Assessment of Heavy Metals Pollution in Sediments of the Lower Orashi and Sombriero Rivers, Southern Nigeria: A Consensus-Based Sediment Quality Guideline Approach.

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ABSTRACT

The monitoring of the ecological health of rivers is key to ensuring optimal quality of water ecosystems. This study examined seasonal heavy metals (Cd, Cr, Cu, Pb, Zn and Fe) pollution in sediments of the lower Orashi and Sombriero Rivers, Southern Nigeria, using the consensus-based sediment quality guidelines (CBSQGs) (TEC and PEC) approach. A quasi-experimental research design approach was adopted for the research. The study area was divided into 10 grids, which constituted the sampling points (Ozuochi, Emesu, Ogbema Corridor, Ogonokom, Hulk-Transition Zone, Atala-Degema Waterfront, Opulogoloboko, Idama Flow Station, Minjidukiri, Ebemaboko). Samples from were collected from each of these 10 grids in the dry and wet seasons in 15ml plastic containers, treated with concentrated nitric acid (HNO_3) to adjust pH to preserve the oxidation states of the metals, and thereafter transported to the laboratory for analyses. PinAAcle 500 Flame Atomic Absorption Spectrometer (AAS) described in API-IA 3111B and ASTM D3651 was used to determine heavy metals concentrations. CBSQGs were used for sediment quality comparison. Results revealed that dry season concentrations of heavy metals were higher in Orashi River compared to the Sombriero River, with concentration values for Cd and Zn exceeding their TEC values in most sites. Wet season concentrations of Cd, Cr and Zn were higher in Sombriero River than Orashi River and transition zone; while concentrations of Pb, Cu and Fe were higher in Orashi River. With exception of Zn whose wet season concentration were above TEC guideline in most stations, concentrations of other metals were below their TEC. All dry and wet seasons concentrations of metals were below their PEC guidelines. This study concludes that Zn is arguably a significant pollutant in the rivers that needs to be monitored to avoid widespread contamination of the entire rivers systems. It is therefore recommended that regular monitoring of both rivers should be prioritised by concerned authorities to track slightest changes.

Keywords: Environmental Quality; River Health; Trace Heavy Metals, Ecosystem Health.

INTRODUCTION

Sediments are a significant element of aquatic ecosystems (Simpson & Batley, 2016; Tytła & Kernert, 2023) and as well are potent media by which pollutants find their way into the open waters and by extension the aquatic ecosystem through the benthic food chain (Simpson & Batley, 2016). So, as the rising consciousness and apprehension of societies about the good quality of rivers and other watercourses subsists, it is anticipated that better water quality will be in place, which ought to also take into account quality of sediments (Simpson & Batley, 2016; Tytła & Kernert, 2023). Generally, sediments are particulate organic and inorganic matter that hang in water or are carried by the water, or amass in a slack unbonded manner at the bottom of water bodies. Hence, in aquatic environment, one could find suspended and bedded sediments (MacDonald et al., 2003, USEPA, 2006).

In every kind of waterbody, suspended and bedded sediments are naturally occurring, and are vital to aquatic ecosystems when found in proper quantities as they contribute to important habitat for aquatic species' growth and reproduction and also support both autotrophic and heterotrophic organisms (MacDonald et al., 2003, USEPA, 2006), in addition to protecting the trophic condition of the aquatic ecosystems (Ergen, 2020). Nonetheless, they can reduce water quality when found in excessive amounts (USEPA, 2006) and also affect the food network and eventually become harmful to aquatic organisms (Ergen, 2020). Sediments are of different sizes such as <0.063 mm, 0.063-0.250 mm, 0.250-2 mm and >2 mm (USEPA, 2025). In situations where regulations are weak and not frequently complied with or enforced, such as the case of developing countries, releases into urban drainage as well as road runoff remain prime ceaseless sources of pollutants that eventually amass in sediments (Simpson & Batley, 2016). Heavy metals have less movement ability in water columns (Custodio et al., 2021) and as they are released into the waterbodies they continuously aggregate in the waterbodies and rapidly flow to sediments (Ergen, 2020; Custodio et al., 2021), which is their major reservoir, and impact the health of the aquatic ecosystem (Ergen, 2020). Also, they can permeate through soil to seed and then cause plants to become toxic, which in turn affect the food chain, because as organisms eat these plants, larger animals eat these organisms (Ergen, 2020).

For over three decades environmental scientists, engineers and regulatory authorities across the world have committed significant resources to assessment and management of pollutants in sediments so as to guarantee protection and usage for numerous purposes. Consequently, to meet collective demands for greater environmental protection of aquatic resources and restoration of degraded rivers and estuaries, scientists in numerous nations have established a variety of methods for evaluating the extent to which sediment-associated substances might harmfully impact aquatic organisms. These methods have brought about chemically based numerical or narrative sediment quality guidelines (SQGs) intended to protect benthic organisms; support or maintain selected uses of freshwater, estuarine, and marine environments; and assist sediment evaluators and managers charged with the interpretation of sediment quality (Wenning & Ingersoll, 2002).

Therefore, sediment quality guidelines (SQGs) "are numerical chemical concentrations intended to be either protective of biological resources, or predictive of adverse effects to those resources, or both". These SQGs have been developed using both mechanistic and empirical methods, for evaluating sediment quality with regard to the likelihood for harmful impacts on organisms that reside in sediment (Wenning & Ingersoll, 2002). One of such SQGs is the consensus-based sediment quality guidelines (CBSQGs) developed by MacDonald et al. (2000). The application of the CBSQGs is in order to not only ascertain the environmental quality of the sediments but to also determine plausible associated risk. The CBSQGs comprise a threshold effect concentration (TEC) and a probable effect concentration (PEC). It is evident from studies that most of the TECs provide an accurate basis for predicting the absence of sediment toxicity, while most of the PECs provide an accurate basis for predicting sediment toxicity (MacDonald et al., 2000). In order words, the CBSQGs (TEC and PEC) collectively provide an accurate basis for predicting the presence or absence of toxicity in sediments.

