community recognises the importance of studying these EPs even if they are only partially or not currently monitored or regulated because of their biosorption, persistence, and negative consequences on organisms, assemblages and ecosystems. Emerging pollutants are new organic chemical compounds of significant environmental concern, often referred to as micropollutants and are found in low concentrations in water bodies (ng/L-µg/L) (Durig et al., 2020; Kong et al., 2013; Ramos et al., 2016). Exposure to endocrine-disrupting chemicals (EDCs) can pose serious dangers to the environment and has been recognized to cause endocrine disruption in humans, including antiestrogenic and antiandrogenic activity (Arman et al., 2021).

Recent studies have identified the presence of these chemical compounds in aquatic environments (surface water, municipal wastewater, groundwater and drinking water), food sources, air and soils (Adesokan et al., 2022; Hu et al., 2021; Arman et al., 2021; Egbuna et al., 2021). Sobus et al. (2019) and Ulrich et al. (2019) reported that EPs are chemicals used widely and enter the environment through different pathways. They frequently enter aquatic ecosystems due to incomplete elimination during wastewater treatment processes (Reemtsma et al., 2016; Li et al., 2018). EPs in the environment are even more alarming because they usually do not appear separately but as combinations of compounds, which likely result in undesirable synergetic consequences.

The universality of the abundance of reasonably noxious EPs in the environment emphasises the importance of measuring and monitoring the occurrence and ecological and health impacts. Endocrine disruptors (EDs), pesticides and pharmaceuticals, and personal care products (PPCPs) are a few EPs documented to affect ecosystems and human health negatively. Endocrine disruptors occur synthetically or naturally as chemical fragments that can negatively impact the homeostasis of endocrine processes, leading to nervous, generative, immunological, and reproductive abnormalities at the organismal level (Kar et al., 2021). Pesticides, fertilisers, PAHs, bisphenol A (BPA), phthalate esters, heavy metals and sex-steroid hormone mimics, for example, have also been linked to EDs that are present in the environment that come from industrial, pharmaceutical, sewage treatment, and agricultural waste.

Endocrine disruptors negatively impact human health and the ecosystem, especially when they bioaccumulate in the environment. A few of the numerous ways humans are exposed to EDs are usually from air, food and water consumption. Additionally, they could enter the body through the skin (Gałazka and Jankiewicz, 2022) and can be found in nearly every aquatic medium facility (Goeury et al., 2022). The vulnerability of fish and other aquatic creatures to EDCs is particularly high. Other health risks posed by exposure to EDs in living organisms include induction abnormalities, changed sex determination, slowed growth, delayed conception, and altered behaviour (Arambula et al., 2018).

Pharmaceuticals have also been identified as an emerging contaminant with potential risks to aquatic systems. Only a few studies have reported the impacts and underlying toxicity processes.  Pharmaceuticals are derived from medications for humans and animals, as well as from food additives, and they are release into the environment through human or animal excreta with little to no alterations to their chemical composition (Lambropoulou et al. 2014), they contain active chemicals that are capable to have pharmacological effects (WHO, 2012). These contaminants can be active at very low concentrations and are usually found in the environment at ng/L to low g/L, even pervasively in drinking waters (Benotti et al., 2008). Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a class of artificial chemicals that are receiving more attentiveness due to their increasingly frequent detection in humans, wildlife, and aquatic environments (Houde et al. 2011; Glover et al. 2018). PFAS contains over 4700 components, accumulating over time in humans and the environment (European Environment Agency, 2023). They are persistent in the environment and humans and are called "forever chemicals." These pollutants were created around the 1950s, and they are actively used in many industries for lowering surface tension in firefighting foam and as water repellents on textiles, rawhide, cooking utensils, and paper (Prevedouros et al. 2006; Wang et al. 2014). They can result in some severe conditions, such as cancerous tumours, thyroiditis, plumpness, decompensated cirrhosis, and reproductive issues (Wang et al., 2023).

The pollution of surface water and wastewater with heavy metals is a serious environmental issue globally, receiving attention from researchers and environmental activists. Past studies have shown that sources of heavy metals include the disintegration of rocks and soils (Samarghandi et al., 2007; Igwe et al., 2008; Al-Juboury, 2009). In the aquatic ecosystem, there have been reports on the increase in the concentrations of heavy metals, and it is fast becoming a harsh threat to human health and aquatic life (Opoku et al., 2020). To reduce the menace of heavy metals, some environmental bodies have provided permissible limits in freshwater, soil, sediment, and wastewater (WHO, 2006; WHO, 2011; USEPA, 2011).

