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Physicochemical Properties of Sediment from Rumuolumeni Axis of New Calabar River, River State, Nigeria

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Abstract
The impact of anthropogenic activities on the aquatic ecosystem of Rumuolumeni axis of New Calabar River was studied for a period of 12 months spanning through wet and dry seasons. Sediment samples were collected and evaluated for physicochemical parameters and the community structures of the benthos following appropriate standard procedures. Physicochemical parameters for sediment were 5.30±0.19 (pH), 26848±1057.11 µS/cm (EC), 0.26±0.2 %(N), 1.20±0.66 mg/kg (NO_{3-}), 4396.06±2054.68 mg/kg (Cl^-), 0.49±0.2 mg/kg (PO_4^{3-}), 1100.78±335.66 mg/kg (SO_4^{2-}), 243.88±53.64 mg/kg (THC), 3.9±0.14 % (TOC), 6.77±0.24 % (TOM) and 118.12±21.53 ppm (TPH). Heavy metal concentration in sediment recorded 8.21±0.55 mg/kg (Zn), 6.73±0.32 mg/kg (Cu), 5.59±0.34 mg/kg (Pb), 9.17±2.3 mg/kg (Ni), 8.0±0.25 mg/kg (Cr) and 0.48±1.59 mg/kg (Cd). Almost all the values of the physicochemical properties and heavy metal sediments were above permissible limits. Based on this finding, we now have an update on the current status of this river which has shown clearly that it is polluted and requires an urgent attention to mitigate further deterioration.

Keywords: Pollution Studies, Heavy Metals, Physicochemical Parameters, New Calabar River, Sediment

Introduction

Anthropogenic activities are human activities associated chiefly with pollutants. There continues to be an increase in these anthropogenic activities with the daily improvements is technology. All these acts continue to put pressure on the ecosystem if there are no checks and plans to remedy their impacts as they confront the system daily. This arises from a range of human activities, including illegal crude oil refining, rapid urbanization and industrialization, efforts to balance the impacts of swift population growth, the unregulated use of substandard equipment that releases waste into the environment, improper application of pesticides and fertilizers in agriculture, infrastructure development such as roads, bridges, dams, and buildings, as well as petroleum exploration, extraction, refining, and the subsequent transportation, storage, marketing, and utilization of petroleum products. The end result of these anthropogenic activities is that the pollutants are washed off into nearby water bodies when it rains from where plants and animals use them for various activities. They can be poisonous to man and other living organisms who come in contact with them. Others leach into the soil and joining the ground water and moving along water pathways to the aquifer. Aquatic species then take up certain quantities of these contaminants alongside their normal essential nutrients and deposit them in their organs and tissues. A swift increase in population, combined with intensified human activities, has driven the growth of various types of industries. This, in turn, has resulted in a greater volume of pollutants being generated and discharged into the environment, placing significant stress on aquatic ecosystems. While this is on, humans end up going back to reap the consequences of their action by going back to the same system they have polluted. This leads to the manifestation of different health issues associated with water usage.

The physicochemical properties of sediment and water, such as temperature, pH, conductivity, salinity, turbidity, total organic carbon, total dissolved solids, total suspended solids, and total organic matter, play a crucial role in determining how pollutants are retained in the environment. These factors influence the adsorption, absorption, desorption, solubility, mobility, and toxicological behavior of the pollutants (Iyama & Edori, 2016). Edori et al.,

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(2019) studied the physicochemical characteristics of surface water and sediment in the Silver River, Southern Ijaw, revealed that parameters such as conductivity, total dissolved solids (TDS), salinity, total hydrocarbon content (THC), sulfate (SO_4^{2-}), dissolved oxygen (DO), biological oxygen demand (BOD), and chemical oxygen demand (COD), were below the recommended standards for domestic water use. However, total suspended solids (TSS), turbidity, pH, nitrate (NO_3^-), and phosphate (PO_4^{3-}) were found to be within the acceptable limits for drinking water as set by the WHO. They concluded that the Silver River, including both its water and sediment, is significantly impacted by human activities. If these influences are not addressed promptly, they could pose a serious environmental and public health risk in the near future.