While the TECs reflect values of contamination of a metal below which harmful effects are not likely to be observed, the PECs reflect values of contamination of a metal above which harmful effects are likely to be observed (MacDonald et al., 2000). A fundamental aspect of the assessment of sediment quality and interaction is the comparison of the concentrations of measured pollutant against sediment quality guideline values (SQGVs) (Simpson & Batley, 2016). To this end, the goal of sediment quality assessment is to protect aquatic life (benthic community) and by so doing ensure that pollutants in sediments would not exist in amounts that, either acting alone or in collaboration, are toxic to benthic communities in bays and estuaries. It also aims at safeguarding human health by guaranteeing that pollutants should not exist in sediments at levels that would bioaccumulate in aquatic life to levels that are detrimental to human health in bays and estuaries. Equally, its goal is the protection of wildlife and resident finfish by ensuring that pollutants would not exist in sediment at levels that either acting alone or in collaboration are toxic to wildlife and resident finfish by direct exposure or bioaccumulate in aquatic life at levels that are harmful to wildlife or resident finfish by indirect exposure in bays and estuaries (California State Water Resources Control Board, 2018).

Within the ecosystems of Orashi and Sombriero Rivers are left footprints of pollution from hydrocarbon-based substances owing to factors such as oil and gas production, pipeline vandalism, gas flaring, pipeline leakages, illegal bunkering and refining of crude oil, locally known as "kpo fire". These scenarios have given impetus to numerous concerns. Studies have reported various assessments of sediment pollution in different regions. Faboya et al. (2012) investigated the sources and concentration of heavy metals in surface sediment samples collected from rivers (Bakkasi, Calabar, Greak Kwa and Qua Ibo) and canals (Ogini, Olomoro and Ughelli) in parts of the Niger Delta. The study found that the mean concentrations of the metals ranged from 0.09 µg/g (Cd) to 19.0 µg/g (Mn) in rivers and 0.11 µg/g (CO) to 24.2 µg/g (Mn) in canals, which were all below the effective range low (ERL) and effect ranges medium (ERM) sediment quality guidelines, as well as the limits set by UK Ministry of Agriculture, Fisheries and Food Action (MAFF) and USEPA; indicating that the levels of heavy metals concentrations in Niger delta sediments do not pose any serious adverse risk to the ecosystem and human health, and as such classified as uncontaminated.

Custodio et al. (2021) evaluated surface sediment quality of Tishgo and Chia Rivers in Peru using indicators of contamination, accumulation and ecological risk of heavy metals. Their findings revealed that the descending order of the mean concentrations of heavy metals and As in the Chia River was Zn>Cu>As>Pb and in Tishgo River was Zn>Pb>As>Cu. The mean concentration ranges of heavy metals and metalloids in Tishgo and Chía Rivers were Cu = 15.58 and 16.30 mg/l; Pb = 19.93 and 7.27 mg/l; Zn = 98.81 and 54.44 mg/l; As = 19.10 and 7.57 mg/l respectively. These values obtained in both rivers were lower than the PEC values. However, whereas the mean concentrations of Cu (19.26 mg kg/l) and As (11.32 mg kg/l) in the Chía River were above the ISQG values (18.70 mg kg/l, 124 mg kg/l, 7.24 mg kg/l respectively); the mean concentrations of Cu (21.17 mg kg/l), Zn (125.08 mg kg/l) and As (19.34 mg kg/l) in the Tishgo River surpassed the ISQG values; concentrations of all elements assessed in the Tishgo River surpassed the UCC reference values; and arsenic concentrations in both rivers exceeded the PEC, UCC and ISQG values.

Ipeaiyeda and Obaje (2019) assessed the upstream and downstream levels of metals pollution in the Onyi River in Obajana community, Nigeria in the wet and dry seasons in order to determine the sediment quality. The results revealed that the concentration level range of Cd (1.7-11.0 µg/g) in downstream sediments was observed to be above the Australia and New Zealand sediment guidelines for the protection of aquatic life. Likewise, the range of lead concentrations (15.0-48.0 µg/g) in some downstream sampling points exceeded the permissible limit of 35.0 µg/g prescribed by the Canadian sediment quality guideline. The typical mean concentrations of heavy metals in the sediment of Onyi River were in the order of Zn≈Pb>Cr>Co>Ni>Cu>Cd.

Archambault et al. (2017), in the Clinch River in Virginia and Tennessee, USA, investigated the toxicity of contaminants of recently-deposited sediments on juveniles of the freshwater mussel Epioblasma brevidens. Their results showed that Zn recorded very low concentration of 1.20 µg/g dry weight, compared to the its PEC value of 459 µg/g; while each PECQs for As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn among treatments ranged from 0.03 to 0.57, with a mean value of 0.13, while average individual PECQs among treatments for each of As, Cr, Cu, Pb, and Zn were less than 0.1. Mn recorded the highest PECQ within each Clinch sediment treatment than other metals, ranging between 0.18 and 0.57 with a mean of 0.34, and this is more than double the control sediment values (SPR = 0.13, WBS = 0.12). Also, PECQ average for Fe (0.20) was also comparatively high than other metals, though was between the control sediment values (SPR = 0.10, WBS = 0.30). The authors further reported that the mean metal PECQs for each treatment were significantly below the set toxicity standard of 1.0 for sediment quality.

