African Scientist Vol. 25, No. 4 December 31, 2024
Printed in Nigeria
1595-6881/2023 $80.00 + 0.00

https://africansciientistjournal.org

afs2024060/25408

Concentrations, Ecological and Health Risk Assessment of Heavy Metals in Surface Water and Sediments of Ogun River in Owode Onirin, Lagos

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(Received December 24, 2024; Accepted in revised form December 31, 2024)

ABSTRACT: Industrial processes, including scrap yards, can contaminate surface waters with heavy metals, posing a risk to aquatic habitat and human health. Thus, the concentrations, ecological and health risks of heavy metals in surface water and sediment of the Ogun River in Lagos was investigated. Surface water and sediments collected from the Ogun River were analyzed for some physicochemical parameters and heavy metals using standard procedures. The results indicated that physicochemical parameters such as temperature and COD were within the standard limits while pH, TDS, EC and TSS for site 1 exceeded the USEPA standard. The distribution of heavy metals at the sampling points was Pb>Cr>As>Cd and Pb>Cr>Cd>As for water and sediments, respectively. The ranges of heavy metals in water were 0.461-0.954, 0.001-0.023, 0.457-1.426 and 0.002-0.645 mg/L and in sediments were 1.034-3.661, 0.882-1.780, 1.005-3.802 and 0.009-0.404 mg/kg for Pb, Cd, Cr and As, respectively. Pb and Cr at all sampling sites exceeded safety limits for drinking water, with the highest concentration found at sites 1 and 4, respectively. The contamination factor (CF) of all the studied heavy metals had a low degree (CF < 1) while geo-accumulation index (Igeo) showed that there was no contamination in the sediment. The values of the pollution load index (PLI) were less than one (<1), indicating moderate contamination of the sediment quality. The results of the HQ and HI values of the heavy metals for dermal and ingestion pathways were below the safety level (HQ and HI < 1) for adults and children. However, the carcinogenic risk of Pb, Cr and As in the sediment exceeds the acceptable limit (1×10^{-6}), suggesting a potential risk to human health in this regard.

Keywords: Heavy metals; Sediment; Ecological risk; Health risk assessment; Ogun River

Introduction

Water constitutes an essential element of both rural and urban environments, and its effective administration plays a pivotal role in preserving a more sustainable and healthier ecosystem. The quality of water undergoes alterations owing to either human-induced or natural occurrences within the upper watershed (Sany *et al*., 2013). Consequently, due to the natural flow of water, a majority of contaminants find their way into a single collection point, such as reservoirs, which can act as a receptacle for various impurities (Nowrouzi and Pourkhabbaz, 2014). Given its potential for adverse environmental and public health impacts, as well as its capacity for accumulation, the issue of heavy metal contamination in aquatic ecosystems is emerging as a potential global challenge (Sharma *et al*., 2015).

Globalization has led in the creation of many other types of garbage, including motor parts, scrap autos, engines, cans, tyres, and so on, in many different areas of the world, particularly in developing nations. Poor water management faces several concerns since human activities have resulted in water resource depletion, increasing pollution, health concerns, and transportation issues, as well as diminished environmental tolerance, all represent substantial threats to sustainable development (van Roosbroeck *et al*., 2006). Human activities, encompassing industrial and agricultural discharges, improper disposal of industrial byproducts, the disposal of domestic and municipal waste, and malfunctioning drainage systems, represent a selection of factors contributing to the contamination of aquatic ecosystems by heavy metals (Hahladakis and Smaragdaki, 2013; Islam *et al*., 2015). Heavy metal concentration in the aquatic habitats is considered in three ways: in the river, in the sediments, and in living creatures. Heavy metals are found in the lowest amounts in water and achieve significant concentration in sediments prior to bioaccumulation in live organisms (Ebrahimpour and Mushrifah, 2008).

Heavy metals present a significant environmental peril to both living organisms and aquatic ecosystems, primarily due to their resistance to biodegradation, propensity for bioaccumulation, environmental stability, enduring nature, and biotoxic properties (Khan *et al*., 2019; Shaheen *et al*., 2019; Zhang *et al*., 2019). Following their release from a source, heavy metals can directly impact the physical and chemical attributes of sediments and water, leading to the suppression of microbial activities (He *et al*., 2019; Omwene *et al*., 2018). Furthermore, they have the potential to inflict harm on the ecological environment through the food chain, resulting in both acute and chronic consequences for human health (Weber *et al*., 2020; Zhang *et al.,* 2019). The non-degradable nature of heavy metals also fosters their accumulation in surface sediments, persisting over an extended period through the amplification effect within the food chain, which, in turn, can give rise to various diseases and complications in the human body (He *et al*., 2019; Idris *et al*., 2019; Wang *et al*., 2019).

Sediment quality influences water quality in the aquatic environment. Heavy metal contamination in the water habitats has recently received a lot of attention due to its long-term persistence in sediment, toxicity, and organic accumulation, all of which can have an impact on human wellbeing and ecosystem (Zhang *et al.*, 2019). Several studies have underscored the elevated concentration of heavy metals in river sediments, primarily attributed to substantial anthropogenic metal inputs conveyed by tributary rivers (Li *et al*., 2011). Consequently, surface sediments may act as a reservoir for metals, with the potential to release them into the overlying water, thereby posing potential adverse consequences for riverine ecosystems (Reda and Ayu, 2016). Risk evaluation entails the systematic examination of pollutant effects, categorizable into human health and ecological assessments based on varying protective targets (Wang *et* al., 2020; Wang *et al*., 2021).

A growing body of research has concentrated on assessing the ecological ramifications of heavy metals in sediment (Liu *et al*., 2018), revealing that these sediment-bound heavy metals can substantially augment waterborne metal concentrations through their liberation into the aquatic milieu. Scholars have documented that cadmium (Cd), lead (Pb), and iron (Fe) in water may give rise to health hazards for human beings (Singh and Kumar, 2017). Hence, it is imperative to take into account the pollution status and potential hazards stemming from heavy metals in water. Recognizing that uncertainties are inherent in any assessment of water quality risks, it becomes essential to conduct an uncertainty analysis as an integral part of risk assessment for a more precise identification and evaluation of high-risk zones to implement effective control measures. Notably, the Monte Carlo simulation technique, acknowledged by the National Academy of Sciences and the United States Environmental Protection Agency (USEPA, 1997) as a potent tool for uncertainty analysis in risk assessments, is frequently employed in evaluating the risks posed by heavy metals (Mukherjee *et al*., 2020). As the concentration of heavy metals in surface waters continues to rise, the significance of risk assessments pertaining to these environmental compartments has become increasingly paramount.

The Ogun River traverses through urban settlements, industrial zones, and agricultural landscapes, all of which depend on the use of agrochemicals and engage in chemical manufacturing. The industrial activities in the Owode Onirin region of Ikorodu, Lagos, home to a population of 989,000, have emerged as a significant source of pollution to the Ogun River. Notably, some residents in this vicinity rely on the Ogun River for drinking, bathing, and culinary purposes. Currently, there exists a dearth of information pertaining to the presence of heavy metal contamination in both the surface water and sediment of the Ogun River, particularly in the Owode Onirin region of Lagos State. Therefore, pollution by heavy metals is a concern, and the risk to this ecosystem needs to be understood. Addressing this knowledge gap could serve as a vital step towards mitigating potential threats to human health and safeguarding the preservation of aquatic ecosystems. In the current study, the distribution and sources in surface sediment and water of globally alarming heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd), and lead (Pb) were evaluated. The geo-accumulation index, pollution load index (PLI) and potential ecological risk assessment were assessed for environmental and ecological risks.