The objectives of this study were to (i) investigate the concentrations and health risk assessment of Fe, Pb, Cd, Cr, Zn, and Mn, categorized as heavy metals in raw effluent, treated effluent, surface/ freshwater and sludge; (ii) examine bisphenol A and phthalate and dioxin classified as endocrine disruptors; (iii) determine paracetamol, diclofenac, diazepam, erythromycin and tramadol known as pharmaceuticals in surface water and wastewater; and (iv) investigate monosodium glutamate a known food additive.

2. material and methods

* 1. **Sampling location**

Samples were collected from Lagos (Apapa and Festac town), Osun (Osun River) and Ekiti (Ureje River) States in Nigeria (Fig. 1). Raw effluent, sludge and treated effluent samples were collected from Apapa, Lagos, the study location coordinates are presented in Table 1. The surface canal water samples were collected from Festac Town, Lagos state (Table 1). The wastewater, sludge, and treated effluent were collected at the Apapa industrial area of Lagos. Apapa is situated west of Lagos Island and houses some industries that discharge contaminants into the lagoon. The discharged contaminants may also affect other water bodies and impact human health. The Festac surface canal houses some aquatic organisms and serves as a livelihood for subsistence fishers; however, houses around the site discharge domestic wastewater into the surface canal water, which is also used by petrol bunkering for crossing.

Osun River lies between Lat 8° 19' 60.00" N and Long: 5° 15' 60.00" E, Osun State. Previous studies showed that the Osun River is currently being polluted by some anthropogenic activities of gold miners in several areas of Osun State. The activities around the study site have further affected the physicochemical and microbiological parameters of the water (Olajire and Imeokparia, 2001; Azeez et al., 2015).  Lake 264 is sited in Saba community Osogbo within Lat 70 79ꞌ 96ꞌꞌ N to 70 77ꞌ 84ꞌꞌ N and Long 40 56ꞌ 22ꞌꞌE to 4054ꞌ 03ꞌꞌ E. The lake is mainly used for irrigation by small-scale vegetable and maize farmers, serves as a water source for fish farming, and finally discharges into the Osun River. In addition, waste generated by mechanic workshops and a significant market along the lake's edge is dumped into the water (Yusuf et al., 2017). Ureje River originates in the mountain ranges that descend into the Afe Babalola University, Ado-Ekiti (ABUAD), Ekiti State. The river lies between longitudes 5°18'25.87" E and latitudes 7°36' 23.82" N.

**Table 1**: Sampling sites and positions

|  |  |  |  |
| --- | --- | --- | --- |
| **Sampling site** | **Sampling location** | **Position**  | **sample matrix** |
| Apapa | Lagos | Lat: 6° 26' 59.99" N Long: 3° 21' 59.99" E | Effluent, treated effluent and slurry sludge effluent |
| Festac Town | Lagos | 6° 27' 59.202" N, 3° 17' 0.6504*"* E | Canal water |
| Osun River  | Oshogbo, Osun State | Lat 8° 19' 60.00" N and Long: 5° 15' 60.00" E | Surface water  |
| Lake 264 | Oshogbo, Osun State | Lat 70 79ꞌ 96ꞌꞌ N - 70 77ꞌ 84ꞌꞌ N and Long 40 56ꞌ 22ꞌꞌE to 4054ꞌ 03ꞌꞌ E.  | Surface water |
| Ureje River | Ekiti State | 5°18'25.87" E and latitudes 7°36' 23.82" N | Surface water |

 

 **Fig 1**: Map of Southwest Nigeria showing the Study location

**2.2 Sampling and sample preparation**

Water samples were collected in triplicate manually from each sample location using amber glass water bottles according to the method described by Hu et al. (2021) and Ogunbanwo et al. (2022). A total of 21 samples were collected from the study locations and transported with ice packs in an igloo cooler to the Department of Animal and Environmental Biology laboratory, Adekunle Ajasin University, Akungba-Akoko, Ondo State. The water samples were stored in the refrigerator (4oC) until analysis. Before the analysis, 1 ml of the triplicate samples from each location was thoroughly mixed with 50 g of the standards of the targeted compounds and stirred to ensure homogenous mixing. Each mixed sample was filtered using a 0.22 mm pore size filter paper into a 5 ml sample bottle.

* 1. **Chemicals and reagents for the determination of pharmaceutical and endocrine disruptors**

HPLC grade reference standards of targeted compounds (paracetamol, diazepam, bisphenol A, phthalates, dioxin, erythromycin, tramadol, paracetamol, diclofenac, diazepam and monosodium glutamate) were procured from Sigma-Aldrich (Steinheim, Germany). They were kept as suggested by the manufacturer. The standard methanol (lichrosolv) stock solutions were prepared and kept at a temperature of – 20 °C in the dark. Other chemicals obtained are LC/ MS-grade formic acid (Sigma-Aldrich, Steinheim, Germany). Acetonitrile, ethylacetate and ammonium acetate, phosphoric acid (analytical grade), and Ethanol (lichrosolv) (HPLC-grade)