Coulibaly et al. (2022) evaluated the distribution, ecological and health risks of arsenic in surface sediment from the Comoe River and the Ebrie Lagoon in Cote d'Ivoire, West Africa. Their findings revealed that overall concentrations of arsenic (2.92 ± 0.27 - 5.42 ± 4.6 mg/kg) were higher than the Upper Continental Crusts value of 2 mg/kg, and these overall concentration values for arsenic were below both the TEC and PEC sediment quality guidelines of 10 mg/kg and 33 mg/kg respectively, indicating that though the sediments were moderately contaminated by arsenic, they may not cause adverse effects to organisms. Moslen et al. (2018) evaluated heavy metals pollution in surface sediments of Azuabie creek in the Niger Delta of Nigeria, while the Okujagu creek was used as a control point. The findings revealed that the concentrations of metals were higher in Azuabie creek compared to the control creek (Okujagu). Mean concentrations of metals were as follows: Zn = 27.5-293.3 mg/kg, Cd = 0.0-0.6 mg/kg, Cr = 2.8-35.7 mg/kg and Pb = 5.7-22.5 mg/kg. The study observed that the concentration of metals was in the decreasing order of Zn>Cr>Pb>Cd.

Madkour et al. (2013) assessed heavy metals concentrations in the marine surface sediments resulting from natural inputs in Wadi El-Gemal area, Egyptian Red Sea coast. The study found that concentration of Fe in sediments ranged between 2266 and 3306 ppm; Mn concentration ranged from 162 to 968 ppm; Zn concentration levels ranged from 18 to 383 ppm; Cu concentration ranged between 5 and 453 ppm; Pb concentration ranged between 12.8 and 96 ppm; Ni concentrations ranged from 11 to 156 ppm; Cobalt (Co) concentrations ranged between 0.2 and 4 ppm; and Cd concentration levels ranged between 0.02 and 0.2 ppm. These high concentrations of heavy metals in sediments were mainly affected by the high sediment depositions from land erosion through the stream of Wadi El-Gemal, and their concentrations decreased as distance from the coastline increased, safe for Pb, which increased as distance from the coastline increased, the study further reported.

Tytła and Kernert (2023) assessed the ecological and human health risks of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in the bottom sediments of the Pławniowice reservoir in the Silesian Voivodeship, Poland. The findings revealed that concentration of metals evaluated ($mg \cdot kg^{-1}$) ranged as follows: Cd 34.0 - 270.8; Cr 32.4 - 44.6; Cu 22.6 - 32.1; Ni 13.9 - 23.7; Pb 29.9 - 60.8; Zn 220.0 - 322.2. These results revealed that Zn had the highest mean concentration, while Cd had the lowest concentration; thus, concentration of the metals was ordered in the decreasing series as: Zn>Pb>Cr>Cu>Ni>Cd. Comparable trend to this was earlier reported by Moslen et al. (2018) in Azuabie creek in Niger Delta. The results of the ecological risk analysis showed that among the evaluated metals, only Cd may pose a potential hazard to the fauna and flora of the reservoir.

Sobhanardakani and Habibi (2016) examined heavy metals content in sediments of Shirin Su wetland, Western Iran February to May of 2013. The findings revealed that the mean concentrations of metals (microgram per gram dry weight = µg/g dry weight) were 0.16 for Cd, 23.07 for Cr, 10.62 for Cu, 689.82 for Fe, 27.9 for Pb, 5.01 for Zn. Thus, the hierarchy of the mean concentration of the metals was in the order of Fe> Cr> Pb> Cu> Zn> Cd. This ranking is contrary to those reported by Moslen et al. (2018) and Tytła and Kernert (2023) in their studies. Further results showed that the mean concentrations of all the metals in all sediment samples were below the TEC and thus no adverse effects are observed, except Fe which surpassed the TEC in all samples, suggestive of potential risk of poisoning. The I-geo values obtained indicated that in most stations the sediments quality was classified as unpolluted; while the Pearson correlation test showed that the anthropogenic sources of Zn, Fe and Cr are closely connected with the sediment from Shirin Su Wetland.

Eke and Iwuoha (2018) evaluated the concentration of heavy metals (Cr, Cu, Fe, Ni, Pb, Hg, Cd and Zn) in fresh water sediments from Oron Channel from 2015 to 2016. The assessment of the sediment quality was done by comparing the derived heavy metal concentrations with the USEPA sediment quality guideline and the CBSQGs as done by Sobhanardakani and Habibi (2016) and Coulibaly et al. (2022). The study found that the concentration levels of metals (mg/kg) in 2015 ranged as follows: Cr: 4.90-5.36; Cu: 0.17-0.22; Fe: 103.94-109.65; Ni: 1.03-1.11; Pb: 0.02-0.02; Zn: 12.02-12.67; and in 2016 ranged as follows: Cr: 6.09-7.1; Cu: 0.129-0.33; Fe: 196.23-199.02; Ni: 156.26-158.63; Pb: 0.02-0.045; Zn: 13.04-13.52; while the concentrations of Hg and Cd were observed to be below detection limit of 0.001mg/kg in both years. The mean metal concentration in both years was in the order of Fe>Zn>Cr>Ni>Cu>Pb and Fe>Ni>Zn>Cr>Cu>Pb, respectively. These series for both years are incongruent with the ranking series reported by Sobhanardakani and Habibi (2016), Moslen et al. (2018) and Tytła and Kernert (2023) in their respective studies.