Materials and methods

Study area: The Ogun River is a waterway in Nigeria that discharges into the Lagos lagoon, the river starts from Oyo state and flows through Ogun state into Lagos state with a length of 480km. The research focuses on the Owode-Onirin axis to Ikorodu, Lagos State, Nigeria, which is located between latitudes 6°36′14.87″N and 6°36′32.4″N and longitudes 3°24′47.05″E and 3°24′48.6″E. The dumping of the scrap metals in Lagos State's Owode-Onirin, Ikorodu neighborhood is widely known for destroying the ecological and harming the scenery. The scrap yard's management has received little attention over the years, leaving the people in the region exposed to heavy metals leaking, notably into surface water. Six (6) water and sediments samples were collected at varying distance along the river flow from upstream to downstream the sample collection area is shown in the Table 1 and distance are stipulated within.

Table 1: Sample collection location and industrial activities carried on there

Sample	Location	Industrial activities/ pollution causes
1	N6 ° 36’44.2188, E 3° 24’50.6052	Scrap dumpsite, Plastic recycling factory, auto parts market, human settlements
2	N 6° 36’36. 9144, E 3° 26’03.156	Mechanic workshop, human settlements
3	N6° 36’40.6836, E 3° 26’43.5192	Farming, fishing, human settlements, Dredging
4	N 6° 37’13.206, E 3° 27’05.8176	Furniture workshop, Fishing
5	N 6° 37’28.0164, E 3° 29’46.7196	Dredging, human settlements, textile factory
6	N 6° 37’07.3164, E 3° 28’11.4132	Major market, human settlements, Refuse dumpsite

Sample collection: Water samples were collected at random distance throughout the Ogun River from upstream to downstream with 2L white plastic containers, leaving a 2 cm gap then adding 2 drops of Nitric acid (HNO_3) before covering it. The samples were labeled S1, S2, S3, S4, S5 and S6. The sediments samples were collected using a plastic scoop at a debt of 10 cm to 30 cm at the edge of the river beds. The samples were scoped in plastic Ziploc bags and labeled S1, S2, S3, S4, S5 and S6. The samples were kept in an ice box at 4°C and transported to the laboratory for analysis.

Determination of water quality parameters: The water quality parameters were determined in accordance with standard methods by APHA (2017).

Determination of metal concentrations in water and sediments: To determine the metal concentrations in the water samples, the water samples were digested with nitric acid as described by Iwegbue *et al*. (2023) and the metal concentrations in the digest were quantified by means of atomic absorption spectrophotometry (AAS) (Perkin Elmer Model 3110). Similarly, the sediments were digested following the procedure of Iwegbue *et al*., 2018) and thereafter the metal concentrations in the digest were quantified by AAS (Perkin Elmer Model 3110).

Quality control and assurance: The reagents used for the analyses were of analytical grade. All samples were analyzed in triplicate and the relative standard deviations (RSD) for the triplicate analyses were < 9 %. The method for metal analysis was validated by using spike recovery method. The percentage recoveries for the metals ranged from 91.3 to 97.5 %.

Statistical analysis: Completely randomized design (CRD) was used for the entire study. All analysis was done with a Statistical Package for the Social Sciences (SPSS) package (SPSS 14.0 for Windows, SPSS Inc, Chicago, IL, USA). One-way Analysis of Variance was used for the analysis of the data and comparison of mean was done using Duncan’s Multiple Range Test (DMRT).

Collection of toxicity data for aquatic life criteria (ALC) and human health ambient water quality criteria prediction: In compliance with the guidelines established by USEPA for ALC as documented in the year 1985, comprehensive data were gathered on no fewer than 33 non-native species. This dataset encompassed toxicity information related to five heavy metals: cadmium (Cd), lead (Pb), chromium (Cr), and arsenic (As), encompassing a total of 27 different species. The acute toxicity data were meticulously sourced from two primary repositories: the Ecotox database, available at https://cfpub.epa.gov/ecotox/, and relevant information published within the scientific literature. These data were sourced from a diverse range of taxonomic groups, including Insecta (e.g., *Chironomus Javanus, Chironomus Plumosus, Culicoids Furens, Chironomus Tetans, Chironomus Kiiensis*), Amphibia (*Rana Huanrenensis*), Pisces (*Salmo Gairdneri, Poecilia Reticulata, Cyprinus Carpio, Misqurnus Anguillicaudatus, Aphyocyoris Chinesis, Carsius Auratus, Colisa Fasciatus, Danio Rerio, Ictalurus Punctatus, Pimephelas Promelas*), Annelida (*Tubifex Tubifex*), Rotifera (*Brachionus calyciflorus*), Crustacea (*Macrobrachium Lanchestri, Gammarus Pseudolimnaeus, Daphnia Magna, Machrobrachium Lamarrei, Arcatia Clausi, Gammarus Sobaegensis*), Mollusca (*Lampsilis Rafinesqueana*), Plants (*Lemna Minor*), and Cnidaria (*Hydra Viridissima*). It is noteworthy that these organisms have also been employed in prior research endeavors to establish aquatic life criteria and ambient water quality standards for chromium, lead, cadmium, and arsenic, as documented in studies by Park *et al.* (2018), Li (2021), Lee *et al*. (2020), Wu *et al*. (2012), and Li *et al*. (2021).

Numerical aquatic life criteria derivation: According to the available data and the 96-h-LC_{50} values, the acute toxicity data was examined. The ALC for the heavy metals was calculated using the US EPA guidelines for aquatic life criteria (US EPA, 1985).

The following formulas were employed to calculate the criterion maximum concentration (CMC).

$$S^2 = \frac{\Sigma[(In\,GMAV)^2] - [\Sigma(In\,GMAV)^2]/4}{\Sigma P - (\Sigma\sqrt{P})^2/4} \quad (1)$$

$$P = \frac{r}{n+1} \quad (2)$$

$$L = \frac{\Sigma(In\,GMAV) - S(\Sigma\sqrt{P})}{4} \quad (3)$$

$$A = S\sqrt{0.05 + L} \quad (4)$$

$$FAV = e^A \quad (5)$$

$$CMC = \frac{FAV}{2} \quad (6)$$

where: GMAV= Genus means acute value, P = cumulative probability, FAV = final acute value

The GMAVs were arranged in an ascending order, with r ranging from 1 to n, indicating the designated order for each GMAV. The FAV was computed by means of four GMAV values with P values close to 0.05. The final acute value (FAV) was calculated in this research using the FAV formula from the guidelines. The FAV was divided by two to derive the criteria for maximum concentration (CMC). The FAV was divided by the acute chronic ratio (ACR) to derive the final chronic value (FCV). ACRs were used to measure chronic toxicity for metals and aquatic organism with known acute toxicity but little or no knowledge of chronic toxicity. Due to deficiency in chronic data for the species adopted in the acute toxicity of this study, a total average value of 8.3 for the ACR was used based on a finding by Raimondo *et al.*, (2016) who deduced an ACR average value focusing on same-species (invertebrate and fish) pairs of acute and maximum acceptable toxicant concentration levels for pesticides, metals, and other organic elements.

Ecological risk assessment: In this research, the pollution load index (PLI), contamination factor, geoaccumulation index and hazard quotient were utilized to review the ecological risk of heavy metals.

Pollution load index (PLI) and contamination factor (CF): According to Islam *et al*. (2015) combined techniques of pollutant load index of the four metals was calculated to evaluate sediment quality. The PLI is described as the nth root of the multiples of the metal contamination factor (CF).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times . . . \times CF_n)^{1/n} \quad (7)$$

where: CF_{metals} is the proportion of each metal's content to the background values in sediment

$CF_{metals} = C_{metal}/C_{background}$.

As a result, a PLI score of zero denotes perfection, a value of one denotes the occurrence of merely baseline levels of contaminants, and values more than one suggest increasing weakening of the site and estuary value (Tomilson *et al*., 1980). The PLI will provide an assessment of the general toxicity of the sample, as well as the contribution of the four metals investigated. For observing the contamination of a single metal through time (Islam *et al*., 2015), the contamination factor (CF) was recommended as the proportion of calculated concentration to high loads of a given metal, which was classed into four grades: low degree (CF 1), moderate degree (1 CF 3), significant degree (3 CF 6), and very high degree (3 CF 7). (CF 6). As a result, CF values may be used to track a metal's concentration in sediments through time.

