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Assessment of Physicochemical Characteristics and Heavy Metals Concentrations in Sediment and Water Samples from Creek Road Market Landing-Bay in the Bonny Estuary Port Harcourt Rivers State, Nigeria

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ABSTRACT: This paper assessed the physicochemical characteristics and heavy metals concentrations in Sediment and water samples from Creek Road Market Landing-Bay in the Bonny Estuary, Port Harcourt Rivers State, Nigeria using standard procedures. Results revealed overall mean values for the analyzed parameters as follows: Temperature: 30.52±0.59°C, pH: 6.78±0.44, Electrical Conductivity: 1593.67±474.60, Total Dissolved Solids: 746.22±138.95, Salinity: 371.33±69.37, Dissolved Oxygen: 3.74±0.36, Nitrate: 26.98±2.78, Phosphate: 2.05±0.25, Hardness: 13.28±0.48 and Biological dissolved oxygen: 0.6±0.17. Heavy metal concentrations showed overall mean values as follows: In water samples –Zinc: 8.97±0.67, and Lead: 1.53±0.23.In sediment samples - Zinc: 8.91±1.04, and Lead: 5.6±0.76. Cadmium and Mercury were below the detection limit of the measuring equipment (<0.001).The concentration levels the physicochemical parameters and heavy metals were found to be higher than the WHO standard limits for water and sediments. It is possible that the food web in this study environment may be at risk of heavy metal contamination.

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In environmental literature, the term "heavy metals" refers to metals and metalloids that are linked with to environmental pollution, toxicity, and adverse effects on biota. These heavy metals have an atomic density greater than 4g/cm^3 or 5 times greater than water (Duruibe *et al.,* 2007).The contamination of heavy metals in the aquatic environment has garnered global attention due to their abundance, persistence, and environmental toxicity (Islam *et al.,* 2015). These metals can come from natural sources (mainly erosion and rock weathering) as well as human activities (e.g., industrial discharge, mining, agriculture, transportation, damage, sewage disposal, and waste run-off) (Cervik *et al*., 2009; Feng *et al*., 2011; Hernandez-Crespo and Martin 2015; Keshavarzi *et al*., 2015; Sun *et al*., 2015; 2015; Xi *et al*., 2016). Heavy metals enter aquatic ecosystems through normal processes like ore formation, rock weathering, and leaching, as well as human activities such as urbanization, industry, agriculture, resource exploration, and exploitation. Both natural and human -induced factors contribute to the presence of heavy

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metals in the environment (Khan *et al*., 2008; Mucha *et al*., 2003) suggests that sediments serve as the main repository for contaminants in water bodies. Sediments play a significant role in heavy metal pollution due to changes in pH, redox potential, diagenesis, or physical disturbances. Elevated levels of heavy metals in sediments are often associated with human activities rather than natural occurrences (Davies *et al*., 1991; Binning and Baird, 2001, Eja *et al.,* 2003).Sedimentary materials are essential components of aquatic environments and play a crucial role in maintaining the ecological balance of water bodies (Singh *et al.,* 1997). Heavy metals present in sediments can contribute greatly to river system pollution. Sediments acts as storage for physical debris and contaminants, making them valuable for pollutant detection and identification of critical pollution sites within a river system are repositories for physical debris and sinks for contaminants. Sediments not only influence pollution levels but also serve as historical records of pollution. They serve as both carriers and sources of contaminants in the aquatic environment (Shuhaiini, 2008). The contamination of sediments with heavy metals can lead to serious environmental issues (Loiziodu *et al.,* 1992) as they accumulate in the sediment through various means such as discharge and surface runoff (Makinde *et al.,* 2015). These metals can be absorbed into the sediments or accumulated by benthic organisms, with their availability and toxicity depending on the specific forms and amounts bound to the sediment matrix (Chukwujindu *et al*., 2007).Analyzing sediment for multiple elements can help identify the presence of heavy metals contaminants that may have adverse effects on groundwater, surface water, plants, animals, and humans (Sucui *et al*., 2008). Sediment analysis is crucial for assessing the overall ecosystem quality of water bodies in conjunction with water sample analysis, as it provides a long-term perspective on pollution levels that is independent of current inputs (Ademayo *et al*., 2008). Therefore, the aim of this study was to evaluate the physicochemical characteristics and concentrations of heavy metals in sediment and water samples from Creek Road Market Landing-Bay in the Bonny Estuary, Port Harcourt, Rivers State, Nigeria.