Comparison with the USEPA SQG for the protection of benthic organisms revealed that the sediments were heavily polluted with Ni in 2016 as against the status of not polluted in 2015. Applying the CBSQG, it was observed that concentration of Cr, Cu, Fe, Pb, Hg, Cd and Zn were below the TEC, thus they are not likely to cause harm to benthic organisms; while Ni concentrations exceeded the PEC value, indicating probable adverse impacts likely to cause of harm to benthic organisms. This results on TEC corroborates the results reported by Archambault et al. (2017); Sobhanardakani and Habibi (2016); and Coulibaly et al. (2022; while the result on PEC agrees with the result of Custodio et al. (2021) on As. The reviewed literature indicates that studies on seasonal pollution by heavy metals in sediments of Lower Orashi and Sombriero Rivers are generally scarce in literature and the use of the consensus-based sediment quality guidelines for assessment of metals in available literature and especially in Lower Orashi and Sombriero Rivers are not prominent in the literature. These are clear gaps in the literature of the subject matter, which this current study seeks to fill.

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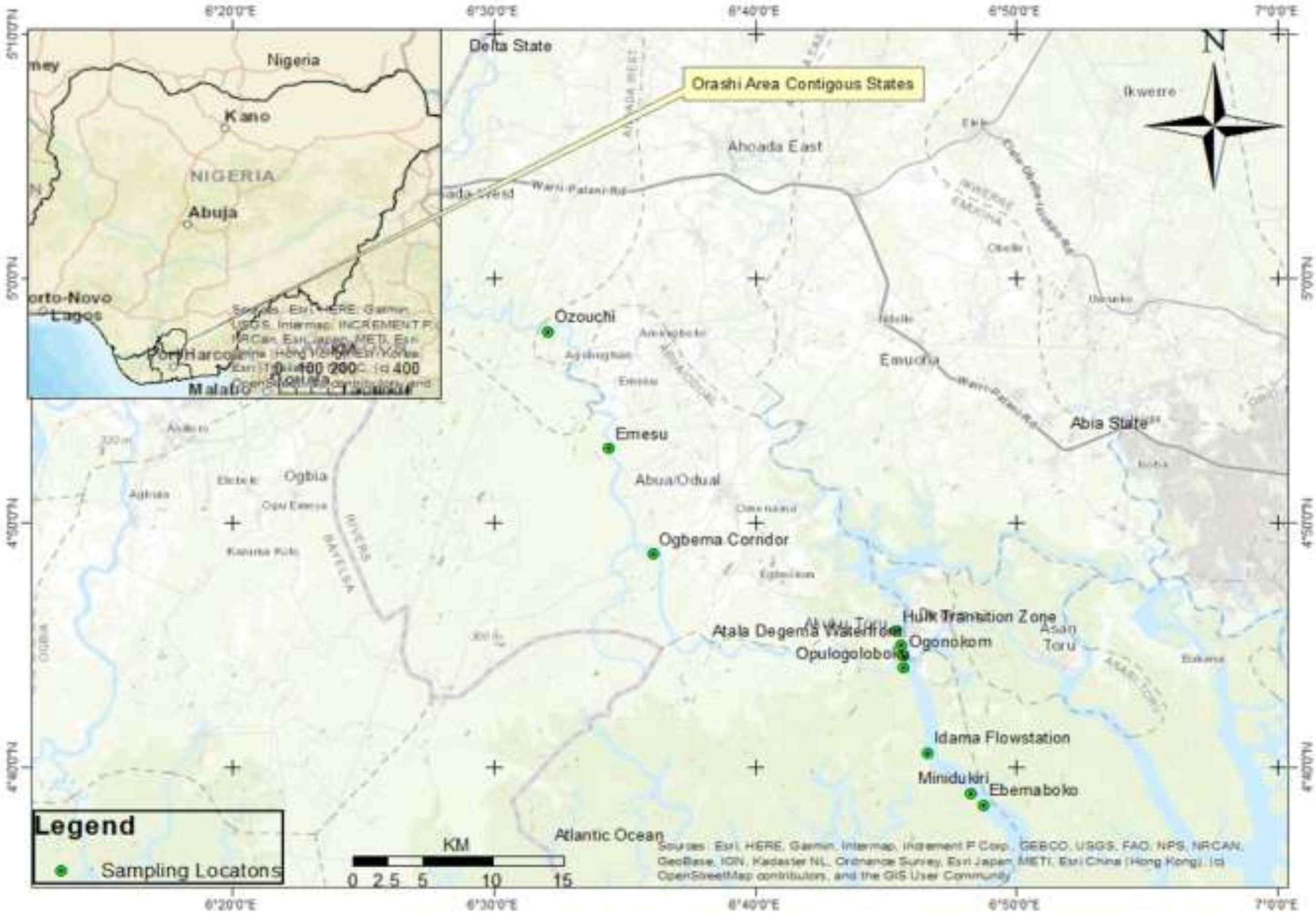
METHODOLOGY

Study Area

Figure 1: Study area showing Lower Orashi and Sombriero River sampling locations



The study area is the Lower Orashi and Sombriero River estuary spanning across Ahoada West, Abua/Odual, Degema, Akuku-Toru and Asari-Toru Local Government Areas of Rivers State. It is bounded by Nembe Local Government Area of Bayelsa State on the west, the Atlantic Ocean on the south of the Sombriero, Emohua Local Government Area on the north and Bonny Local Government Area on the east, all of Rivers State. The climate is predominantly humid tropical climate which is typical of the Niger Delta region. The mean annual rainfall is 2800 mm, and the average temperature is 27ºC (Oyegun, 1997). It is a low-lying plain of fresh unconsolidated fluvial sediments of Quaternary Age (Clinton-Ezekwe et al., 2022), characterised by layered heterogeneous sediment structure of alternating sands, silts and clay of the Benin, Agbada and Akata formations (Abam & Okagbue, 1997).