Geoaccumulation index (i_{geo}): The geoaccumulation index was used to measure the degree of heavy metal pollution (I_{geo}). The geoaccumulation index has been frequently utilized to analyze sediment pollution (Santos Bermejo *et al*., 2003; Saleem *et al*., 2015). Geoaccumulation index (I_{geo}) values will be determined using the equation to quantify the degree of contamination in the sediment,

$$I_{geo} = Log_2[\,Cn / 1.5B_n\,] \quad (8)$$

where Cn is the determined metal concentration in the sediment, and In the back - ground sample, Bn represents the biogeochemical background level for element n (Yu *et al*., 2011). The factor 1.5 is used to reduce the possibility of fluctuations in background values that might be credited to lithogenic processes.
The probable effects of heavy metal pollution on the organisms in the research region were assessed using an ecological risk assessment. The Hazard Quotient (HQ) procedure was used to determine ecological risk by dividing the heavy metal concentration in water by the pertinent long-term aquatic life criteria (CCC) values and is frequently employed in ecological risk assessments of aquatic environments (Gao *et al.*, 2020, Suter, 2008; Wang *et al.*, 2020) using equation (9).

$$HQ = \frac{EC}{CCC} \quad (9)$$

Ecological risk was divided into 2 categories HQ < 1 (No Risk); HQ > 1 (High Risk) (Dong *et al.*, 2020; Li *et al.*, 2019c)
Human risk assessment: A human health risk assessment was undertaken to establish if the present amounts of heavy metals discovered in surface water samples are detrimental to people's health. The USEPA provided the methodology used to review the non-carcinogenic and carcinogenic risk of newly identified heavy metals. Adults and children who utilize the river's water make up the target demographic. Human exposure to harmful causes is defined in terms of average daily dose (ADD), which is the amount of contaminants ingested into the human body on every day basis throughout the determined exposure time.

$$ADDinjestion = \frac{C \times IR \times EF \times ED}{(BW) \times AT} \quad (10)$$

$$ADDdermal = \frac{DAevent \times SA \times EV \times EF \times ED}{BW \times AT} \quad (11)$$

Non-carcinogenic effects: The Hazard Quotient (HQ) test was used to determine if excessive metal levels in humans have non-cancer consequences. The ADD was divided by the reference dosage for ingestion or cutaneous encounters (RfD), as given in Equation (3). Any hazard quotient less than one is deemed harmless for long-term exposure:

$$HR = \frac{ADD}{RfD} \quad (12)$$

The hazard index (HI) of the various exposure scenarios, counting oral ingestions and dermal pathways, was determined using;

$$HI = \sum_{i=0}^{n} HQ \quad (13)$$

Carcinogenic potential: The carcinogenic risk of heavy metals identified in water that have the potential to cause cancer was evaluated using the Equations below;

$$RISK = \beta \times LADD \quad (14)$$

$$TR = \sum R \quad (15)$$

where: Risk = the possibility of developing cancer as a product of oral or cutaneous exposure with heavy metal-contaminated water.
LADD is an abbreviation for lifetime average daily dose exposure via oral or cutaneous routes; β = slope factor; TR = total risk.
In terms of noncarcinogenic risk indices, hazard quotient (HQ), or hazard index (HI) values greater than one indicate that the contaminant in the environmental matrix has a significant public health risk, whilst values less than one imply tolerable risk. Cancer risk scores more than $1x10^{-4}$ indicate unacceptable health concerns, whereas values less than $1x10^{-6}$ are deemed to offer a tolerable health risk.

Results

Water Quality Parameters: Table 2 lists the physical parameters of the water column, such as, pH, temperature, Electric Conductivity (EC), Total Dissolved Solids (TDS), Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD). The mean temperature of the collected water samples at the six points ranged from 27.51°C to 28.17°C. The mean pH values varied from 5.88 to 6.74, which indicated that the water was slightly acidic to alkaline. The EC measurements obtained at Ogun River ranged from 406.2 to 1513 µS/cm. Highest EC value of 1513 µS/cm was obtained in sampling site 1. The TDS obtained from the sampled sites in Ogun River ranged from 255.26 to 862.96 mg/L while the total suspended solid (TSS) concentrations were found to be in the range of 247.16 to 420.63 mg/L. Among all the sampling sites, sampling site 2 consistently exhibited the highest TSS concentration, recording 420.63 mg/L. Chemical oxygen demand (COD) of the water samples ranged from 0.43 to 1.68 mg/L. Of all the water samples sample, sampling site 1 had the highest COD (1.68 mg/L).

Table 2: Physical parameters of water samples collected

Samples	pH	TEMP (ºC)	EC (µS cm⁻¹)	TDS (mg/L)	TSS (mg/L)	COD (mg/L)
1	5.88±0.02[e]	27.51±0.02[e]	1513±288[a]	862.96±2.57[a]	382.11±1.63[b]	1.68±0.29[a]
2	6.04±0.02[d]	27.87±0.01[cd]	1008±298[ab]	539.27±7.69[b]	420.63±0.51[a]	1.18±0.30[ab]
3	6.45±0.02[c]	28.03±0.03[b]	590±230[bc]	286.75±12.49[e]	247.16±0.28[f]	0.72±0.23[ab]
4	6.59±0.02[b]	27.81±0.02[d]	406.2±20.2[c]	255.26±5.49[f]	288.47±0.42[d]	0.43±0.04[b]
5	6.74±0.03[a]	28.17±0.05[a]	549.1±123.6[bc]	394.55±5.58[c]	302.77±1.78[c]	0.48±0.13[b]
6	6.57±0.01[b]	27.88±0.01[c]	524.1±0.42[bc]	335.44±0.27[d]	274.99±0.10[e]	1.02±0.71[ab]
WHO (2017)	6.5-8.5	20-30	1,000	600	150	4
USEPA (2012)	6.5-8.5	25	1,000	500	-	-

Values represent mean and standard deviation (n=3). Different lowercase letters within the same column indicate significant difference ($p<0.05$).

Metal concentration in water: Table 3 lists the results of heavy metal concentrations in the surface waters of the Ogun River. Concentrations of Pb, Cd, Cr and As were ranging from 0.461 to 0.954, 0.001 to 0.023, 0.457 to 1.426 and 0.002 to 0.645 mg/L, respectively.

Table 3: Heavy metal concentration (in mg/L) in waters of Ogun River and comparison to other studies and different international guidelines

Sampling sites	Pb	Cd	Cr	As
1	0.909±0.002[b]	0.023±0.002[a]	1.233±0.002[c]	0.068±0.003[bc]
2	0.954±0.001[a]	0.004±0.000[bc]	0.575±0.003[e]	0.031±0.001[cd]
3	0.755±0.002[d]	0.002±0.000[cd]	0.684±0.004[d]	0.645±0.047[a]
4	0.885±0.004[c]	0.001±0.000[d]	1.426±0.002[a]	0.030±0.002[cd]
5	0.461±0.002[f]	0.006±0.000[b]	0.457±0.001[f]	0.094±0.006[b]
6	0.701±0.002[e]	0.003±0.000[cd]	1.306±0.001[b]	0.002±0.006[d]
Average	0.778±0.002	0.007±0.000	0.947±0.002	0.145±0.011
[a]Karnaphuli River (Bangladesh)	5.29-27.45	2.54-18.34	51.76-112.43	13.31-53.87
[b]Kodikkarai River (India)	1.4	0.1	2.9	NA
[c]Tembi River (Iran)	0.59-1.91	0.07-0.35	0.13-0.58	NA
[d]New Calabar River (Nigeria)	<0.001-0.06	<0.001	0.03-0.18	NA
[e]EC 98/83	0.01	0.005	0.05	0.01
[f]FTRV	0.002	0.002	0.011	0.15

Values represent mean and standard deviation (n=3). Different lowercase letters within the same column indicate significant difference ($p<0.05$). [a]Ali *et al*. (2016); [b]Pandiyan *et al*. (2021); [c]Shanbehzadeh *et al*. (2014); [d]Davies and Ekperusi (2021); [e]EU Directive 1998/83 Drinking Water Standards; [f]Fresh water toxicity reference value proposed by USEPA (2020).