MATERIALS AND METHOD

*Study Area:*The study area investigated in the research was the Bonny Estuary, Port Harcourt (Figure 1). Between latitudes 4º 25" to 4º 45" N and longitudes 7º 00" to 7º 15" E is where the Estuary is located. The estuary is a mangrove swamp that is brackish and intertidal.

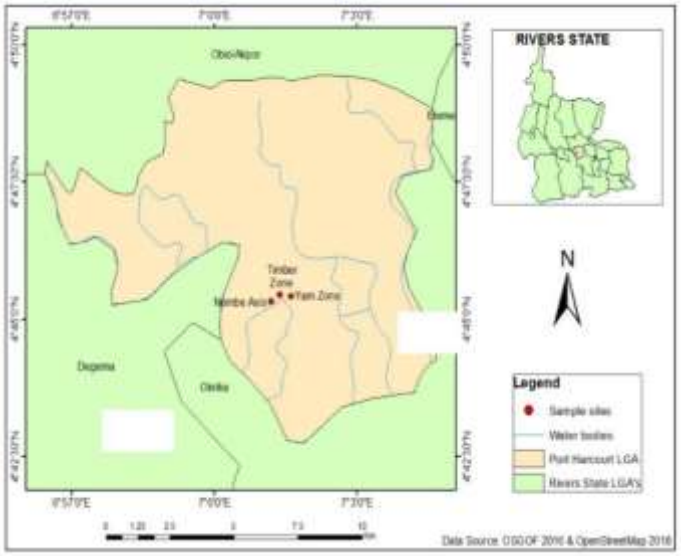

Fig 1: Map of the study area with sampling stations; sources: Open Street Map of 2018 and OSGOF, 2016.

The greenery of the estuary is dominated by mangrove species such as *Rhizophora racemose, Nypafructan, R. racemose, Avicennia Africana,* etc. Point sources of industrial effluent discharge, sand mining or dredging, fishing, navigation, washing, bathing, recreational, and illicit bunkering operations are examples of anthropogenic activity along the creek. A total of three sampling stations were strategically established around the creek at the Jetty, Timber, and Yam Zone areas of the estuary.

Experimental design: Along the creek's path, sample stations were set up. The biological environments and local human activity were taken into consideration

when selecting the sampling stations. Triplicate samples of water were gathered from each station. Chemical factors like pH and temperature, DO, TDS, as well as conductivity were measured on-site utilizing a multi-parameter water checker.

Triplicate sediment samples were collected from every station. To ensure that there were no remnants of heavy metal contamination, the sediment samples were gathered into plastic containers that had all been thoroughly cleaned with powerful nitric acid.

pH: Using an Ultra Metre 116pfcs-Plate 3.1 multi-parameter instrument, the pH was measured in-situ.

Temperature: An Ultra Metre 116pfcs-Plate 3.1 multi-parameter water checker was used to measure the temperature in-situ.

Conductivity: An Ultra Metre 116pfc-Plate 3.1 multi-parameter water checker was used to assess conductivity in-situ.

Salinity: The SPER BENCH-TOP WATER QUALITY METRE was used to measure it. After inserting the metre's probe into a beaker holding the test solution, the metre was turned on and given ten minutes to stabilise. A salinity reading was taken. In grams of salt, it is expressed

Total Dissolved Solids (TDS): An Ultra Metre 116pfc-Plate 3.1 multi-parameter water checker was used to test TDS in-situ.

Dissolved Oxygen (DO): The JPB607A dissolved oxygen analyzer was used to measure in-situ. After stabilizing the DO analyzer for ten minutes, the probe was submerged in the water holding the test solution to a depth of ten to fifteen centimeters. After turning on the analysis, the reading was stable enough to take the DO. The same procedure was carried out three times, and the results were noted. Plate 3.3)

Transparency (m): It uses a Secchi disk to measure the amount of light that reaches through the water body. The secchi disc was submerged in water, and the exact moment it was submerged was also noted. The values of appearance and disappearance were added and divided by two. The average was recorded.

Biochemical Oxygen Demand (BOD): A 250-ml dark Amber bottle was used to collect the sample, wrapped with an aluminum foil, kept in the BOD chamber, and then incubated at 20 OC for five days. The dissolved oxygen (DO) metre was used to examine the sample. 50 milliliters of the sample solution were contained in a beaker when the probe was put inside. After turning on the metre, the reading was taken as soon as it stabilized

Laboratory Examination of Water for Heavy Metals: After the sample's volume was measured, 50 ml was added to a 250 ml volumetric flask. The samples in the flask were filled with 3 ml of nitric acid before being placed inside the fume hood. Using a hot plate, the solution was heated for around 15 to 20 minutes to dissolve the metals. Afterward, it was taken off the hot plate and let to cool for five minutes. After adding distilled water to the 50 ml volumetric flask to make it full, the solution was filtered using Hartman (41) filter paper and placed inside a 100 ml plastic container for an atomic absorption spectrophotometer (AAS).