Metals are substances characterized by high electrical conductivity, malleability, and a shiny appearance, with the tendency to readily lose electrons and form cations. They occur naturally in the Earth's crust, with their composition varying by location, leading to spatial differences in their surrounding concentrations (Khlifi & Hamza-Chaffai, 2010). To support essential biochemical and physiological functions in living organisms, these metals are required in trace amounts. However, when their concentrations surpass certain thresholds, they can become harmful. Due to their persistence and wide range of adverse health effects, exposure to heavy metals is on the rise globally. Recognized as major environmental pollutants, heavy metals pose growing concerns because of their toxicity, with implications that extend across evolutionary, nutritional, ecological, and environmental dimensions (Jaishankar et al., 2014; Nagajyoti et al., 2010). Heavy metals find their way into the surroundings by natural means and also by anthropogenic sources. Heavy metals are released into the environment through various sources, including industrial effluents, mining activities, natural weathering of the Earth's crust, soil erosion, urban runoff, pesticides and disease-control chemicals used on crops and in the environment, sewage discharge, among others (Morais et al., 2012). Copper, cadmium, mercury, nickel, arsenic, chromium, and lead are among the most commonly occurring heavy metals that pollute the environment (Hazrat et al., 2019).

The various water bodies get dosed with heavy metals through various sources primarily natural and anthropogenic sources. Volcanoes, forest fires and weathering are the major natural sources. Some important anthropogenic sources of heavy metals include effluents (both mining and industrial), urban storm-water run-off and domestic effluents, garbage and solid water dump sites, metals in pesticides, petroleum industry activities etc. Upon entry into the aquatic environment, then heavy metals cross into the various components of the aquatic environment: water, sediments and organisms present (Masindi & Muedi, 2018). A study by Adaobi et al. (2019) on heavy metals (Cd, Pb, Fe, Al, and V) in the water and sediment of the Soku oil field area in the Niger Delta revealed that all measured values exceeded permissible limits, except for aluminum in the water samples. They also observed that heavy metal concentrations were generally higher during the dry season and lower in the wet season, likely due to dilution from heavy rainfall. Additionally, their findings showed that heavy metals were more concentrated in the sediments than in the surface water, indicating long-term pollution, with sediments acting as sinks for these contaminants. Adesuyi et al. (2016) examined the physicochemical properties of sediment from Nwaja Creek in the Niger Delta and concluded that these characteristics are shaped primarily by human activities rather than natural sources. This was evident in the elevated levels of phosphate and nitrate, with the authors noting that the geology of the Niger Delta is not naturally rich in nitrate. Therefore, any excess presence of nitrate in surface or groundwater is considered a sign of pollution.

Daka et al., (2018) stated that the sediments have been contaminated with hydrocarbons and heavy metals when compared with the control used for this research. This was attributed to anthropogenic activities going on in Kolo Creek. Butu and Iguisi (2013) reported that the sediments of River Kubanni contained heavy metals—such as manganese (Mn), chromium (Cr), zinc (Zn), and iron (Fe)—at levels exceeding WHO safety standards. They identified the sources of these contaminants as human-related activities, including waste dumps, agricultural runoff, public drainage systems, and local effluent discharges. The study emphasized that this pollution poses serious health risks to communities living along the river who rely on it for drinking water, potentially leading to severe illnesses. Edward et al. (2013) investigated the concentrations of Zn, Mn, Cu, Fe, Pb, and Cd in the sediment, water, and various fish organs (including gills, flesh, kidneys, and liver) from the Odo-Ayo River in Ado-Ekiti, Ekiti State, Nigeria. Their findings revealed that heavy metal levels were lowest in the water, higher in the sediments, and highest in the fish samples. The heavy metals levels were however below WHO and FEPA acceptable limits hence the water was fit for consumption but the fish samples were unsafe for human consumption. Warmate et al. (2011) examined the concentrations of Cu, Ni, Pb, and Zn in soil and water exposed to used engine oil in Port Harcourt. Their study found that the levels of these heavy metals in both soil and water samples exceeded permissible limits.