The area is of freshwater and marine forest ecology with fresh and saline water on the Orashi and Sombriero respectively. The Orashi River, particularly from Mbiama to Hulk is fresh water, while the Sombriero River from Degema where it beheaded the Orashi River (Transition Zone) to Ebemaboko is saline water. The ecosystem is highly diverse and support various terrestrial and aquatic fauna, flora, economic trees that support human livelihoods (Ekundayo & Obuekwe, 2001; Nduka et al., 2012). Major occupations of the people in the area include fishing, farming, sand mining, tash making, hunting, palm oil production, timber logging, trading, canoe-carving and wine tapping. In addition, the area is endowed with mineral resource chief amongst which is crude oil and gas deposits (Reigers et al., 1996 cited in Nduka et al., 2012); and this has occasioned oil and gas exploration and production activities, and the attendant incidences of oil spillages and gas flaring and their negative impact of pollution and degradation to ecosystem and public health (Nduka et al., 2012).

Sampling and Data

The study adopted the quasi-experimental research design. The study area was divided into ten (10) grids, which constituted the sampling points and sediment samples were collected from each of these 10 grids. The sampling sites spanned from Mbiama water front to Hulk (Agada)/Degema which is in the transitional zone between the two River systems, and from there down through the Sombriero to the mouth of the Atlantic Ocean. Sediment samples were collected in all ten sites in the dry and wet seasons. Dry season sampling was carried out on the 3rd February, 2022, while wet season sampling was done on 23rd July, 2022. Samples were collected in 15 ml plastic containers, treated with concentrated nitric acid (HNO_3) to adjust pH to preserve the oxidation states of the metals, and thereafter transported to the laboratory for further analyses.

Table 1: Sampling Sites and Coordinates

S/N	Sampling Sites	Codes	Coordinates
1	Ozuochi	OR1	E006º 32 02.0" N04º57 45.5"
2	Emesu	OR2	E006º 34 29.9" N04º53 03.1"
3	Ogbema Corridor	OR3	E006º 36 07.0" N04º48 44.3"
4	Ogonokom	OR4	E006º 45 06.0" N04º 45.33.0"
5	Hulk-Transition Zone	TZ1	E006º 45 31.4" N04º45 46.7"
6	Atala-Degema Waterfront	TZ2	E006º 45 51.4" N04º45 40.4"
7	Opulogoloboko	SR1	E006º 45 34.1" N04º44 08.3"
8	Idama Flow Station	SR2	E006º 46 34.7" N04º44 38 3"
9	Minjidukiri	SR3	E006º 46 52.5" N04º40 36.9"
10	Ebemaboko	SR4	E006º 48 08.0" N04º38 38.7"

Data Analysis

Laboratory Procedures and Analysis

To determine the concentrations of heavy metals (Cr, Cu, Pb, Fe, Cd, Zn and Ni) in the sediment samples, the PinAAcle 500 Flame Atomic Absorption Spectrometer (AAS) described in API-IA 3111B and ASTM D3651 was used, which involved direct aspiration of the sample into air/acetylene or nitrous oxide/acetylene flame generated by a hollow cathode lamp at specific wavelength applicable only to the metal under analysis. Standards and blanks were prepared and applied for calibration for any metal analysed before samples were aspirated. Respective concentrations at specific absorbance were equally shown on the data system monitor for need of printout at less than 0.001 mg/l detection limit.

Descriptive Analyses and Data Interpretation

The consensus-based sediment quality guidelines (CBSQGs) (TEC and PEC) were used for sediment quality toxicity assessment. The CBSQGs are numerical values used to assess the concentrations of the selected metals in the sediments (Harikumar et al., 2010). The procedure involved comparison of the CBSQGs' numerical values with concentration levels of the pollutants of interest obtained from laboratory analysis. The CBSQGs (TEC and PEC) collectively provide an accurate basis for predicting the presence or absence of toxicity in sediments. If the concentrations of metals in sediments are below the TEC, then it is unlikely that harmful effects would be observed, whereas in the case of PEC, if the concentrations of metals are above the PEC, then it is likely that harmful effects would be observed (MacDonald et al., 2000). Descriptive statistics such as mean scores, simple percentages, and frequency tables were used to present and interpret the results.

RESULTS

Tables 2 and 3 shows the comparison of concentration of heavy metals in sediments from the Orashi and Sombriero Rivers with CBSQGs for the dry and wet seasons respectively.

Dry Season Concentration Levels of Heavy Metals in Sediments

The dry season result revealed that cadmium (Cd) concentration level ranged from the lowest of 0.40 mg/l at SR1 to its highest level of 1.73 mg/l at TZ2, with a mean value of 0.934 mg/l. Chromium (Cr) concentration level ranged from the lowest of 2.66 mg/l at SR1 to its highest value of 19.40 mg/l at SR3, with a mean value of 7.654 mg/l. Concentration levels of lead (Pb) ranged from the lowest of <0.001 mg/l at OR1 to its highest value of 13.62 mg/l at TZ1, with a mean concentration value of 5.447 mg/l. Copper (Cu) concentration levels ranged from the lowest of 0.87 mg/l at SR1 to its highest value of 5.06 mg/l at OR3, with a mean concentration value of 2.381 mg/l. Concentration levels of zinc ranged from its lowest of 0.72 mg/l at OR2 to its highest value of 29.57 mg/l at OR3, with a mean concentration value of 14.536 mg/l. Iron (Fe) concentration levels ranged from its lowest value of 365.75 mg/l at SR1 to its highest value of 8,073.7 mg/l at OR3, with a mean concentration value of 3,917.24 mg/l.