* 1. **Determination of Heavy Metals**

The metals were analysed using the AOAC Manual (2015) protocol. Before the digestion of samples, the water samples were filtered with Whatman filter paper 41 (60 mm). During sample digestion, 0.75 L of each filtrate was measured in the digestion flask. Thereafter, 9 ml and 3 ml of concentrated HNO3 and HCl were added to the sample in the digestion flask and boiled on the hot plate in a fume cupboard. The samples were allowed to cool down. The cooled samples were later placed in the Atomic Absorption Spectrophotometer (AAS) modelled by AA990 PG Instrument Ltd, England, for heavy metal detection. The metals analysed were Fe, Pb, Cd, Cr, Zn, Ni and Mn. The concentration of each metal was measured in parts per million (ppm). Before the determination of each metal analysis, calibration was done with standards and the AAS detection limits for Fe, Pb, Cd, Cr, Zn, Ni, and Mn were 0.0046 ppm, 0.012 ppm, 0.0028 ppm, 0.005 ppm, 0.003 ppm, 0.008 ppm and 0.002 ppm, respectively.

* 1. **Determination of pharmaceutical and endocrine disruptor pollutants**

Instrumentation analysis was carried out using the high-performance liquid chromatography (HPLC) attached to an ultraviolet (UV) detector to determine the pharmaceutical and endocrine disruptor pollutants content in the sample. The HPLC system (Hangzhou LC-8518, column size 150 x 4.6 mm) with a low-pressure gradient, solvent delivery pump with high-pressure switching valves, and a high-sensitivity ultraviolet (UV) detector. The mobile phases were prepared with acetonitrile/0.1% phosphoric acid (30:70) for bisphenol A, diazepam and tramadol; acetonitrile/0.1% Phosphoric acid (35:65) for diclofenac; acetonitrile/0.1% ammonium acetate (50:50) erythromycin; acetonitrile/10 ml Phosphate buffer (25:75) for monosodium glutamate; acetonitrile/0.1% phosphoric acid (60:40) for dioxane, acetonitrile/0.1% phosphoric acid (40:60) for phthalate and methanol/0.1% ammonium acetate (15:85) for paracetamol. The gradients of each chemical increased within 7 min while the column temperature was 30-35 0C. The retention time of each standard was compared with that of the chromatogram obtained from the sample to determine the chemical contents in the sample.

**2.6 Data Analysis**

**2.6.1 Statistical Analysis**

Data from this study were analyzed using R version 4.3.2 (2023-10-31). The means and standard deviations of each pollutant were presented in tables. In addition, a one-way ANOVA was used to determine the statistical difference values (p-values) between heavy metals from each study location.

**2.6.2** **Health risk assessment of metals in surface and wastewater**

**The chronic daily intake limit**

The chronic daily intake (CDI) limit is also known as exposure assessment. The CDI may also be referred to as an “absorbed” dose that is metabolised into the body. The chronic daily intake (CDI) of metals in surface and wastewater via oral ingestion route was calculated using Equation 1 below:

$ CDI=\frac{CxIRxEFxED}{BWxAT}$ (1)

CDI (mg/kg-day)

C = Concentration of metal in water samples (ppm/mg/l)

IR = Ingestion Rate (l/day) = 1 L for children 2.2 for adult

EF = Exposure Frequency (days/yr) = 365 days

ED = Exposure Duration (yr) 15 years for children, 64.4 years for adults (WHO)

BW = Body Weight (kg) 6kg and 70 kg for children and adults, respectively

AT = Averaging Time (period over which exposure is averaged) (days) (for carcinogens, AT = 70 × 365 = 2550 days for both children and adults; for non-carcinogens, AT = ED x 365 = 2190 days and 10950 days for children and adults, respectively)

For noncarcinogens: AT = ED \* 365 days per year and intake is called Chronic Daily Intake (CDI).

For carcinogens: AT = Lifetime (70 years) \* 365 days per year and intake is called Lifetime Average Daily Dose (LADD). (Bamuwuwamye et al., 2017)

**Non-carcinogenic risk assessment**

For the non-carcinogenic risk assessment, it is calculated as hazardous quotient (HQ) in contaminated surface and wastewater for non-cancer risk is calculated using equation 2 below:

$HQ=\frac{CDI}{RfD}$ (2)

HQ is the non-cancer hazard quotient

CDI is the chronic daily intake (mg metal/kg/day); and

RfD (oral reference dose) represents the chronic oral reference dose (Bamuwamye et al., 2015).

The RfD equivalents for Cd, Zn, Fe, Mn, Pb, Cr and Ni are 0.001, 0.3, 0.7, 0.14, 0.0036, 0.003 and 0.011, respectively. In addition, the hazard index is evaluated by adding all of the calculated hazard quotients (HQ) for each heavy metal. No significant non-cancer risk is observed if the HQ or HI < 1 and if >1 it means significant non-cancer risks, which increase with the increasing value of HQ or HI (Wei et al., 2015).