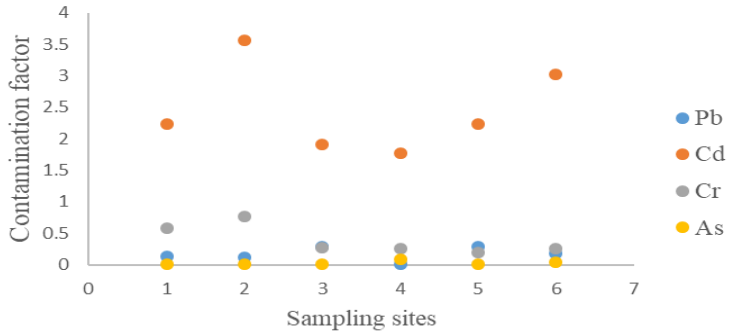
Metal concentration in sediment: Table 4 lists the concentrations of heavy metals in sediment. Concentrations of Pb, Cd, Cr and As were ranging from 1.034 to 3.661, 0.882 to 1.780, 1.005 to 3.802 and 0.009 to 0.404 mg/kg, respectively.

Table 4: Heavy metal concentration (in mg/kg dw) in sediment of Ogun River and comparison to other studies and different international guidelines

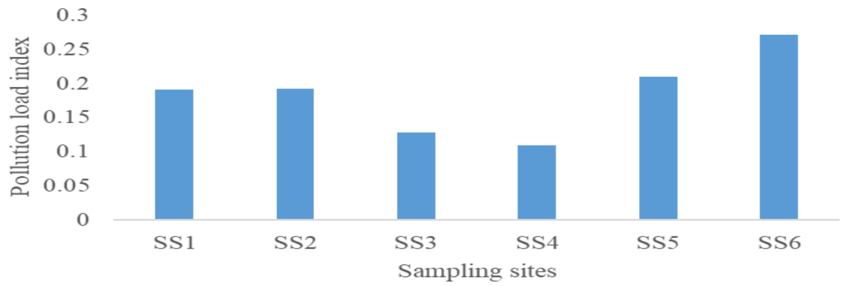
Sampling sites	Pb	Cd	Cr	As
1	1.359±0.011[d]	1.120±0.000[c]	2.905±0.004[b]	0.038±0.000[d]
2	2.905±0.004[b]	1.780±0.002[a]	3.802±0.005[a]	0.022±0.000[e]
3	1.285±0.069[d]	0.955±0.000[d]	1.346±0.001[c]	0.009±0.000[f]
4	1.034±0.000[e]	0.882±0.000[e]	1.316±0.001[d]	0.404±0.007[a]
5	3.661±0.000[a]	1.118±0.000[c]	1.005±0.002[f]	0.074±0.000[c]
6	1.576±0.000[c]	1.515±0.013[b]	1.256±0.001[e]	0.198±0.000[b]
Average	1.970±0.002	1.228±0.003	1.938±0.002	0.124±0.000
[a]Karnaphuli River (Bangladesh)	21.69-73.42	0.63-3.56	11.56-35.48	37.23-160.32
[b]Kodikkaral River (India)	2.5	0.3	0.8	NA
[c]Tembi River (Iran)	141-270	10-40	11-74	NA
[d]New Calabar River (Nigeria)	0.14-0.32	<0.001	0.17-0.22	NA
[e]FTRV	31	0.6	26	6

Values represent mean and standard deviation (n=3). Different lowercase letters within the same column indicate significant difference (p<0.05); [a]Ali *et al*. (2016); [b]Pandiyan *et al*. (2021); [c]Shanbehzadeh *et al*. (2014); [d]Davies and Ekperusi (2021); [e]Fresh water toxicity reference value proposed by USEPA (USEPA, 2020).

Contamination status of the sediments: The values of PI for Pb, Cd, Cr, and As are shown in Figure 1. As seen in figure 1, all the sites were contaminated by Cd. The results revealed that sites 2 and 6 were heavily contaminated by Cd.



(a)



(b)

Figure 1: (a) Contamination factor (CF) and (2) Pollution Load Index (PLI) values in the surface sediments of the Ogun River. Low degree, CF < 1; moderate degree, 1 < 3; considerable degree, 3 < 6; very high degree, CF > 6 (Loska and Wiechuła, 2003). PLI =1, baseline level; PLI > 1, progressive deterioration (Tomlinson *et al*., 1980).

Geo-accumulation Index: Figure 2 shows the Igeo value for Pb, Cd, Cr and As in the Ogun River. The geo-accumulation index (Igeo) for Pb, Cr and As in Ogun River sediment ranged from -2.3685 to 3.7433, -0.9802 to -2.8993 and -4.2136 to -9.6868, respectively.

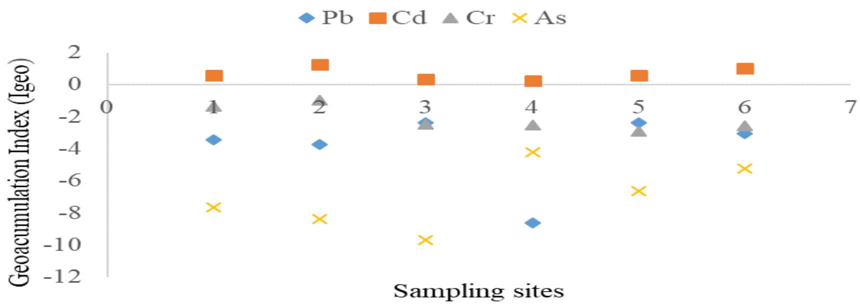


Figure 2: Geoaccumulation index (Igeo) for heavy metals in Ogun River sediments. Igeo ≤ 0, practically uncontaminated; 0 ≤ Igeo ≤ 1, uncontaminated to moderately contaminated; 1 ≤ Igeo ≤ 2, moderately contaminated; 2 ≤ Igeo ≤ 3, moderately to heavily contaminated; 3 ≤ Igeo ≤ 4, heavily contaminated; 4 ≤ Igeo ≤ 5, heavily to extremely contaminated; 5 ≤ Igeo, extremely contaminated

Aquatic life criteria for four heavy metals: In this research study, toxicity data was exclusively gathered based on the 96-hour LC50, resulting in eight data sets for each of the heavy metals: lead (Pb), cadmium (Cd), hexavalent chromium (Cr(VI)), and arsenic trioxide (As(III)). A detailed account of the collected toxicity data is provided in Table 5. These 32 data points, spanning the four heavy metals, were obtained from a total of 27 species, encompassing fishes, invertebrates, and plants. The analysis of acute toxicity data, as presented in Table 5, revealed that *M. lanchesteri, H. Virisdissima, C. Tetan,* and *G. Sobaegensis* exhibited the highest sensitivity to Pb, Cd, Cr(VI), and As(III), respectively, while P. *Reticulata, D. Rerio, S. Gairdneri*, and *R. Haunrensis* were the most resilient to these heavy metals. Significant variation was observed in the LC50 values for Cr(VI), ranging from 0.65 to 65.5 mg/L, with a mean of 34.81 mg/L. For Cd, concentrations spanned from 0.0078 to 0.603 mg/L, with an average of 0.14 mg/L, while Pb exhibited concentrations ranging from 0.035 to 20.6 mg/L, with an average of 7.39 mg/L. As for As(III), concentrations ranged from 0.72 to 38.43 mg/L, with an average of 3678.4 µg/L. The short-term and long-term aquatic life criteria were derived using acute toxicity data from aquatic organisms. Employing the FAV equation from the USEPA (1985), we estimated a final acute value (FAV) for Pb, Cd, Cr(VI), and As(III) as 15.40, 3.16, 102.09, and 339.35 µg/L, respectively. A Criterion Maximum Concentration (CMC) was obtained by dividing the FAV values by 2, resulting in values of 7.70, 1.58, 51.05, and 169.68 µg/L for Pb, Cd, Cr(VI), and As(III), respectively (as shown in Table 2). A criterion Continuous Concentration (CCC) was derived by dividing the FAV values by an ACR (Aquatic Chronic Ratio) of 8.3, yielding CCC values of 1.86, 0.38, 12.30, and 40.89 µg/L for Pb, Cd, Cr(VI), and As(III), respectively.