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Aghoghovwia et al., (2015), in their study on heavy metal concentrations in the sediment of the Warri River, found that levels of Fe, Cu, Zn, Ni, Pb, Cd, and Cr had increased compared to baseline data from 1994. Similarly, Barakat et al., (2012) investigated the Day River, which receives untreated domestic and industrial wastewater from Beni-Mellal city and nearby villages, to assess the distribution of Cd, Cr, Cu, Pb, Zn, and Fe in the sediments. Their results showed significant spatial variation in metal concentrations, with correlation analysis indicating that sediment metal content was influenced by organic matter and iron levels. They concluded that both the pollution load index and sediment quality guidelines confirmed that metal concentrations exceeded local and regional background levels, suggesting the contamination poses a potential threat to human health and the ecosystem. Wokoma (2014) examined total hydrocarbon content (THC) in the sediments of a polluted tidal creek along the Bonny River in the Niger Delta, Nigeria. The study revealed that THC levels ranged from $1,403 \pm 80.61$ to $3,755 \pm 113.14$ mg/kg—significantly exceeding the permissible limit of 30 mg/kg for sediment. Similarly, Daka and Adaobi (2013) analyzed polycyclic aromatic hydrocarbons (PAHs) in both the sediments and tissues of the crab *Callinectes pallidus* from Azuabie Creek in the Upper Bonny Estuary. Their findings confirmed the presence of major PAH compounds, including naphthalene, benzo(a)pyrene, benzo(a)anthracene, and phenanthrene. These were carcinogens and were usually higher during the rainy season due to anthropogenic activities from a nearby abattoir leading to more contaminated runoffs into the river especially the sampling station close to the abattoir.

Materials and Methods

Study Area

The study area is a section of the New Calabar River located in Rumuolumeni in the city of Port Harcourt, in the coastal area of Niger Delta, precisely Rivers State and empties into the Atlantic Ocean as seen in Figure 1. This River is one of the important water resources that the Niger Delta can boast of in the southern part of Nigeria. It is located between latitude 4º25’ N and longitude 7º1’60” E with the Delta itself having a bearing of 5º45’ N and 6º35’ N in latitude and 4º50’ E and 5º15’ E in longitude. The New Calabar River region has an annual rainfall ranging between 2000 – 3000 mm with dry season months lasting from December to May with occasional rainfall and raining season months from June to November. The water is black in color and tidal, being fresh water at its upper and middle reaches but brackish towards the mouth (Akankali & Davies, 2018). A total of six different stations were established along the Rumuolumeni Axis of the river for the purpose of this research. They were selected based on anthropogenic activities like sand dredging, illegal bunkering, washing and cleaning of petroleum vessels after discharge of products into approved storage tanks, discharge of waste from industries around among other action that impact on the rivers. The geographic coordinates of the sampling stations were determined in-situ with hand- held GPS equipment – Garmin Extrex. The GPS was switched on at each station and allowed to stabilize for about 2 – 3 minutes, after which the coordinates were read – off and recorded.