3. results and discussion

* 1. **Heavy metal concentrations**

Figure 2 shows that the concentration of cadmium (Cd) from all sampling locations was 0.00 ppm. These results implied the obtained concentration was below the detection limits of 0.0028 ppm. In addition, when the obtained concentration was compared with the Standard Organisation of Nigeria’s (SON) limit of 0.003, World Health Organisation (WHO) and the United States Environmental Protection Agency (USEPA) acceptable limits shown in Table 2 (SON, 2015; WHO, 2021; USEPA, 2023), the obtained result was below the limits. Cadmium is sometimes alluded to as a poisonous trace element that may be present in rocks, coal, and gasoline in low concentrations and occasionally in association with Zn (Sobha et al., 2016).  It may also be released into the environment through mining processes, metal coating, batteries, rain, cigarette smoke, waste disposal and wind (MDHHS, 2014). According to WHO (2011), drinking water may be contaminated with Cd from zinc galvanized pipelines with cadmium impurities or fittings, water heaters, water coolers, and taps with cadmium-containing solders. The non-detection of cadmium in all samples collected in this study might be due to the scarcity of cadmium in soils or activities carried out around the locations, hence, the surface water and treated effluent might be safe for humans and aquatic biota at the location. At higher concentrations, Cd may affect the kidneys, livers, hearts and bones of fish (Obahiagbon and Olowojoba, 2007).

Chromium values from all study sites were 0.00 ppm (Fig. 1). The result revealed that the observed concentration was below the detection limit of 0.005 ppm and below the allowable limits presented in Table 2 by the SON, WHO and USEPA. Chromium is one of the most important elements and pollutants found in the ecosystem. It may be used as pigments in cement, paper, rubber, and paints (Olayinka-Olagunju et al., 2021).   Chishti et al. (2011) argued that chromium plays an important part in the digestion of cholesterol, fat, and glucose at low concentrations. The authors further claimed that the absence of Cr may result in high blood sugar, obesity, and oligospermia. However, it may be hazardous and carcinogenic at higher concentrations (Chishti et al., 2011). Chromium, specifically its hexavalent (VI) form, is a noxious pollutant that may harm human health (Abagale et al., 2013). Even at low concentrations, contact with Cr may result in skin rashes and infection. In addition, long-term exposure to Cr may cause kidney and liver damage, circulatory system interruption and nervous system breakdown (ATSDR 2000). In the aquatic ecosystem, Cr bioaccumulates and may pose a danger to the fish. Results from this study differ from the findings of Emmanuel et al. (2022) and Lu and Ma (2020), who observed the presence of Chromium in their surface water assessment in Anambra and China North plain respectively.

The concentration of iron from the study locations ranged from 0.00-28.33 ppm. The highest concentration was seen in the slurry sludge from Lagos, while the lowest was seen in the treated effluent. When the results in Table 1 were compared to the recommended limits in Table 2, it was observed that the concentration of Fe in the slurry sludge, treated effluent, Lake 264, Rivers Ureje and Osun were below the permissible limit. However, the concentrations of Fe in the raw effluent were higher than the recommended limit of 2 ppm. Iron is an essential element, but at high concentrations in wastewater, it contributes to soil acidification and loss of phosphorus and molybdenum in the soil, suggesting that discharging wastewater into the soil would increase its acidity and reduce its phosphorus. Iron is also essential for structural materials and equipment coated as steel or alloy (Imai et al., 2020). The result from this study is similar to the findings of Akter et al. (2021), whose concentration of iron wastewater ranged from 0.0305 to 4.1466 ppm, which implies that the industrial effluent was within the permissible limit but differs from the study of Lu and Ma (2020) whose did not detect the presence of iron in China North plain. The presence of iron is this study may be due to the parent soil and rocks of Nigeria.

From Fig. 2, the zinc concentrations ranged from 0.00-6.50 ppm. The highest concentration was observed in the slurry sludge, while the lowest value was recorded in the Ureje River. The results further showed that Zn concentration in the raw effluent and slurry sludge were higher than the permissible limits of WHO and USEPA, shown in Table 2, while Lake 264, Osun River and Ureje River values were within the permissible limits. One of the common elements found in wastewater facilities is zinc. Although Zn is an essential element in water, it may be dangerous at high concentrations (Advanced Chemical Systems, 2023). The toxic level of zinc in the wastewater may be due to Cd impurities (Essumang et al., 2008). This result implied that the low cadmium concentrations contributed to the low zinc concentration. The result also shows that the various activities along the study location did not contribute to the pollution of the study site.