Table. 5: Acute toxicity of Pb, Cd, Cr(VI), and As(III), to 27 freshwater species

Metals	**Ranks**	**Species**	**96h-LC$_{50}$ (mgL^{-1})**
	1	*M. Lanchestri*	0.035
	2	*C. Furens*	0.4
	3	*A. Clausi*	0.668
Lead	4	*D. Magna*	0.93
	5	*P. Promelas*	7.48
	6	*M. Anguillicaudatus*	12.77
	7	*C. Plumosus*	16.2
	8	*P. Reticulata*	20.6
	1	*H. Viridissima*	0.0078
	2	*S. Gairdneri*	0.01
	3	*L. Rafinesqueana*	0.0228
Cadmium	4	*G. Pseudolimnaeus*	0.05
	5	*C. Javanus*	0.06
	6	*P. Reticulata*	0.17
	7	*L. Minor*	0.21
	8	*D. Rerio*	0.603
	1	*C. Tetans*	0.65
	2	*M. Lamarrei*	1.84
	3	*B. Calyciflorus*	2.61
Chromium (VI)	4	*C. Auratus*	37.5
	5	*D. Magna*	51.4
	6	*P. Promelas*	59.0
	7	*C. Fasciatus*	60
	8	*S. Gairdneri*	65.5
	1	*G. Sobaegensis*	0.72
	2	*C. Carpio*	2.52
	3	*D. Magna*	5.278
Arsenic (III)	4	*T. Tubifex*	8.87
	5	*C. Kiinesis*	9.63
	6	*I. Punctatus*	18.093
	7	*A. Chinesis*	26.13
	8	*R. Huanrenensis*	38.43

Table. 6: FAV, CMC and CCC value for Pb, Cd, Cr(IV), and As(III)

	Pb(µL^{-1})	**Cd(µL^{-1})**	**Cr(VI) (µL^{-1})**	**As(III) (µL^{-1})**
This Stud				
FAV	15.40	3.16	102.09	339.35
CMC = 1/2FAV	7.70	1.58	51.05	169.68
CCC = FAV/ACR*	1.86	0.38	12.30	40.89
CCME	1	0.008	1	5
UNECE (Class 1)	<0.1	0.007	<1	3-10
USEPA (CMC)	10.8	0.4	16	340
CCC	0.42	0.2	11	150

*ACR = 8.3 (from Raimondo *et al*. (2007).

Ecological risk assessment: The HQ values, as outlined in Table 7, were determined by normalizing the concentrations of heavy metals in the water, using the Chronic Concentration Criteria (CCC) method (Wang *et al*., 2020). This approach utilizes the Hazard Quotient (HQ) method for assessment. Upon comparing the concentrations of heavy metals in surface waters with the CCC, it was observed that the calculated HQ values for lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As) all remained below 1 at all sampling sites.

Table 7: Ecological risk assessment of four heavy metals

Sample	Pb		Cd		Cr		As	
	EEC (mg/L	HQ	EEC (mg/L)	HQ	EEC (mg/L	HQ	EEC (mg/L)	HQ
SS1	0.909	0.49	0.0219	0.058	1.233	0.10	0.0680	0.0017
SS2	0.954	0.51	0.0038	0.010	0.575	0.05	0.0310	0.00080
SS3	0.755	0.41	0.00213	0.0060	0.684	0.06	0.645	0.016
SS4	0.885	0.48	0.00117	0.0030	1.426	0.12	0.0297	0.00070
SS5	0.461	0.25	0.00627	0.016	0.457	0.04	0.0940	0.0023
SS6	0.701	0.38	0.00287	0.0080	1.306	0.11	0.00167	0.0000401
Average	0.780	0.42	0.00640	0.017	0.950	0.080	0.140	0.0036

Health risk assessment: The non-carcinogenic health risks associated with the presence of heavy metals in sediment, impacting both children and adult groups is presented in Table 8. The calculated total HI values for the children's group, considering both ingestion and dermal adsorption, were found to be 5.072×10^{-2}, 7.776×10^{-2}, 3.728×10^{-2}, 5.252×10^{-2}, 5.178×10^{-2}, and 6.180×10^{-23} for sites 1, 2, 3, 4, 5, and 6, respectively. Similarly, for the adult group, the total HI values, encompassing ingestion and dermal adsorption, were determined as 5.578×10^{-3}, 8.535×10^{-3}, 4.088×10^{-3}, 6.477×10^{-3}, 5.657×10^{-3}, and 6.780×10^{-3} for sites 1, 2, 3, 4, 5, and 6, respectively.

The mean Total Lifetime Cancer Risk (TLCR) values for sediment samples collected from both the children and adult groups are summarized in Table 9. In the children group, the TLCR values of Pb, Cr and As ranged from 1.128×10^{-7} to 3.990×10^{-7}, 2.065×10^{-5} to 9.569×10^{-6} and 1.535×10^{-6} to 7.797×10^{-7}, respectively. In the adult group, it varied from 1.209×10^{-8} to 4.280×10^{-8}, 1.045×10^{-6} to 9.978×10^{-8}, and 1.698×10^{-7} to 8.628×10^{-8}, respectively, in all sites.

Table 8: Hazard Quotient (HQ) and Hazard Index (HI) For Non-Carcinogenic Risk for Children and adult Groups in Sediment

Sites	Heavy metal	HQ_{ing}	HQ_{der}	HI=∑HQ	∑HI	HQ_{ing}	HQ_{der}	HI=∑HQ	∑HI
Site-1	Pb	4.965E-03	1.390E-05	4.979E-03	5.072E-02	5.320E-04	2.123E-06	5.341E-04	5.578E-03
	Cd	2.864E-02	1.604E-03	3.025E-02		3.069E-03	2.449E-04	3.314E-03	
	Cr	1.238E-02	1.386E-03	1.377E-02		1.326E-03	2.117E-04	1.538E-03	
	As	1.598E-03	1.342E-04	1.732E-03		1.712E-04	2.050E-05	1.917E-04	
Site-2	Pb	1.061E-02	2.971E-05	1.064E-02	7.776E-02	1.137E-03	4.536E-06	1.141E-03	8.535E-03
	Cd	4.552E-02	2.549E-03	4.807E-02		4.878E-03	3.892E-04	5.267E-03	
	Cr	1.620E-02	1.815E-03	1.802E-02		1.736E-03	2.771E-04	2.013E-03	
	As	9.475E-04	7.959E-05	1.027E-03		1.015E-04	1.215E-05	1.137E-04	
Site-3	Pb	4.692E-03	1.314E-05	4.705E-03	3.728E-02	5.027E-04	2.006E-06	5.047E-04	4.088E-03
	Cd	2.441E-02	1.367E-03	2.578E-02		2.615E-03	2.087E-04	2.824E-03	
	Cr	5.736E-03	6.424E-04	6.378E-03		6.146E-04	9.808E-05	7.127E-04	
	As	3.878E-04	3.258E-05	4.204E-04		4.155E-05	4.974E-06	4.653E-05	
Site-4	Pb	3.779E-03	1.058E-05	3.789E-03	5.252E-02	4.049E-04	1.615E-06	4.065E-04	6.477E-03
	Cd	2.256E-02	1.263E-03	2.383E-02		2.417E-03	1.929E-04	2.610E-03	
	Cr	5.607E-03	6.280E-04	6.235E-03		6.007E-04	9.588E-05	6.966E-04	
	As	1.723E-02	1.447E-03	1.867E-02		1.846E-03	2.209E-04	2.067E-03	
Site-5	Pb	1.337E-02	3.745E-05	1.341E-02	5.178E-02	1.433E-03	5.718E-06	1.439E-03	5.657E-03
	Cd	2.859E-02	1.601E-03	3.019E-02		3.064E-03	2.445E-04	3.308E-03	
	Cr	4.284E-03	4.799E-04	4.764E-03		4.590E-04	7.326E-05	5.323E-04	
	As	3.147E-03	2.643E-04	3.411E-03		3.371E-04	4.036E-05	3.775E-04	
Site-6	Pb	5.756E-03	1.612E-05	5.772E-03	6.180E-02	6.167E-04	2.461E-06	6.192E-04	6.780E-03
	Cd	3.875E-02	2.170E-03	4.092E-02		4.152E-03	3.313E-04	4.483E-03	
	Cr	5.355E-03	5.997E-04	5.954E-03		5.737E-04	9.156E-05	6.653E-04	
	As	8.443E-03	7.092E-04	9.152E-03		9.046E-04	1.083E-04	1.013E-03	