Heavy Metal Analysis for Sediment Samples: In 15 cm3 of a tri-acid combination (HNO3, HClO4, H2SO4, in a 5:1:1 ratio) at 80°C, about 2.0g of dry silt were digested until a translucent solution emerged. Following cooling, Hartman No. 41 filter paper was used to filter the digested sample, and the filtrate was ultimately kept at 50 cm3 of distilled water. After that, sample bottles containing the transparent solution were filled so that the Atomic Absorption Spectrometer could measure it (Mir *etal.*, 2016).

Statistical Analysis: Data collected from the physiochemical parameters and the heavy metals were evaluated using Analysis of Variance (ANOVA) and descriptive statistics to identify any differences in mean values between months and stations. The sample mean and standard deviation are computed as additional statistical metrics.

RESULTS AND DISCUSSION

Physiochemical Parameters of Creek Road Market Landing-Bay in the Bonny Estuary: The findings of the physiochemical parameters indicated that the mean temperature ranged from 30.43+ 0.49ºC at station 1 to 31.3+ 0.40ºC at station 3, with an overall mean value of 30.52+ 0.590ºC. There was no notable difference in temperature variation (4.1). The pH levels ranged from 6.6+ 0.44 at station 1 to 7+0.17 at station 2, with an overall average of 6.78+ 0.44. There was a significant difference in pH variation (4.1). The electrical conductivity levels varied from 1395+ 325.89 ms/cm at station 1 to 1845.33+ 764.42 ms/cm at station 2, with an overall average of 1593.67+ 474.60, showing a significant difference in conductivity variation. The total dissolved solids ranged from 693.33+ 57.76 ppm at station 1 to 805.67+ 187.99 ppm at station 2, with an overall average of 746.22+138.95, also indicating a significant difference. Salinity levels varied from 350.67+ 5.13 ppm at station 1 to 400+108.57 ppm at

station 2, with an overall average of 371.33+69.37, with a significant difference in salinity variation (4.1). Dissolved solids ranged from 3.30+0.50mg/l at station 3 to 3.90+0.15mg/l at station 2, with an overall average of 3.74+0.36, showing no significant difference in dissolved oxygen variation (4.1). Phosphate levels varied from 1.93+0.06mg/l at station 1 to 2.11+0.59mg/l at station 2, with an overall average of 2.05+0.25, showing a significant difference in phosphate variation (4.1). Hardness levels ranged from 13.17+0.35mg/l at station 2 to 13.47+0.60mg/l at station 1, with an overall average of 13.28+0.48, indicating a significant difference in hardness variation (4.1). The biological oxygen demand ranged from 0.50+0.00mg/l at station 3 to 0.55+0.21mg/l at station 2, with an overall average of 0.6+0.17, showing no significant difference in BOD variation (4.1).

Table 1: Range mean and standard deviation of the physiochemical parameters of the Creek Road Market Landing-Bay in the Bonny Estuary across stations and comparison with National and International Standard

Parameter	Station 1	Station 2	Station 3	ACMS	DPR	WHO
Temperature ºC	30.1-31.0	30.3-31.5	29.7-30.5	30.52	30	25-32
	30.43±0.49	31±0.62	31.3±0.40			
PH	6.3-7.1	6.8-7.1	6.0-7.3	6.78	6.0	6.5
	6.6±0.44	7±0.17	6.73±0.67			
Electrical	1097-1743	1024-2536	1367-1799	1593.67		2
Conductivity	1395±325.89	1845.33±764.42	1540.67±228.106			
TDS (ppm)	639-754	642-1011	612-933	746.22	2	0.25
	693.33±57.76	805.67±187.99	739.67±170.28			
Salinity (ppm)	345-355	322-524	301-445	371.33	-	-
	350.67±5.13	400±108.57	363.33±73.92			
DO (mg/L)	3.50-4.10	3.80-4.10	3.00-4.00	3.74	5	<4
	3.85±0.32	3.90±0.15	3.30±0.50			
Nitrate (mg/L)	28.6-30.1	22.6-26.5	23.0-28.8	26.98	-	1
	29.43±0.76	24.83±2.01	26.67±3.19			
Phosphate (mg/L)	1.80-2.10	1.75-25.9	2.00-2.20	2.05	5	-
	1.93±0.06	2.11+0.59	2.10±0.07			
Hardness (mg/L)	12.9-14.1	12.8-13.5	12.6-13.8	13.28	-	-
	13.47±0.60	13.17±0.35	13.2±0.60			
BOD (mg/L)	0.40-0.80	0.60-0.90	0.40-0.50	0.6	10	0.0-6.0
	0.55+0.21	0.75+0.21	0.50+0			