The manganese concentrations ranged from 0.00-9.50 ppm, with the highest concentration observed in the slurry sludge and the least from Lake 264. Table 2 also shows that the concentrations of Mn in the raw and treated effluent were above the permissible limit of 5.00 ppm. With an increase in the concentration of Fe, the concentration of Mn increases. In this study, the concentration of Fe was high, which may contribute to the concentration of Mn (Abagale et al., 2013). In addition, high concentrations of Mn in the aquatic environment can result in the iron deficiency needed by the green algae, which will inhibit chlorophyll (Abagale et al., 2013). According to MDHHS (2022), drinking water with excessive concentrations of Mn will cause difficulties with recollection, alertness and motor abilities in children and adults.

Figure 2 also revealed that Pb was observed in the sludge, raw and treated effluents. The concentrations of Pb ranged from 0.00-5.00 ppm, with the lowest concentrations seen in water collected from the lake and rivers, while the highest concentration was observed in the sludge. The concentrations of sludge, raw and treated effluent were higher than the permissible limits of 0.001-0.10 ppm of the WHO, while the other samples were within the limits. Lead is a poisonous metal that is not safe for consumption at high concentrations. Even at low concentrations, Pb can damage the human central nervous system, brain, kidneys, and liver and cause genetic damage. Lead can also bioaccumulate and may result in irreversible harm or death (Olatunji-Ojo et al., 2020).

In addition, Figure 2 shows that no statistically significant difference (p>0.05) was observed between the heavy metals obtained from the six study locations. This result implies that there is no evidence to suggest that the samples were contaminated with heavy metals.

Fig. **2** Heavy metal concentration (mean ± sd) and p-values from study sites

**Table 2.** Permissible limit of heavy metals in drinking/surface water

|  |  |  |  |
| --- | --- | --- | --- |
| **Heavy metal**  | **WHO**  | **US EPA (2003)** | **Standard Org. Nigeria** |
|  | **Drinking/surface water** |  |  |
| Zinc Zn | 1.00- 15 ppm (WHO, 2021) | 0.010 ppm (EPA, 2003) | 3.00 ppm (SON, 2015) |
| Cadmium (Cd) | 0.005-0.15 ppm (WHO, 2021)  | 0.005 ppm (Martin & Griswold, 2009) | 0.003 ppm (SON, 2015) |
| Chromium  | 0.001-0.5 ppm (WHO, 2021) | 0.01 ppm (EPA, 2003) | 0.05 ppm (SON, 2015) |
| Nickel (Ni) | 0.01-0.25 ppm (WHO, 2021) | 0.10 ppm (EPA, 2003) | 0.02 ppm (SON, 2015) |
| Lead (Pb) | 0.005-0.1 ppm (WHO, 2021) | 0.015 ppm (EPA, 2003) | 0.01 ppm (SON, 2015) |
| Manganese  | 0.01-0.5 ppm (WHO, 2021) |  | 0.2 ppm (SON, 2015) |
| Iron (Fe) | 0.30 ppm (WHO, 2021) | 0.30 ppm (EPA 2011) | 0.30 ppm (SON, 2015) |
|  | **Effluent/wastewater** |  |  |
| Cadmium | 0.003 ppm (Aneyo *et al*., 2016) | 0.005 ppm (EPA 2011) | - |
| Chromium | 0.05 ppm Aneyo et al., 2016) | - | - |
| Nickel | 0.02 ppm (Aneyo *et al*., 2016) | 0.10 ppm (EPA 2011) | - |
| Manganese | 0.04 ppm (WHO, 2006) | - | - |
| Iron | 2.00 ppm (WHO, 2006) | -  | - |
| Lead  | 0.01-0.1 ppm (Khan et al., 2005; Aneyo *et al*., 2016) | 0.015 ppm (EPA 2011) | - |
| Zinc  | 3.00 ppm (WHO 2002) | 5.00 ppm (EPA 2011) | - |

**3.2 Health risk assessment of heavy metals**

The results for the chronic daily intake (CDI) for the non-carcinogenic oral ingestion for children and adults in all study locations are presented in Table 3. From the results, the CDI values calculated in the slurry sludge and raw effluents were above the reference dose. Iron from the slurry sludge had the highest CDI in the wastewater for both children and adults, while in surface water, Lake 264 showed the highest CDI in adults. The findings from this study differ from those of Emmanuel et al. (2022), whose findings revealed that their highest CDI value was recorded in Pb from drinking water from Anambra. The CDI indices for the HMs in the study areas were found to be in the order Fe > Mn >Zn>Pb>Ni>Cd>Cr for the children and adult population. The overall results showed the highest CDI in the adult population. This result, however, differs from the findings of Ghosh et al. (2023), who observed high CDI in children. The CDI order may be due to the level of wastewater generated by the industry, which is most likely from the essential nutrients iron, zinc, and manganese used in food industries.  Essential metals are important in water, but must not exceed the permissible limits stipulated by SON. They may have contributed most to the high CDI values observed in the study and could be a significant health risk.