Table 9: Total Lifetime Cancer risk (TLCR) for Sediment

Sites	Heavy metal	TLCR (Children)	TLCR (Adult)
Site 1	Pb	1.481E-07	1.589E-08
	Cr	2.065E-05	2.307E-06
	As	7.797E-07	8.628E-08
	∑TLCR	2.158E-05	2.409E-06
Site 2	Pb	3.166E-07	3.396E-08
	Cr	2.703E-05	3.020E-06
	As	4.623E-07	5.116E-08
	∑TLCR	2.781E-05	3.105E-06
Site 3	Pb	1.400E-07	1.502E-08
	Cr	9.569E-06	1.069E-06
	As	1.891E-07	2.094E-08
	∑TLCR	9.898E-06	1.105E-06
Site 4	Pb	1.128E-07	1.209E-08
	Cr	9.352E-06	1.045E-06
	As	8.403E-06	9.300E-07
	∑TLCR	1.787E-05	1.987E-06
Site 5	Pb	3.990E-07	4.280E-08
	Cr	7.145E-06	7.984E-07
	As	1.535E-06	1.698E-07
	∑TLCR	9.079E-06	1.011E-06
Site 6	Pb	1.718E-07	1.842E-08
	Cr	8.930E-06	9.978E-07
	As	4.119E-06	4.558E-07
	∑TLCR	1.322E-05	1.472E-06

Discussion

Water quality parameters: According to the standards of the World Health Organization (WHO, 2017), these values were acceptable for aquatic life and household activities, including drinking purposes. Ajagbe *et al*. (2018) reported that the temperature of the Ogun River ranged from 27.21 - 28.53 °C, which agreed with the findings of this study. There was a significant difference in the water temperature among the different sampling sites. The variation in temperature observed in the Ogun River water may not act as a limiting factor for the survival of aquatic populations and the biotic community because of the wide range of temperature tolerance in aquatic life (Rahman *et al*., 2021). According to Table 1, the mean pH value with respect to the different sampling sites was within the permissible limit (except for sampling site 1) for diverse uses such as irrigation, domestic purposes, and recreational purposes. The deviation in pH at sampling site 1 from the standard could be attributed to the presence of various industrial and human activities, including the scrap dumpsite, plastic recycling factory, auto parts market, and human settlements. These activities might introduce chemicals or pollutants into the water, altering its pH. These results correlate with the findings of Ojekunle *et al*. (2020). The normal range of pH for surface water systems is 6.5-8.5, and the optimum limit for irrigation and fish culture is from 6.5 to 8.0 (Rahman *et al*., 2021). Consumption of acidic water, as observed in the sampling site 1 can lead to negative effect on gastrointestinal tract which has potential to result in diarrhea. Continuous consumption of such samples of water with pH below the acceptable limits (acidic pH) is capable of causing acidosis (Asamoah *et al*., 2011).

Electrical Conductivity (EC), an indicator of total dissolved solids, measures the presence of ions in water. According to the standards of the World Health Organization (WHO, 2017) and USEPA (2012), this value was above the acceptable limit. This may be attributed to the range of activities taking place in the sampling site, including the presence of a scrap dumpsite, plastic recycling factory, auto parts market, and human settlements. These activities can introduce various dissolved substances into the water, such as chemicals, heavy metals, and salts, which can collectively contribute to the elevated EC. The electrical conductivity range (406.2 to 1513 µS cm^{-1}) recorded in the Ogun River was greater than that of Ogun River Basin (range, 25-64.63 µS cm^{-1}) in Ogun, Nigeria obtained by Awomeso *et al*. (2019). In a river basin, electrical conductivity typically remains low in the upper regions but escalates downstream as the river water accumulates ions from soil biota and other debris (Sila, 2019). The average EC value of uncontaminated standard river water is approximately 350 µScm^{-1} (Sila, 2019). Consequently, the rise in electrical conductivities of rivers due to pollution is a cause for concern, as it renders the river water unsuitable for household use prior to treatment. The mean electrical conductivity across all sampling sites is slightly beneath the typical EC (350 µS cm^{-1}) of an unpolluted river. Nevertheless, Sampling sites 1 and 2 registered comparatively elevated EC levels (1513 and 1008 µS cm^{-1}, respectively), signifying pollution.

Total dissolved solid (TDS) is a measure of inorganic salts. The observed TDS values (except for sampling site 1) were within 500 mg/L and 600 mg/L stipulated by USEPA (2012) and WHO (2017), respectively. The presence of a scrap dumpsite, plastic recycling factory, auto parts market, and human settlements at sampling site 1 may have introduced various inorganic salts and chemical residues into the river, elevating TDS levels. Total dissolved solid of Ogun River from this study (255.26 to 862.96 mg/L) was greater than that of Woji Creek (range, 6.52 to 17.53 mg/L) in Rivers State, Nigeria obtained by Woke (2019). The observed TSS concentration in the Ogun River during this study, exceeded the minimum threshold of 150 mg/L deemed essential for the protection of aquatic life, as recommended by WHO guidelines (WHO, 2017). It is worth noting that the TSS levels in this study, were notably higher than those reported for the Ogun River Basin in Ogun State, Nigeria, with a range of 678.32 to 179.25 mg/L according to the findings by Awomeso *et al*. (2019). Activities associated with the mechanic workshop in this site, such as vehicle maintenance and repairs, could contribute to the release of oil, grease, and particulate matter into the surrounding environment. These contaminants may then find their way into the water, increasing TSS levels. The COD concentration range for the all the sampling sites (0.43-1.68 mg/L) were almost within the same range with no significant ($p<0.05$) observed for sampling sites 1, 2, 3 and 6. Thus, the rate of oxygen required to chemically oxidize and break down organic and inorganic substances in the water samples were more less the same. The COD concentration recorded in the water samples studied is within the expected range for excellent quality potable water for domestic supply and for recreational purposes (USEPA, 2012; WHO, 2017). The COD concentration ranges (0.43 and 1.68 mg L^{-1}) in the water samples sampled closely align with the COD concentrations found in other rivers in Nigeria, such as the River Benue, which was reported to have concentrations ranging from 0.89 to 3.72 mg/L (Maitera *et al*., 2010). Notably, the COD concentrations observed in the sampled water were considerably lower than those reported by Davies and Ekperusi (2021) for New Calabar River, Nigeria, where COD levels ranged between 52 and 76 mg/L.