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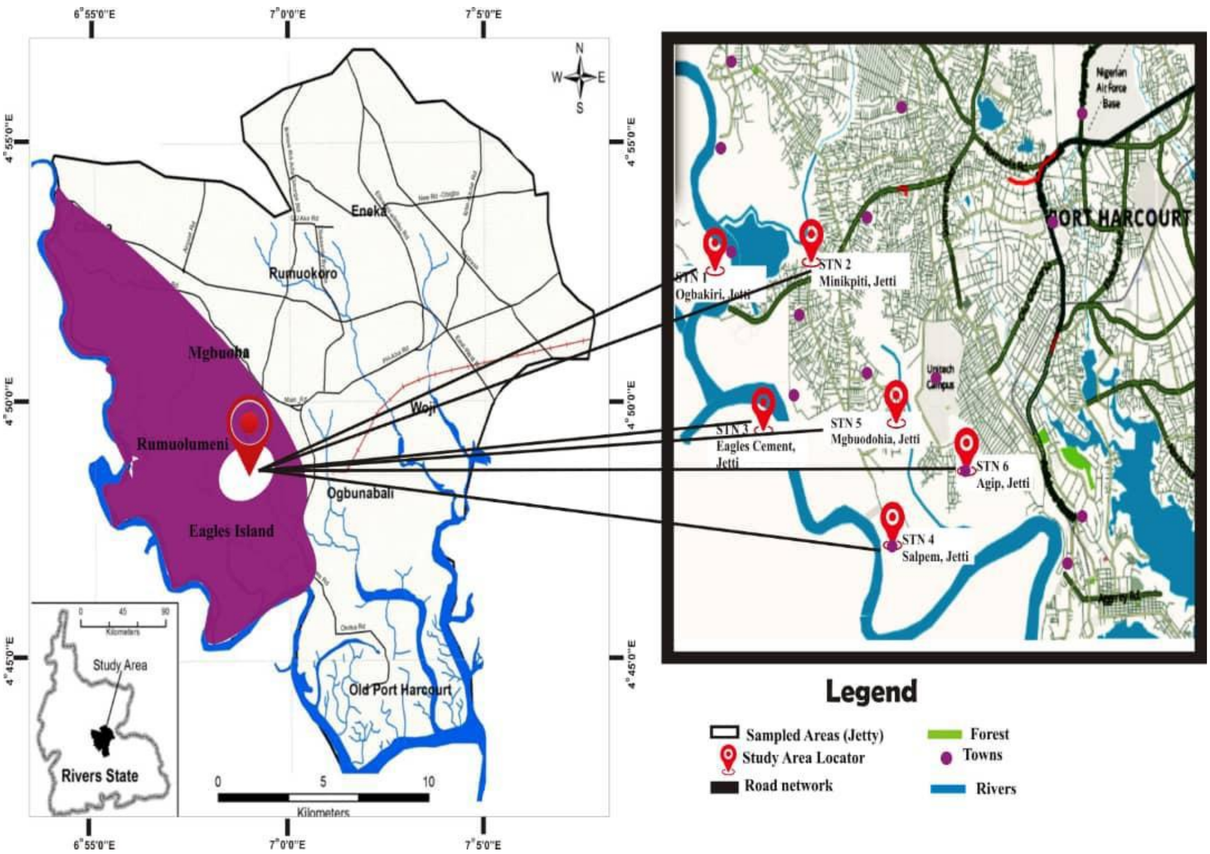

Figure 1: Map of Rumuolumeni Axis of New Calabar River Showing Sampling Stations

Sampling and Sampling Techniques

Before the main sampling began, a reconnaissance survey was conducted along the designated stretch of the New Calabar River. During this preliminary assessment, six sampling stations were established to encompass all observed activities along both sides of the river's shoreline (Figure 1). Initial samples were taken during this visit to familiarize the team with field procedures, identify the sampling locations, and ensure proper use of equipment—thereby minimizing potential sampling and handling errors. Sediment samples were collected for physicochemical analysis following standard procedures outlined by APHA (2005). Sampling was conducted over a 12-month period to account for seasonal variations. At each station, two replicate seabed sediment samples were collected using an Eckman Grab for physicochemical analysis. Samples intended for hydrocarbon and organic content analysis were wrapped in aluminum foil, while those for heavy metal, particle size analysis, and other parameters were placed in black polyethylene bags and transported to the laboratory. A composite sample was collected from each station specifically for particle size analysis.