Note: DO-Dissolved Oxygen; BOD-Biological Oxygen Demand; TDS-Total Dissolved Solids; AMCS-Average Mean Concentration across the stations; WHO (2005)-World Health Organization; DPR-Department of Petroleum Resources (2002) limits for particles in surface water.

Variation of Heavy Metals in Water of Creek Road Market Landing-Bay in the Bonny Estuary: Examination of heavy metals in water from the Bonny Estuary revealed that the average concentrations of zinc ranged from 8.53±0.81 mg/l at station 2 to 8.97±0.86 mg/l at station 1, with an overall average of 8.74±0.67. There was a notable variation in zinc levels. The average concentration of lead varied from 1.37±0.15 mg/l at station 3 to 1.77±0.06 mg/l at station 2, with an average value of 1.53±0.23. There was a significant difference in lead concentrations. Cadmium and Mercury levels were below the detection limit of the equipment (0.001).

Table 2: Range, mean and standard deviation of heavy metals in water of the Creek Road Market Landing-Bay in the Bonny Estuary across stations in comparison with International Standard.

	Station 1	Station 2	Station 3	WHO Standard	AMCS
Zinc (mg/l)	8.20-9.20	7.80-9.40	8.20-9.20	0.001	8.74
	8.97±0.86	8.53±0.81	8.73±0.50		
Lead (mg/l)	1.20-1.60	1.70-1.80	1.20-1.50	0.01	1.53
	1.47±0.23	1.77±0.06	1.37±0.15		
Cadmium (mg/l)	<0.001	<0.001	<0.001	0.003	0
Mercury (mg/l)	<0.001	<0.001	<0.001		0

Note: AMCS-Average Mean Concentration across the stations; WHO (2008, 2011) - World Health Organization.

Variation of Heavy Metals in Sediment of Creek Road Market Landing-Bay in the Bonny Estuary: The study findings indicated that the average zinc concentration varied from 8.63±0.49mg/kg at station 3 to 9.03±0.44mg/kg at station 2, with an overall average of 8.91± 0.04. There was noticeable variability in the levels of zinc. In terms of lead, the mean values ranged from 4.93±0.21mg/kg at station 3 to 6.03±0.57mg/kg at station 2, with an overall mean of 5.6±0.76. The variation in lead concentrations was not found to be significant. Cadmium and Mercury levels were below the detection limit of the equipment (0.001).

Table 3: Range, mean and standard deviation of heavy metals in sediment of the Creek Road Market Landing-Bay in the Bonny Estuary across stations in comparison with International Standard

	Station 1	Station 2	Station 3	WHO Standard	AMCS
Zinc (mg/kg)	6.7-10.3	8.8-9.6	8.3±9.2	0.001	8.91
	8.8±1.87	9.03±0.44	8.63±0.49		
Lead (mg/kg)	4.8-6.8	5.4-6.5	4.8-5.2	0.01	5.6
	5.8±1.00	6.03±0.59	4.97±0.21		
Cadmium (mg/kg)	<0.001	<0.001	<0.001	0.003	0
Mercury (mg/kg)	<0.001	<0.001	<0.001		0

Note: AMCS-Average Mean Concentration across the stations; WHO (2008, 2011) - World Health Organization.

Physicochemical Parameters of Water: The examination of the physicochemical properties (including Temperature, pH, Electrical conductivity, Total dissolved solids, Salinity, Dissolved oxygen, Nitrate, Phosphate, Nitrate, hardness, and biological oxygen demand) of the water was conducted.