Metal concentration in water: The results of heavy metal concentrations in the surface waters of the Ogun River, reveal a significant variation ($p < 0.05$) between the sampling sites. Decreasing order of Cr > Pb > As > Cd was found in the average concentration of the studied metals in water. The observed order in average metal concentrations aligns with the findings of a previous study conducted by Ali *et al*. (2021), indicating the persistence of these contamination patterns over time. The mean ± SD concentration of Cr in water was 0.947 ± 0.002 mg/L, which was higher than the value of USEPA (1999) standard (0.011 mg/L), suggesting potential environmental risks. The mean ± SD concentration of As was significantly ($p<0.05$) higher (0.645 ± 0.047 mg/L) in SS3 than other sampling sites, which also exceeded the USEPA (1999) standard (0.15 mg/L) while As concentration in other sampling sites did not exceed the standard. This sampling point is associated with farming practices, human settlements and dredging. The use of pesticides and herbicides containing arsenic compounds in agriculture can lead to the runoff of arsenic into the river. Additionally, irrigation with arsenic-contaminated water may contribute to increase in As levels in soil and subsequently in river water (Altowayti *et al*., 2022; Bjørklund *et al*., 2020). Dredging, a common practice in this sampling site, can disturb the riverbed sediments. If the riverbed sediments contain naturally occurring arsenic or have accumulated arsenic from previous pollution sources, dredging can re-suspend and release this arsenic into the water column. Human settlements in this sampling site may also have inadequate sewage treatment facilities, leading to the release of arsenic-contaminated wastewater into the river. The concentration of cadmium (Cd) in the surface waters of the Ogun River, as indicated by the mean ± SD value of 0.007 ± 0.000 mg/L, falls below the fresh water toxicity reference value (TRV) of 0.002 mg/L. This suggests that Cd levels in the river water do not pose an immediate toxicity concern to aquatic life. The study's assessment of heavy metal concentrations in the surface waters of the Ogun River, particularly with regard to chromium (Cr) and lead (Pb), reveals that these metals significantly exceeded the maximum concentration limits set by the U.S. Environmental Protection Agency (USEPA) in 1999 (USEPA, 2020). This has profound implications for the safety of water from the Ogun River for human consumption and cooking purposes.

Metal concentration in sediment: There was a significant ($p<0.05$) variation in the heavy metals across the sampling sites. The mean heavy metal concentration in the sediment followed the decreasing order of Pb > Cr > Cd > As. Concentrations of Pb was significantly ($p<0.05$) high at site 5 while Cd and Cr were high at site 2. The high concentrations of Cd and Cr at site 2 could be attributed to activities associated with mechanic workshops, which may involve the use of heavy metals in vehicle maintenance. Additionally, human settlements in the site might contribute to heavy metal inputs through domestic and waste-related activities. The concentration of Cd in the sediments from all the sampling sites are higher than the Sediment Quality Guidelines (SQG) values set by USEPA water quality criteria (USEPA, 2020). The elevated Pb levels at site 5 may be linked to dredging activities, which can disturb sediments and release previously buried pollutants. The presence of a textile factory may also contribute to heavy metal discharges into the river, particularly Pb. The highest value (0.404 mg/kg) of As is found at sampling site 4, which could be attributed to the presence of a furniture workshop which may involve the use of wood preservatives or coatings that contain arsenic compounds (Altowayti *et al*., 2022). Such materials can leach arsenic into the environment, potentially contaminating sediment. The concentrations of Pb, Cr and As in this study were found to be within acceptable limits (USEPA, 2020). The elevated concentration of the heavy metals in the sediment in contrast to its concentrations in the water is a predictable occurrence for sediments characterized as a repository or storage site for contaminants in water (Topi *et al*., 2012).

Contamination status of the sediments: As seen in Figure 1, the high values of PI may have come from the geological composition of the region (Malsiu *et al*., 2020) as well as the industrial activity in this area such as mechanic workshop, major markets and refuse dumpsites. Among the relevant heavy metals, As exhibited low contamination, while Pb showed moderate contamination at all the sites. The PI values of the heavy metals (except for Cd) at all the sites were much less than 1, which indicates that the contamination levels of Pb, Cr, and As were low. The moderate contamination of Pb at all sites is in line with the literature, as lead contamination is commonly associated with historical use of lead-based products and vehicle emissions. Although the contamination is moderate, continuous monitoring and remediation efforts are necessary to prevent health risks, especially in areas with higher population density. Arsenic contamination is often linked to specific geological conditions, and the findings suggest that it may not be a significant concern in this study area. On the other hand, all the sites were moderately contaminated with Cd because their PI values are greater than 1. This finding underscores the urgent need for measures to reduce Cd emissions and its impact on human health. The contamination status of the study area can also be demonstrated by considering the load of all the heavy metals in the sediment. Here, the pollution load index (PLI) was used to assess the overall contamination status, which was calculated using equation (2). The PLI values being less than 1 for all the heavy metals indicate that the contamination levels of Pb, Cr, and As are relatively low. Li *et al*. (2022) on the other hand reported moderate contamination (PLI > 1) of heavy metal pollution in surface sediments of the Chishui River Basin, China. The PLI values for sites with dredging, human settlements, and a textile factory (0.2096) and the sites with major markets, human settlements, and a refuse dumpsite (0.2707) were the highest among the study locations.

Geo-accumulation index: The negative Igeo values of Pb, Cr and As indicated that there was no contamination in the sediment. These results suggest that the sources of Pb, Cr and As pollution in the studied areas are likely minimal or well-contained. The Igeo values among the studied metals show a decreasing order of Cd > Pb > Cr > As. The geo-accumulation index (Igeo) for Cd ranged from 0.2344 to 1.2472. The median calculated geo-accumulation index (Igeo) values for Cd showed that the sediments of the Ogun River were unpolluted (Igeo ≤ 0) for all study sites except for SS2 and SS6. This indicates that these sites were practically contaminated with anthropogenic sources of Cd. The presence of Cd contamination in these areas raises concerns for both the ecosystem and human health, as Cd is a known toxic heavy metal. Differences in waste management practices play a pivotal role in Cd contamination. SS2, characterized by mechanic workshops, and SS6, featuring major markets and refuse dumpsites, likely have inadequate waste disposal measures. This allows Cd to accumulate in the sediments over time. The type and magnitude of anthropogenic pressures in these sites are also significant contributors to Cd contamination. These activities generate waste products containing Cd, which can leach into sediments, leading to elevated Igeo values. Şimşek *et al*. (2022) also reported considerably high contamination of Cd in some sites in the river sediments in Samsun-Tekkeköy district located in the Mid-Black Sea Region of Turkey.

Aquatic life criteria for four heavy metals: Notably, crustaceans, represented by *M. Lanchestri* and *G. Sobaegensis,* emerged as the most sensitive species to Pb and As(III). The sensitivity of crustacean species relative to one another and to Daphnia magna aligns with findings by Von Der Ohe and Liess (2004), who demonstrated that 13 crustacea taxa were among the most susceptible to metal compounds. The inclusion of non-native species in this analysis was necessitated by the limited availability of toxicity data for native species. Interestingly, a recent study found no statistically significant differences ($p > 0.05$) in the criterion values between native and non-native species. It is worth noting that applying a single ACR value to all four metals has limitations and may occasionally underestimate the chronic toxicity of metals to aquatic organisms. However, the ACR method enables the estimation of chronic values for acutely sensitive species lacking chronic data. The short-term (CMC) and long-term (CCC) aquatic life values obtained in this study were consistent with values reported by other researchers, such as Shauhaimi-Othman et al. (2012a; b), FengChang et al. (2012), and Zheng et al. (2017). Furthermore, the results from this study were in alignment with metal criteria from various countries, including the United States (USEPA, 2005), Europe (UNECE, 1994), and Canada (CCME, 1999). It should be noted that the ACR value of 8.3 used in this study was higher than the ACR value employed by USEPA to derive CCC for copper, which stands at 3.22 (USEPA, 2005).