Physicochemical analysis of Surface Water Samples

Sediment particle size was determined by the Hydrometer method, electrical conductivity was determined using the Lovibond conductivity/TDS meter (Type Cm- 21), salinity was measured by using the HACH salinity measuring device, Nitrate ions in sediment samples were determined by the cadmium reduction method, Phosphate was determined by the PhosVer 3 method, Total hydrocarbon content (THC) is measured spectrophotometrically at 420nm with spectrophotometer 41D, Total Organic carbon (TOC) was analyzed using a LECO CR-412 Carbon Analyzer and Total organic Matter (TOM) was determined using sequential Weight Loss On Ignition (WLOI) method. Others include Total Petroleum Hydrocarbon (TPH) which was analyzed using Soxhlet extraction and analysis process while heavy metal analysis was done using atomic absorption spectrophotometer (AAS) UNICAM 919 model.

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Statistical Analysis
This was done using MS Excel, analysis of variance (ANOVA) was performed to compare the means and the statistical significance was considered at $p<0.05$.

Results and Discussions
Physicochemical Parameters
The results are as reported in Tables 1 and 2 below. The mean pH of the sub tidal sediment of the Rumuolumeni axis of New Calabar River fluctuated between 4.75±0.0 – 5.69±0.01. Adesuyi et al., (2016) documented a range of 3.90 – 8.50, Wokoma and Friday (2017) got 6.61±0.175 – 7.16±0.03 and Vincent-Akpu (2015) found 5.70 – 8.00. These ranges are higher than that got from this study indicating that this sediment is acidic compared to those with the results above. However, Ezekiel et al., (2011) who reported 5.06 – 5.85 in the Sombreiro River. This range are close to that got in this study. A two-way ANOVA showed that the seasons and stations were significantly different at $p<0.05$ and supported by Adesuyi et al., (2016). Seiyaboh et al., (2016) also found that the seasons differed significantly. The wet season had more mean values than that of the dry season but remained acidic all through the period of study, a position affirmed by Seiyaboh et al., (2016). The variation observed in the pH among the seasons goes to suggest the effect the weather has in water pH. During the dry season, water volume is observed to decrease, whereas in the wet season, it increases due to rainfall and flooding along the coastal waterways.

Conductivity for the sediment under the study ranged from 25106±799.03 – 28268.5±202.94 µS/cm. This value is far higher than the approved WHO limit of 1500.0 µS/cm. Other studies showed lower ranges as seen in the work by Adesuya et al., (2016) who measured 23.0 – 567.0 µS/cm, Wokoma and Friday (2017) who had a range of 4798.0±408 – 10836.0±158 µS/cm, Edori et al., (2019) who reported 16100.0 – 17355.0 µS/cm and Ebong and John (2021) who measured 554.74 – 573.62 µS/cm. The seasons and station for this study did not vary significantly at $p<0.05$. Adesuya et al., (2016) and Seiyaboh et al., (2016) reported on the contrary that the stations varied significantly. Higher values were recorded during the dry season compared to the wet season, likely due to the dilution effect caused by rainfall during the latter. This observation aligns with the findings of Seiyaboh et al., (2016). Conductivity refers to the ability of a material—whether liquid or solid—to conduct electricity. It is influenced by the presence of dissolved solids and charged ions, such as calcium, magnesium, sodium, potassium, and chloride, in water or sediment samples (Nazir et al., 2015). The conductivity of a substance depends on the concentration of ions present and can be used to estimate the overall ionic or mineral content of a sample, although it does not identify specific ions. The elevated conductivity values observed in this study may be attributed to the intrusion of seawater into the river during high tides.