**Table 3. Chronic daily Intake limits of heavy metals in children and adults** (mg/kg body weight/day)

|  |
| --- |
| **Children** |
| **Sample type/location** | Fe  | Zn | Mn  | Ni | Pb | Cd | Cr |
| Raw Effluent | 1.145 | 0.286 | 0.515 | 0.038 | 0.191 | 0.000 | 0.000 |
| Slurry sludge | 1.620 | 0.372 | 0.544 | 0.029 | 0.286 | 0.000 | 0.000 |
| Treated Effluent | 0.000 | 0.153 | 0.000 | 0.038 | 0.021 | 0.000 | 0.000 |
| River Osun | 0.057 | 0.038 | 0.038 | 0.000 | 0.000 | 0.000 | 0.000 |
| Lake 264  | 0.096 | 0.038 | 0.000 | 0.057 | 0.000 | 0.000 | 0.000 |
| River Ureje  | 0.210 | 0.000 | 0.038 | 0.057 | 0.000 | 0.000 | 0.000 |
| **Adult** |
| **Sample type/location** | Fe | Zn  | Mn  | Ni  | Pb | Cd  | Cr |
| Raw Effluent | 5.798 | 1.450 | 2.609 | 1.942 | 0.965 | 0.000 | 0.000 |
| Slurry sludge | 8.204 | 1.884 | 2.754 | 0.145 | 1.445 | 0.000 | 0.000 |
| Treated Effluent | 0.000 | 0.774 | 0.000 | 0.194 | 0.104 | 0.000 | 0.000 |
| River Osun | 0.290 | 0.194 | 0.194 | 0.000 | 0.000 | 0.000 | 0.000 |
| Lake 264  | 0.484 | 0.194 | 0.000 | 0.290 | 0.000 | 0.000 | 0.000 |
| River Ureje  | 1.061 | 0.000 | 0.194 | 0.290 | 0.000 | 0.000 | 0.000 |

**3.3 Hazard quotients and hazard index**

Table 4 shows the hazard quotient (HQ) and hazard index (HI) values of the heavy metal samples. The result showed that the HQ of Fe, Zn, Mn and Pb were greater than one (>1) in the children's population in the effluents, while in the adult population, Fe, Zn, Mn, Ni and Pb were greater than one (>1). The results implied significant non-cancer risks in the effluents (Wei et al., 2015). The results from this study agreed with the findings of Wu et al. (2009) and Emmanuel et al. (2022), who reported that HQ greater than 1 may show high carcinogenic/non-carcinogenic risk to the adult and children population in the study areas. Meanwhile, in the surface water, among the children population, HQ were less than one (1<), implying no significant non-cancer risk to the population. The adult population showed that in Ureje River, the HQ of Fe, Mn and Ni were greater than one (>1), and in Osun River, Mn and Lake 264, Ni was greater than 1 (>1).

On the other hand, the hazard index (HI) in the three effluent samples calculated in children and adults was greater than one (HI > 1). The HI of the surface water in the adult population was greater than one (>1), but was less than one (HI < 1) in the children's population, signifying that the population would experience non-cancer risks due to exposure to effluent and surface water metals. The result from this study corroborates the study of Lee et al. (2021) and Emmanuel et al. (2022), who reported HI greater than one from Rivers Buntal, Penambir and Demak, Malaysia and Anambra drinking water in Nigeria, respectively.

**Table 4.** Hazard quotients and hazard index

|  |  |
| --- | --- |
| **Hazard quotient in children** |  |
| **Sample type/location** | Fe  | Zn  | Mn  | Ni | Pb | Cd  | Cr  | **Hazard Index (HI)** |
| Raw Effluent | 1.636 | 0.954 | 3.681 | 0.038 | 52.972 | 0.000 | 0.000 | 59.281 |
| Slurry sludge | 2.315 | 1.241 | 3.885 | 0.029 | 79.528 | 0.000 | 0.000 | 86.997 |
| Treated Effluent | 0.000 | 0.510 | 0.000 | 0.000 | 5.726 | 0.000 | 0.000 | 6.274 |
| River Osun | 0.082 | 0.128 | 0.274 | 0.000 | 0.000 | 0.000 | 0.000 | 0.356 |
| Lake 264  | 0.137 | 0.128 | 0.000 | 0.057 | 0.000 | 0.000 | 0.000 | 0.322 |
| River Ureje  | 0.299 | 0.000 | 0.274 | 0.057 | 0.000 | 0.000 | 0.000 | 0.759 |
| **Hazard quotient in adults** |  |
| **Sample type/location** | Fe | Zn  | Mn  | Ni  | Pb  | Cd | Cr  | **Hazard Index (HI)** |
| Raw Effluent | 8.283 | 4.832 | 18.64 | 3.491 | 268.14 | 0.000 | 0.000 | 303.38 |
| Slurry sludge | 11.72 | 6.281 | 19.67 | 2.600 | 402.62 | 0.000 | 0.000 | 442.90 |
| Treated Effluent | 0.000 | 2.580 | 0.000 | 3.487 | 29.00 | 0.000 | 0.000 | 35.07 |
| River Osun | 0.414 | 0.647 | 1.387 | 0.000 | 0.000 | 0.000 | 0.000 | 1.801 |
| Lake 264  | 0.692 | 0.647 | 0.000 | 5.205 | 0.000 | 0.000 | 0.000 | 6.544 |
| River Ureje  | 1.516 | 0.000 | 1.387 | 5.205 | 0.000 | 0.000 | 0.000 | 8.755 |