An assessment of metal toxicity to freshwater organisms indicated that among the four metals studied, cadmium (Cd) exhibited the highest toxicity to these organisms, followed by lead (Pb), chromium (Cr(VI)), and arsenic trioxide (As(III)). This finding corresponds with international standards (Table 6), where all the standards (USEPA, CCME, and UNECE) categorically position Cd as more toxic than Pb, Cr(VI), and As(III) to freshwater organisms. Additionally, several studies have also shown that Cd is more toxic than Pb to various freshwater organisms, such as *insecta Chironomus tendipes, worm Tubifex tubifex, fish P. reticulata, snail Lymnaea acuminata, and crustacea Mytilus edulis.* The toxic effects of cadmium can manifest through multiple mechanisms in both short-term and long-term exposures. In short-term (acute) exposures, cadmium disrupts the calcium balance in aquatic organisms by acting as a calcium antagonist, competing with calcium on ionoregulatory cells, leading to hypocalcemia and potential mortality. Cadmium can cause death in aquatic organisms after just a few hours of exposure, although the timing of such deaths may lag behind exposures by up to at least a day. Small-bodied fish, particularly fry stages of some salmonids and sculpin, appear to be particularly sensitive to acute cadmium exposure. The general mechanism of ionoregulatory disruption as the cause of acute cadmium toxicity to freshwater fish is well understood. However, there are significant variations in life-stage- and species-specific sensitivities to cadmium, and the physiological mechanisms underlying these differences are not fully understood. For instance, early fry stages of certain fish taxa, like sculpin and sturgeon, are most sensitive, while some salmonids become more sensitive to cadmium as they increase in size up to a certain point (~0.5 to 2g), after which they become less sensitive as they further grow in size.

According to Luoma & Rainbow (2008), the relative toxicity of metals can vary among different organisms due to factors affecting metal uptake rates. When metals accumulate in undesired locations within organisms, they can disrupt vital molecular functions, resulting in toxicity. Toxic effects occur when the availability of metals exceeds a certain threshold, indicating that the rate of uptake surpasses both excretion and detoxification processes. Khangarot (1991) noted that the toxicity of heavy metal ions is attributed to their ability to bind with enzyme ligands essential for biological processes. Although enzyme inhibition may not be the primary factor determining the toxicity of non-transitional metal cations, other colligative factors, such as osmotic pressure, can lead to physical damage within cellular systems.

The CMC and CCC values for Pb, Cd, Cr(VI), and As(III) obtained in our study provide valuable data for the establishment of national and local water quality criteria for these metals. Water quality criteria represent the highest permissible concentration of a particular substance that will not lead to unacceptable short-term or long-term effects on aquatic organisms or their intended uses. Aquatic ecosystems exhibit varying levels of resilience and can tolerate some degree of stress and negative impacts. Therefore, the primary objective of establishing numerical national water quality criteria is not to maintain uniform concentrations at all time to support the survival and reproduction of all species within a specific ecosystem. Instead, its purpose is to ensure adequate protection for ecologically significant organisms and commercially valuable species in aquatic environments most of the time, while avoiding both over-protection and under-protection (USEPA 1985).

Ecological risk assessment: The HQ values were below 1 and indicates that there is no significant ecological risk to aquatic organisms within the Ogun River due to these heavy metals. The HQ values calculated within the scope of this study emphasize the need for continued monitoring of the ecological risk associated with heavy metal exposure to aquatic organisms in the Ogun River. This consideration should be extended to account for potential long-term effects on aquatic life, making periodic assessment an imperative aspect of environmental management and protection.

Health risk assessment: The heavy metals identified in the water samples have the potential to infiltrate the human body through dermal/skin contact and ingestion (Balali-Mood *et al*., 2021). As shown in Tables 8 and 9, the Hazard Quotient (HQ) values for heavy metals in the ingestion pathway consistently exceeded those for dermal pathway across all examined sites and age groups. This result implies that the non-carcinogenic risk of diseases caused by the ingestion of all heavy metals from the riverine sediment of the region is much more hazardous than that of dermal contact. In all the sediments and heavy metals analyzed, it was evident that children exhibited a notably elevated susceptibility to non-carcinogenic health risks in comparison to adults. This finding is supported by the research conducted by Rezapour *et al*. (2022). The increased vulnerability of children to the adverse health effects of heavy metals can be attributed to their behavioral traits, such as engaging in more outdoor activities and frequent oral and manual contact (Liu *et al*., 2016). These heavy metals have the potential to precipitate a spectrum of health concerns in children, including but not limited to musculoskeletal injuries, cardiovascular disorders, respiratory ailments, and impaired productivity (Madrigal *et al*., 2018). Within the children's group, Cd exhibited the highest HQing values at sites 1, 2, 4, 5 and 6, while As presented the highest HQing at sites 3. Similarly, in the adult group, Cd displayed the highest HQing values at all sampling sites. All examined heavy metals exhibited cumulative HQs below 1, indicative of an acceptable level of non-carcinogenic health risk across the entire water distribution network of the Ogun River. The findings obtained suggest that the assessed sediment samples do not pose a significant non-carcinogenic health risk, in accordance with the health risk assessment conducted for all analyzed heavy metals (Mohammadi *et al*.,

2019). Notably, all of these calculated values remained below 1, illustrating no significant non-carcinogenic risk in the analyzed sediments (Guerra *et al*., 2012). Based on the obtained results, the hierarchy of contributions from the analyzed heavy metals to the non-carcinogenic health risk is as follows: Cd > Cr > Pb > As.
As shown in the Table 9, the TLCR values for the children's group exceeded those of the adult group at all surveyed sites. This observation is consistent with the anticipated elevated carcinogenic risk at these specific sites, owing to their association with mechanic workshop activities. The heightened TLCR values align logically with the increased likelihood of exposure to potentially carcinogenic substances in these particular areas. In the context of this study, the assessment of Total Lifetime Cancer Risk (TLCR) for heavy metals is guided by specific thresholds. Based on prior research findings, when the carcinogenic risk (CR) falls below 10^{-6}, there is no evident threat to health. When CR falls within the range of 10^{-6} to 10^{-4}, it is considered an acceptable level of risk. Conversely, when CR exceeds 10^{-4}, it becomes an unacceptable level of risk (Luo and Jia, 2019; Mohammadi *et al*., 2019). As shown in Table 7, the TLCR of Pb, Cr and As in the Ogun River sediment at all sampling sites for children and adults exceeded the threshold of 10^{-4}, indicating the presence of a discernible carcinogenic hazard for children exposed to this particular area.

Conclusion

Based on the obtained results from the analysis of waters and sediment of the Ogun River, it was found that the concentrations of Pb and Cr in the water exceed the safety limits for drinking water as well as the concentration of Cd in the sediment. The temperature and COD values for Ogun River were within the permissible limits of WHO and USEPA while the values of pH, TDS, EC and TSS for sampling site 1 were above the permissible limits. The concentration of the metals in water and sediments, respectively decreased in the order of Pb>Cr>As>Cd and Pb>Cr>Cd>As. The concentrations of heavy metals in the Ogun River water and sediments also varied among sampling points with sampling sites 1 and 4 having the highest concentrations of Pb and Cr, respectively for drinking water. The data analyses by Igeo, CF, and PLI values showed no contamination of the sediments by all the studied heavy metals. The HI for exposure of both children and adults to heavy metals fell within the accepted standard levels ($HI < 1$), signifying no non-carcinogenic risk of the metals in the study region. Moreover, the results of total risk via ingestion and dermal contact showed that the ingestion was the predominant pathway. On the other hand, carcinogenic risk for Pb, Cr and As were observed higher than the acceptable limit. This underscores the necessity for continuous monitoring of heavy metals in the Ogun River's water and sediment to ensure the health and welfare of both humans and the ecosystem.

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