Table 2: Comparison of Dry Season Concentrations of Heavy Metals with Consensus-Based Sediment Quality Guidelines.

	Metals Concentrations					
Sampling sites	**Cd**	**Cr**	**Pb**	**Cu**	**Zn**	**Fe**
SR1	0.40	4.70	8.07	0.87	4.85	365.75
SR2	0.46	3.62	1.18	2.20	14.35	5,497.7
SR3	0.72	11.66	1.44	2.21	2.28	395.66
SR4	0.57	7.02	6.35	0.99	22.33	4,217.0
OR1	0.87	2.66	<0.001	0.89	2.78	860.51
OR2	0.63	3.89	5.90	1.72	0.72	1,339.9
OR3	1.56	19.40	6.28	5.06	29.57	8,073.7
OR4	1.33	7.20	10.20	4.49	23.27	7,691.5
TZ1	1.07	11.39	13.62	3.10	23.10	7,847.6
TZ2	1.73	5.00	1.43	2.28	22.11	2,883.1
Mean	0.934	7.654	5.447	2.381	14.536	3,917.24
TEC (CBSQG)	0.99[a]	43.4[a]	35.8[a]	31.6[a]	12[a]	20,000 (2%)[b]
PEC (CBSQG)	4.98[a]	111[a]	128[a]	149[a]	459[a]	40,000 (4%)[b]

NB: CBSQG = consensus-based sediment quality guideline; TEC = threshold effect concentration; PEC = probable effect concentration; a = MacDonald et al. (2000); b = Persaud et al. (1993).

Wet Season Concentration Levels of Heavy Metals in Sediments

The result revealed that Cd concentration level for the wet season ranged from the lowest of <0.001 mg/l at SR1, OR1, OR3, OR4 and TZ2 respectively, to its highest level of 0.54 mg/l at TZ2, with a mean value of 0.156 mg/l. Cr concentration level ranged from the lowest of <0.001 mg/l at SR2, SR4, OR1, OR2 and OR3 respectively, to its highest value of 8.05 mg/l at OR4, with a mean concentration value of 2.692 mg/l. Concentration levels of Pb ranged from the lowest of <0.001 mg/l at SR1, SR2, SR4 and OR4 respectively to its highest value of 15.14 mg/l at OR1, with a mean concentration value of 3.550 mg/l. Cu concentration levels ranged from the lowest of

<0.001 mg/l at SR1, SR4, OR1, OR3 and TZ2 respectively, to its highest value of 5.06 mg/l at OR3, with a mean concentration value of 1.096 mg/l. Concentration levels of Zn ranged from its lowest of <0.001 mg/l at OR3 to its highest concentration value of 18.18 mg/l at TZ2, with a mean concentration value of 8.872 mg/l. Fe concentration levels ranged from its lowest value of 588.84 mg/l at OR1 to its highest value of 7,826.7 mg/l at OR2, with a mean concentration value of 4,288.4 mg/l.

Table 3: Comparison of Wet Season Concentration of Heavy Metals with Consensus-Based Sediment Quality Guidelines (CBSQG).

	Metals Concentrations					
Sampling Sites	**Cd**	**Cr**	**Pb**	**Cu**	**Zn**	**Fe**
SR1	<0.001	5.18	<0.001	<0.001	11.59	4,541.7
SR2	0.07	<0.001	<0.001	0.24	5.39	4,053.6
SR3	0.54	5.12	8.93	2.82	12.72	6,273.5
SR4	0.09	<0.001	<0.001	<0.001	13.56	2,402.1
OR1	<0.001	<0.001	15.14	<0.001	0.76	2,428.8
OR2	0.45	<0.001	3.35	4.13	0.85	7,826.7
OR3	<0.001	<0.001	4.60	<0.001	<0.001	588.84
OR4	<0.001	8.05	<0.001	3.17	13.11	7,429.1
TZ1	0.40	7.52	1.58	0.59	12.56	5,690.6
TZ2	<0.001	1.04	1.90	<0.001	18.18	1,648.7
Mean	0.156	2.692	3.550	1.096	8.872	4,288.4
TEC (CBSQG)	0.99[a]	43.4[a]	35.8[a]	31.6[a]	12[a]	20,000 (2%)[b]
PEC (CBSQG)	4.98[a]	111[a]	128[a]	149[a]	459[a]	40,000 (4%)[b]

NB: CBSQG = consensus-based sediment quality guideline; TEC = threshold effect concentration; PEC = probable effect concentration; a = MacDonald et al. (2000); b = Persaud et al. (1993).

Comparison of Dry and Wet Seasons Mean Concentrations of Heavy Metals

The result revealed that the overall mean concentration values for Cd, Cr, Pb, Cu, Zn and Fe for dry season were 0.934 mg/l, 7.654 mg/l, 5.447 mg/l, 2.381 mg/l, 14.536 mg/l and 3,917.24 mg/l, respectively; while their wet season concentration levels were 0.156, 2.692, 3.550, 1.096, 8.872 and 4,288.4 respectively. These dry and wet seasons mean concentration values for all the metals were all below their respective TEC and PEC guideline values, with exception of zinc whose dry season mean concentration value of 14.536 mg/l was higher than its PEC value of 12 mg/l.