**3.4 Emerging contaminant concentrations**

The emerging contaminants detected from the study sites are presented in Table 5. From the Table, the concentrations of 1,4-Dioxane ranged from 55.8873-168.899 μg/kg. The highest concentration was detected in raw effluent, while the lowest was observed in slurry sludge. Dioxins are known as persistent organic pollutants (POPs), which implies they do not degrade easily in the environment. Dioxins are highly hazardous and carcinogenic. They can disrupt the immune system, affect the hormones, and cause human reproductive issues (EPA, 2025). These pollutants are found across terrestrial and aquatic environments, at the top of the food chain, and in animals, where they are in fatty tissues. In addition, more than 90% of human contact, according to the USEPA, comes from consuming meat, dairy products, fish, and shellfish (USEPA, 2023). In groundwater, the USEPA’s permissible limit of 1,4-Dioxane in children’s drinking water should not be 0.4 mg/L (400ug/kg) per day for 10 days (McElroy et al., 2019). However, the results from this study are within the limits of USEPA.

**Table 5.** Concentrations of emerging contaminants

|  |
| --- |
| **Contaminants (ug/kg)** |
| Sampling site | 1,4-Dioxine  | bisphenol A | Monosodium gluthamate | Diazepam | Diclofenac | Paracetamol | Tramadol  | Erthryo-mycin  |
| Raw Eff. Apapa  | 168.90 | 57.167 | 0.559 | NT | NT | NT | NT | NT |
| Sludge Apapa | 55.887 | 38.028 | 0.781 | NT | NT | NT | NT | NT |
| Treat Eff Apapa | 67.234 | 27.870 | 8.226 | NT | NT | NT | NT | NT |
| Lake 264 | 82.749 | 46.639 | NT | NT | NT | NT | NT | 76.821 |
| Osun River | 62.012 | 73.109 | NT | NT | NT | NT | NT | 63.922 |
| Ureje River | 90.094 | 45.423 | NT | NT | NT | NT | NT | 53.017 |
| Festac Town Canal  | NT | 26.260 | NT | 17.805 | 59.286 | 34.849 | NT | NT |

\*NT - Not Tested

Bisphenol A ranged from 26.2596-57.1674 ug/kg. The highest concentration was measured in the raw effluent, while the lowest was detected in the Festac surface canal.   Bisphenol A (BPA) is referred to as an endocrine disruptor and plastic additive often found in surface water, sediment, sewage and sludge. In the natural environment, the presence of BPA could serve as a threat to the aquatic ecosystem and human health (Liu et al., 2021). People ingest BPA through contaminated food and beverages. Previous studies have reported that BPA has shown genetic toxicity, reproductive toxicity, endocrine-disrupting effects, cytotoxicity and neurological toxicity (Chen et al., 2016). The total allowed concentration (TAC) for the oral reference dose of BPA was 100 g/L. At the same time, the temporary tolerated daily intake (t-TDI) of BPA, according to the EFSA, is 4 g/kg body weight/day (Muhamad et al., 2016; Correia-Sá et al., 2017).

Monosodium Glutamate ranged from 0.5591 ug/kg in the raw effluent to 8.2269 ug/kg in the treated effluent. Monosodium glutamate is used globally as a food additive and is the most abundant non-essential amino acid. In Japan, MSG was found in seaweed and pesticides/fertilizers.  The average intake of MGS in the United Kingdom for the general population was 580 mg/day while 4.68 g/day for serious users (Rhodes et al. 1991). According to Niaz et al. (2018), the consequences of excess MGS include disorder of the central nervous system, cytokine release syndrome**,** obesity and reproductive problems.