In this investigation, the concentration of nitrate fluctuated from 0.12±0.01 – 3.44±0.30 mg/kg, which is lower than 40.00 mg/kg WHO permissible limit. Seiyaboh et al., (2016) reported a range of 2.23 – 3.30 mg/kg, which falls within that found in this study. This is contrary to the higher ranges of 1.34±0.04 – 4.00±0.135 mg/kg reported by Wokoma and Friday (2017), 0.45 - 11.9 mg/kg found by Adesuya et al., (2016), 0.495 – 5.210 mg/kg by Edori et al., (2019) and 57.54 – 68.28 mg/kg reported by Ebong and John (2021). A two-way ANOVA at $p<0.05$ showed that the seasons were significantly different while the stations weren't. Adesuya et al., (2016) and Seiyaboh et al., (2016). found significant differences across the stations as against the findings of this study while Obunwo et al., (2004) did not indicate any significant seasonal variation. Values recorded during the dry season were higher than those observed in the wet season as also found by Seiyaboh et al., (2016).

The mean concentration of phosphate was investigated and found to range around 0.04±0.01 – 0.92±0.04 mg/kg. This value is lower that WHO limit of 5.0mg/kg. Seiyaboh et al., (2016) got 0.14 – 0.34 mg/kg while Edori et al., (2019) found a range of 0.247 - 0.268 mg/kg, both of which fall within that of this study. However, these values are lower compared to those of Adesuya et al., (2016) who measured 5.5 - 15.5 mg/kg, Wokoma and Friday (2017) who reported 0.39±0.01 – 2.97±0.03 mg/kg, and Ebong and John (2021) who found 2.71 – 3.54 mg/kg. More mean values were recorded during the dry season as the seasons and stations did not show any significant variation during the period under study. Seiyaboh et al., (2016) noted on the contrary that there was significant difference across the stations but confirmed that the mean values recorded during the dry season were higher than those in the wet season. Phosphate present in the water samples may have originated from several sources, including the breakdown of organic matter, surface runoff from agricultural lands treated with phosphate-based fertilizers, and animal waste from pig and poultry farms, among others. An increase in phosphate concentration in aquatic environments—whether in water or sediment—can trigger algal blooms (excessive algae growth), which often result in eutrophication, particularly in lakes and stagnant water bodies (Edori & Kpee, 2016). Over time, this process can cause the river to become shallower, thereby leading to the withdrawal of most specie that dwells in

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the bottom and require certain level of depth for their habitation in the aquatic environment. However, the value of this study is within safe limits and may not cause eutrophication.

The obtained value for sulphate during the period of this study ranged from 223.5±4.95 – 1897.5±10.61. This value significantly exceeds the WHO recommended limit of 240 mg/kg, indicating a high level of pollution in the sediment. Seiyaboh et al., (2016) found a lower variation of 0.28 – 1.31 mg/kg, Edori et al., (2019) reported 0.247 – 25.90 mg/kg while Ebong and John (2021) gave 83.72 – 89.56 mg/kg all of which fall within the above permissible limit. The seasons and stations varied significantly at $p<0.05$. Seiyaboh et al., (2016) affirmed a significant difference in the stations but found no significant difference for the seasons. The wet season recorded higher mean values compared to the dry season, which contrasts with the findings of Seiyaboh et al. (2016), who reported higher values during the dry season.