DISCUSSION OF RESULTS

The results showed that generally, Cd concentrations were higher in the Orashi River and transition zones compared to the Sombriero River; with the highest values of 1.73 mg/l and 1.56 mg/l being recorded at TZ2 and OR3 respectively, and these values are above the TEC value of 0.99 mg/l. These values indicate that cadmium contamination in these locations exceeded levels that harmful effects would not likely to be observed; implying that these locations are contaminated with cadmium for which likely harmful effects could be observed. The implication of this is that both aquatic organisms and humans alike who depend on the ecosystems of these rivers for sustenance could become vulnerable to attendant ecological and health impacts of cadmium poisoning. Contrary to this result, Faboya et al. (2012) elsewhere in the Niger Delta region reported Cd concentration that was below the effective range low (ERL) and effect ranges medium (ERM) sediment quality guidelines.

However, all values obtained in the Sombriero River (SR1, SR2, SR3 and SR4) and those obtained in OR1 and OR2 are below the TEC value of 0.99 mg/l. Nonetheless, all values of cadmium obtained in all the sampling points were below the PEC value of 4.98 mg/l. This PEC result is inconsistent with the result reported by Custodio et al. (2021) who in their study in the Tishgo and Chia Rivers in Peru found As values that surpassed the PEC value. On the contrary, Coulibaly et al. (2022) in their study in the Comoe River and the Ebrie Lagoon in Cote d'Ivoire, West Africa reported As levels (2.92 ± 0.27 - 5.42 ± 4.6 mg/kg) that were below the TEC and PEC standards of 10 mg/kg and 33 mg/kg respectively.

Also, dry season Cr concentration was largely higher in the Orashi River than in the Sombriero River, with both the least value of 2.66 mg/l and the highest value of 19.40 mg/l recorded in the Orashi River. All concentration values of chromium obtained in all the sampling points were observed to be below the TEC and PEC values of 43.4 mg/l and 76.5mg/l respectively. Pb concentration was mainly higher in the Orashi River than in the Sombriero River; however, <0.001 mg/l was recorded still at the Orashi River at OR1, while the transition zone 1 (TZ1) recorded the single highest concentration level of 13.62 mg/l. All concentration levels recorded for lead in all the sampling stations were below its TEC and PEC values of 35.8 mg/l and 128 mg/l respectively. Cu concentration was observed to be higher in the Orashi River than in the Sombriero River and transition zones, with the highest value of 5.06 mg/l being observed at OR3; albeit, the concentration values obtained for Cu in all the sampling sites are below its respective TEC and PEC values of 31.6 mg/l and 149 mg/l. Eke and Iwuoha (2018) in their study of sediment in the Oron Channel had reported comparable low (mg/l) Cr (7.654), Pb (5.447) and Cu (2.381) concentration levels that were below their TEC values (mg/l) of 43.4, 35.8 and 31.6.

Zn concentration was found to be higher in the Orashi River and transition zones than in the Sombriero River, with the highest values of 29.57 mg/l, 23.27 mg/l and 23.10 mg/l being recorded at OR3, OR4 and TZ1 respectively. It was further observed that the cumulative concentration levels of zinc pollution in Orashi River (56.34 mg/l) and transition zones (45.21 mg/l) are almost similar. The findings further reveal that the concentration values obtained for Zn in SR2 (14.35 mg/l), SR4 (22.33 mg/l), OR3 (29.57 mg/l), OR4 (23.27 mg/l), TZ (23.10 mg/l) and TZ2 (22.11 mg/) including the mean value of 14.536 mg/l exceeded its TEC value of 12 mg/l. Again, this result connotes that these zones are polluted with zinc and could be harmful to both marine and human population. At all other stations, the concentration values obtained are below the TEC value. Sobhanardakani and Habibi (2016) in their study in sediments of Shirin Su wetland, Western Iran had reported contrary concentration level of Zn that was below the TEC threshold. Furthermore, in all sampling station, zinc concentration values are less that its PEC value of 459 mg/l, indicating that harmful effects are not likely to be observed among marine species and human population. This result on Zn is analogous to the value of 1.20 µg/g dry weight reported by Archambault et al. (2017) in the Clinch River in Virginia and Tennessee, USA, which was less than PEC value of 459 µg/g.

Fe concentration is observed to be higher in the Orashi River than in the Sombriero River, with the highest value of 8,073.7 mg/l, 7,847.6mg/l and 7,691.5 mg/l being observed at OR3, TZ1 and OR4 respectively; though, all the obtained concentration values at all the sampling sites are below its TEC and PEC values of 20,000 (2%) and 40,000 (4%) respectively. A critical look at the results for all the metals at all the sampling stations reveals that per unit basis, the Orashi River and the transition zones are more polluted with heavy metals than the Sombriero River, with cadmium, lead, zinc and iron being the most notorious pollutants in these areas. The result on Fe with respect to comparison with TEC conflicts with the finding of Sobhanardakani and Habibi (2016), which reported high concentration values that exceeded the TEC limit.

It was observed that wet season Cd concentrations were higher in the Sombriero River than in the Orashi River and transition zones, with the highest value of 0.54 mg/l being recorded at SR3, and all the cadmium values in all the sampling sites are below the TEC value of 0.99 mg/l. These values therefore signify that cadmium contamination in these locations are detected at levels that harmful effects are not likely to be observed. The implication of this is that both aquatic organisms and humans alike who depend on the ecosystems of these rivers for sustenance are not at risk of the associated ecological and health impacts of cadmium pollution. Comparable low values of Cd that were below the TEC limit were reported by Sobhanardakani and Habibi (2016). However, Ipeaiyeda and Obaje (2019) in the Onyi River in Obajana community, Nigeria reported Cd concentration range of Cd (1.7-11.0 µg/g) in downstream sediments that was above the Australia and New Zealand sediment guidelines for the protection of aquatic life. Similarly, all values of CD obtained in all the sampling points were below the PEC value of 4.98 mg/l, also indicating that no harmful effects would be experienced.