The pharmaceutical concentrations examined in this study were paracetamol, diazepam, diclofenac, tramadol, and erythromycin. The result showed that tramadol was not measured but undetected in the water samples. The highest concentration of erythromycin was measured in Lake 264 with 76.8211 ug/kg, while the lowest was seen in Ureje River.  Erythromycin is an antibiotic and may be present in the environment because all medicines in Nigeria are sold as over-the-counter drugs. The concentrations of paracetamol, diclofenac and diazepam measured in this study differ from the findings of Ogunbanwo et al., 2021.

Due to the discharge of wastewater into the terrestrial and aquatic environment, pharmaceuticals, endocrine disruptors, monosodium glutamate, and dioxin are present in the ecosystem, and they may pose serious health issues to humans (Burns et al., 2018; Huang et al., 2021). The presence of these contaminants in these study areas proved that contaminants are present in Nigeria's wastewater and freshwater bodies. No pharmaceutical or plastic industries were sited closer to the study locations, yet contaminants were detected. Previous studies have discovered some of these contaminants, but they were done in areas where pharmaceutical companies discharge effluent into the rivers. In addition to the over-the-counter sale of medicine in Nigeria, the indiscriminate disposal of waste and unused medication could be another reason for this detection.

Eight types of phthalate compounds shown in Table 6 were detected from all locations, and they are as follows: dibutyl phthalate (DBP), diethyl hexyl phthalate (DEHP), diethyl phthalate (DEP), dimethyl phthalate (DMP), diisononyl adipate, dicyclohexyl phthalate, Diisodecyl phthalate and Benzyl butyl phthalate were determined from all study sites. However, not all classes were found in all sites. Phthalates are chemicals used for items' flexibility, durability, and other desired qualities. An example of phthalate is polyvinyl chloride (PVC) polymers used as plasticizers. Other products that contain phthalates are children's toys, paints, fabrics, food packaging, dental materials, perfumes, nail polish, and other cosmetics all contain phthalates (Li et al., 2010). The aquatic environment is usually open to phthalate pollution because approximately 1% of the phthalate components are found in plastic materials, which later find their way into the aquatic environment (Huang et al., 2013). Humans are widely exposed to phthalates through drinking water, which may lead to serious health risks like the disruption of the endocrine system, cancer, developmental abnormalities, and polyneuropathy (Lee and Koo, 2007).

**Table 6.** Concentrations of phthalate compounds

|  |  |
| --- | --- |
|  | **Phthalate compounds** |
| Sampling site | Dibutyl phthalate  | Diethyl phth*alate* | Di-n-hexyl phthalate | Diisononyl adipate | Benzyl butyl phthalate | Dicyclohexyl phthalate | Diisodecyl phthalate | Dimethyl phthalate |
| Raw Eff.  | 60.778 | 31.978 | 5.625 | ND | 0.049 | 1.459 | ND | ND |
| Treat Eff | 44.156 | 15.100 | ND | ND | ND | ND | ND | ND |
| 264 | 36.725 | 43.647 | 14.28 | ND | 4.806 | ND | 0.543 |  |
| Osun | 44.651 | 46.965 | 0.283 | ND | ND | ND | ND | 0.011 |
| Ureje |  | 39.617 | 12.92 | 47.003 | ND | ND | ND | ND |
| Fst Canal  | 8.299 | 39.524 | 52.11 | ND | ND | ND | ND | ND |

\*ND – Not Detected

4. Conclusion

High concentrations of heavy metals in any aquatic or terrestrial ecosystem have been associated with different environmental and health impacts, which natural or anthropogenic causes could cause. This study assessed heavy metals in two rivers and a lake and treated raw and slurry effluent. It was observed that cadmium and chromium were below the equipment's detection limits in all the sites. Fe, Zn, Mn, Pb and Ni concentrations were observed at all locations, while higher concentrations were observed in raw effluent and slurry sludge.  Raw effluent collected from Lagos was the most contaminated with heavy metals, which may be the key source of contamination in Lagos. The heavy metals had no significant difference, implying that the locations were not severely polluted.

On the other hand, the emerging contaminant results showed the presence of some pharmaceuticals and endocrine disruptors in Nigeria's aquatic ecosystem. The presence of phthalates and bisphenol A implies that these plastic additives can hinder the growth of plants and hormone development in animals and humans, hindering reproduction. Although the pollutants observed in this study were not significantly different when the samples were collected, further studies should be conducted to cover various contaminants. In addition, further study on the risk assessment of emerging contaminants should be focused on, as a few authors have detected different contaminants in several aquatic bodies.

The key limitations of not testing some pollutants in this study were lack of equipment and funding. The study recommends that the use of plastics and the indiscriminate disposal be properly managed. More so, we encouraged the use of glass or alumnium water bottles for drinking water as this will limit the consumption of these additives through PET bottles. Lastly, the communities around the study location should be educated on the dangers associated with the discharge and disposal of waste into the environment

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