The total hydrocarbon content (THC) obtained in the sediment of the Rumuoluemni axis of New Calabar River during the period under investigation fluctuated from 138.88±0.04 - 785.06±7 mg/kg. The value observed was significantly higher than the WHO's recommended limit of 30 mg/kg for sediments and soil. Similar findings were reported by Howard et al., (2012), who recorded a range of 400.6 - 6205.5 mg/kg from the upper reaches of the Sombreiro River. Etesin et al. (2013) found levels between 274.5-403.7 mg/kg in the Iko River, while Doherty and Otitoloju (2016) reported a maximum concentration of 450.53 mg/kg in the Lagos Lagoon. In contrast, Seiyaboh et al. (2016) documented much lower values, ranging from 2.31-6.81 mg/kg in Ikoli Creek while Ebong and John (2021) reported 32.04 – 61.85 mg/kg from some major rivers estuaries within Niger Delta Region. Station 5 had a relatively higher value compared to other sampling stations this may be unconnected to the fact that it became the major logistic base for the transportation of illegally refined petroleum products due the clamp down on illegal bunkering activities that took place during the period when other sites suddenly had less activities. The location is inside a community and there were challenges for security agencies to the reach this area easily. Owing to the high values obtained round the stations all through the period of research, one can say that the entire stretch of the sub tidal sediment of the area is polluted with petroleum. Howard et al. (2012) reported that the petroleum industry, including both legal and illegal refineries, is responsible for producing the majority of the 5,500 tons of hazardous waste generated annually in Rivers State, a fact which corroborated the finding of the study. These observed pollutions could be linked to the observed leaf loss or complete defoliation of the mangrove vegetation seedlings in some impacted areas not forgetting the near absence of mudskipper and crabs on mud flats during low tide in the study area as against what it used to be prior to this time. This will also be posing a great danger to benthic fauna and by extension top predators such as fishes and other consumers of marine resources. There was a significant difference in THC values between the dry and wet seasons, with higher concentrations generally recorded during the dry season. This observation is supported by findings from Etesin et al., (2013) and Doherty and Otitoloju (2016). Both seasonal and station-based variations were statistically significant, with $p < 0.05$. On a general note, this study found that concentration of THC in this study was higher in the sediment samples compared to those of This can be attributed to the volatile nature of hydrocarbons, which causes them to evaporate from the surface water, while the remaining fraction gradually settles at the riverbed, leading to an accumulation and increased concentration in the sediment over time. The concentration of THC which is quite higher than approved limits may be from various anthropogenic sources like oil spills, oil slicks and seepages.

The obtained value for %TOC during the period of this study ranged from 2.34±0.04 – 4.88±0.04%. This can be compared to the 2.020 – 4.134% found by Ezekiel et al., (2011) in Sombreiro River. This value shows that there is high organic carbon content in the sediment. Adesuya et al., (2016) measured a range of 1.99±0.50 – 3.65±1.79%, Wokoma and Friday (2017) reported a range of 0.87±0.15 – 2.69±0.1% in their study and Edori et al., (2019) gave 2.32 – 2.44% range. All these ranges did not go above the range got in this work but all exceed 1%. However, studies by Umesi et al., (2013) on the contrary, showed higher values such as 2.67±2.08 – 16.00±5.00%. The seasons had an insignificant variation whereas the stations varied significantly at $p<0.05$. Adesuya et al., (2016) observed a significant difference between stations in line with this work. These values may vary because of the level of bacteria decomposition of organic matters in the sediment. The types of anthropogenic perturbations can also affect the value of the TOC. This study did not reveal a trend seasonally as the difference in mean value between wet and dry season were not significant.

%TOM for this study was got and ranged from 4.2±0.06 – 8.33±0.06%. Contrary reports were got by Edori et al., (2019) with a range of 4.00 – 4.21%, Edori and Marcus (2019) that measured 2.01± 0.06 – 4.13±1.38% and Onajite and Ovie (2022) that got 2.78±0.44 – 4.38±0.87. These ranges were lower than those observed in the present study. There were significant differences across seasons and stations, with the dry season showing slightly higher mean values. Edori and Marcus (2019) reported higher values during the dry season, consistent with the findings of this study, while Onajite and Ovie (2022) confirmed a significant variation across different stations. The amount of organic matter present in sediment is closely related to the proportion of silt and clay it contains.

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Finer particles provide a greater surface area for organic matter to adhere to, compared to coarser particles that offer fewer adsorption sites for the binding of colloids and organic materials. Once deposited, these complexes help attract, bind, and retain organic matter within the sediment.