Temperature: The results revealed that the average temperature in the Bonny estuary varied, with a range of 30.43+0.49ºC to 31.3+0.40ºC in station 3, indicating fluctuations due to water discharge. The temperature levels remained within the acceptable range set by WHO (25-32) and DPR (30), it shows that Bonny Estuary is well within WHO and DPR (WHO 2005, DPR 2002). This aligns with previous studies in the estuary, this work agrees strongly with Sikoki and Veen (2004), where the water temperature obtained for the new Calabar-Bonny River during the study ranged between 26.2 and 30.10ºC with a mean of 28.22+0.16. Chindah (2003) reported a temperature range between 26 and 35ºC, while Hart and Zabbey (2005) reported a temperature range of between 25.8 and 30.4ºC.

pH: The Bonny Estuary displayed a neutral pH, with values ranging from 6.66+0.44 in station 1 to 7+0.17 in station 2, attributed to rainfall patterns during sampling. The pH levels were found to be suitable for aquatic life according to DPR 2002 (6.0) and WHO 2005 (6.5) standards, and in line with earlier research in the Niger Delta waters by Hart and Zabey (2005), Deekae, Abowewi and Chindah (2005) and Edogbolu and Aleleye-Wokoma (2007).

Total Dissolved Solids (TDS): The mean TDS values in the Bonny Estuary ranged from 639.33+57.76 ppm in station 1 to 805.67+18799 ppm in station 2, suggesting low water particle content possibly due to sediment accumulation. The TDS levels were higher than the recommended values from DPR 2002(2) and WHO 2005 (0.25).

Salinity: The salinity levels in the Bonny Estuary varied, ranging from 350.67+5.13 ppm in station 1 to 400+108.57 ppm in station 2, indicating neutral salinity levels impacted by seasonal rainfall.

Dissolved Oxygen (DO): The mean dissolved oxygen levels in the Bonny Estuary ranged from 3.30+0.50mg/l in station 3 to 3.90+0.15mg/l in station 2, suggesting lower oxygen content possibly due to limited atmospheric oxygen penetration. The levels were below the minimum requirements outlined by DPR 2002 (5) and WHO 2005 (<4) standards. This result is in line with work by Emmanuel and Onyema (2007), where the dissolved oxygen range was 3.4–4.5 mg/l.

Biological Oxygen Demand (BOD): The estuary exhibited varying BOD values, ranging from 0.50+0.0mg/l in station 3 to 0.75+0.21mg/l in station 2, indicating the presence of organisms consuming oxygen. In comparison to DPR 2002 (10) and WHO 2005 (0–6), BOD levels were below the DPR standard of 10mg/l, they fell within the WHO standard range of 0–6 mg/l.

Heavy metal concentrations in water: The study compared the bioaccumulation of heavy metals (Zinc, Lead, Cadmium, and Mercury) in water collected from three sampling stations in the Bonny Estuary using the standard set by the World Health Organization (WHO).The concentration of zinc in the water samples ranged from 8.53±0.81mg/l in station 2 to 8.97±0.86mg/l in station 1. These levels were found to be relatively high across all stations compared to the WHO 2005 (0.001), indicating a significant presence of zinc. Lead concentrations ranged from 1.37±0.15mg/l in station 3 to 1.77±0.06mg/l in station 2, which exceeded the WHO standard of 0.01 due to the disposal of lead-containing waste. Cadmium and Mercury levels were undetectable in the water samples. They were below the detection limit of the equipment (0.001).

Heavy metals in sediment: The study also examined the concentrations of zinc, lead, cadmium, and mercury in the sediments collected from the study area during July to September 2019. The sediment analysis revealed higher levels of heavy metals compared to the water samples, indicating potential environmental pollution. The presence of heavy metal ions in the sediment at the ppm level suggested industrial pollution (Gobo *et al*., 2008).The mean values of zinc

in the sediment ranged from 8.53±0.81mg/kg in station 2 to 8.97±0.86mg/kg in station 1, with significant differences noted($p>5$). In comparison with WHO standard 2005 (0.001), which shows that zinc was relatively high, indicating the presence of industrial pollution in these stations. Lead concentrations ranged from 1.37±0.15mg/kg in station 3 to 1.77±0.06mg/kg in station 2, exceeding the WHO (2005) standard of 0.01, indicating potential oil pollution in the estuary. Cadmium and Mercury levels in the sediment samples were below the detection limit of the equipment (0.001)

Conclusion: The study emphasizes the importance of monitoring the environmental health of the Bonny Estuary. The presence of heavy metals in both water and sediment samples indicates potential environmental pollution with adverse effects on aquatic life and human health. Continuous monitoring, remediation efforts, and public awareness are crucial for protecting the ecosystem and ensuring a healthier environment in the Bonny Estuary.

Abbreviations: AMCS: Average Mean Concentration across the stations; WHO: World Health Organization; DPR: Department of Petroleum Resources.

Declaration of Conflict of Interest: The authors declare no conflict of interest

Data Availability Statement: Data are available upon request from the first author or corresponding author.

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