Chromium (Cr) concentration levels in the wet season on the aggregate were higher in the Sombriero River than in the Orashi River and transition zones, although the single highest values of 8.05 mg/l and 7.52 mg/l were recorded at OR4 and TZ1 respectively. All the chromium concentration values obtained in all the sampling sites are below the CBSQG TEC and PEC values of 43.4 mg/l and 111 mg/l; however, at SR2, SR4, OR1, OR2 and OR3 it was found below detection limit of <0.001 mg/l. This result on Cr confirms the earlier finding reported by Sobhanardakani and Habibi (2016) in Shirin Su wetland, Western Iran. Lead (Pb) concentration level in the wet season on the whole was higher in the Orashi River than in the Sombriero River and transition zones, with the highest value of 15.14 mg/l being observed at OR1. Nevertheless, all the obtained concentration values are below its TEC and PEC guideline values of 35.8 mg/l and 128 mg/l respectively, all indicating to harm to the marine and human population. Contrary to this result, Ipeaiyeda and Obaje (2019) reported concentrations range of Pb (15.0-48.0 µg/g) in some downstream sampling points that exceeded the permissible limit of 35.0 µg/g prescribed by the Canadian sediment quality guideline. More so, At SR1, SR2, SR4 and OR4 lead was found below detection limit of <0.001 mg/l. Copper (Cu) overall wet season concentration level was higher in the Orashi River compared to the Sombriero River and transition zones, with the highest single concentration values of 4.13 mg/l and 3.17 mg/l being observed at OR2 and OR4 respectively. All concentration values of copper obtained at all sampling points were less than its TEC and PEC guideline values of 31.6 mg/l and 149 mg/l respectively; which collectively implies no harmful effects. Custodio et al. (2021) in the Tishgo and Chia Rivers in Peru reported Cu and Pb concentration levels that were below their PEC guideline values of 149 mg/l and 128 mg/l.

Zn concentration on the aggregate was higher in the Sombriero River and transition zone than in the Orashi River, with the highest single concentration values of 18.18 mg/l, 13.56 mg/l, 13.11 mg/l, 12.72 mg/l and 12.56 mg/l being observed at TZ2, SR4, OR4, SR3 and TZ1 respectively. These concentration values obtained at these sampling points (TZ2, SR4, OR4, SR3 and TZ1) are above Zn's TEC guideline value of 12 mg/l, indicating probable harmful effect experience both for the marine species and human population who depend on the resources therein for survival. The study of Eke and Iwuoha (2018) in the Oron Channel had earlier reported a contrary low concentration level of Zn that was below the TEC threshold. However, at other sampling sites, the obtained Zn concentration values are below the TEC guideline value. All concentration levels obtained at all the sampling stations are less than Zn's PEC guideline value of 459 mg/l, implying no experience of harmful effects. Cumulative concentration level of Fe for the wet season was slightly higher in the Orashi River compared to the Sombriero River, with the single highest concentration values of 7,826.7 mg/l, 7,429.1 mg/l, 6,273.5 mg/l and 5,690.6 mg/l being recorded at OR2, OR4, SR3 and TZ1 respectively. These wet season concentration values for Fe in all the sampling stations are below its TEC and PEC guideline values of 20,000 (2%) and 40,000 (4%) respectively; signifying no likely harmful effects to be observed. The study of Eke and Iwuoha (2018) in the Oron Channel had earlier reported similar low concentration levels of Fe that were below the TEC threshold.

CONCLUSIONS AND RECOMMENDATIONS

This study applied the consensus-based sediment quality guidelines (CBSQGs) (TEC and PEC) approach to assess seasonal heavy metals pollution in sediments of the lower Orashi and Sombriero Rivers, in the Southern part of Nigeria. The results of the study showed that in the dry season, concentration levels of the sampled heavy metal (Cd, Cr, Pb, Cu, Zn and Fe) were higher in the Orashi River compared to the Sombriero River, with concentration values obtained for cadmium and zinc exceeding their respective TEC values. This may imply that likely harmful effects may befall aquatic organisms in the river ecosystems. The wet season, concentration levels of Cd, Cr and Zn were higher in Sombriero River than Orashi River and transition zones; while concentrations of lead, copper and iron were higher in the Orashi River. With the exception of zinc whose wet season concentration values at some sites were above its TEC of 12 mg/l; the wet season concentration values obtained for other heavy metals (Cd, Cr, Pb, Cu and Fe) were below their respective TEC and PEC values. This study concludes that Zn is arguably a significant pollutant in the rivers that needs to be monitored to avoid widespread contamination of the entire rivers systems. It is therefore recommended that regular monitoring of both rivers should be prioritised by concerned authorities especially in the context of the sustainable development goals #6 and ~1. Other crude oil related activities such as illegal oil bunkering and refining activities should be checked; and the oil and gas companies operating in the areas should regularly service their facilities to avert or reduce discharges from failed or obsolete equipment.

Data Availability Statement

The data sources that support the findings of this study have been provided in the body of the study.

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Declaration of generative AI in scientific writing

The authors declare that AI was not used in the writing of this article

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