Table 1: Mean Concentration (±SD) of Physicochemical Parameter of Sediment from Rumuolumeni Axis of New Calabar River

S/No	Parameter	Range of Concentration (Unit)
1	pH	4.75±0.0 – 5.69±0.01
2	Conductivity	25106±799.03 – 28268.5±202.94 µS/cm
3	Nitrate	0.12±0.01 – 3.44±0.30 mg/kg
4	Phosphate	0.04±0.01 – 0.92±0.04 mg/kg
5	Sulphate	223.5±4.95 – 1897.5±10.61 mg/kg
6	Total Hydrocarbon Content (THC)	138.88±0.04 - 785.06±7 mg/kg
7	% Total Organic Carbon (TOC)	2.34±0.04 – 4.88±0.04 %
8	% Total Organic Matter (TOM)	4.2±0.06 – 8.33±0.06 %

The results for select heavy metal is as seen in figure 2 below. The mean zinc concentration in the subtidal sediment of the study area ranged from 4.08 ± 0.04 to 11.89 ± 0.17 mg/kg, which is below the WHO's permissible limit of 123 mg/kg for unpolluted sediment. These findings are comparable to those of Wokoma and Friday (2017), who reported values between 2.70 ± 0.007 and 10.42 ± 0.01 mg/kg. In contrast, higher concentrations were reported by Vincent-Akpu (2015), with values ranging from 1.4 to 18.0 mg/kg, Ebong and John (2021), who found levels between 23.46 and 67.36 mg/kg, and Sani et al. (2022), who recorded a range of 13.94 ± 3.88 to 39.91 ± 10.27 mg/kg. While seasonal differences were not statistically significant, there was a significant variation across stations ($p < 0.05$). This aligns with the findings of Onajite and Ovie (2022) and Sani et al. (2022), who also reported significant station-based differences. However, Edokpayi et al. (2017) found no significant seasonal variation. Although no clear seasonal trend was observed in the present study, Sani et al. (2022) reported higher values during the dry season compared to the wet season. Based on WHO recommendation, Zn may not pose any threat yet to lives exposed to this environment but continue to safely play its role as a macro element.

Copper mean values for this research ranged from 3.79±2.22 – 9.61±0.34 mg/kg. This range is below 25mg/kg permissible limit approved by WHO for unpolluted sediment. Ebong and John (2021) measured 6.75 to 8.06 mg/kg which can be compared to the range found in this study. A higher range of 8.8 – 12.0 mg/kg was reported by Vincent-Akpu et al., (2015) while Wokoma and Friday (2017) reported a lower value of 0.15 to 0.30 mg/kg. In this study, the seasons did not differ significantly but it was found that the stations did at $p<0.05$. Akankali and Davies (2021) stated that Cu differed significantly across the seasons but was silent about stations. No trend was spotted during the course of this research but Edokpayi et al., (2017) stated that the wet season had more values.

Cadmium mean concentration for the period under study ranged from 0±0 – 0.43±0.37 mg/kg. This figure is lower than the limit of 3.0 mg/kg recommended by WHO for unpolluted sediment. Wokoma and Friday (2017) recorded a lower range of 0.001±0 – 0.095±0.001 mg/kg, whereas higher ranges of 0.70 to 2.11 mg/kg were recorded by Ebong and John (2021), 2.603±1.10 – 4.09±2.40 mg/kg recorded by Sani et al., (2022), 0.33±0.42 – 0.67±0.87 mg\kg found by Onajite and Ovie (2022). Based on the values found, the sediment isn't polluted with Cd at the moment and so will be of no effect on it. This study showed higher mean concentrations of Cd in the wet season compared to the dry season, consistent with the findings of Chinda et al. (2009). At $p<0.05$, the seasons were significantly different while the stations did not show any significant difference. Sani et al., (2022) and Onajite and Ovie (2022) concurred to a insignificant difference across the station but was silent on seasons. Edokpayi et al., (2017) however found a significant difference at $p<0.01$.

Lead was investigated in this study and was found to range between 3.61±0.33 – 7.21±0.16 mg/kg. Ebong and John (2021) also reported a range of 2.34 – 6.33 mg/kg which falls within the range of this work but is however lower than the 10.00 mg/kg limit approved by WHO for unpolluted sediment. This range may not yet pose a threat but needs to be closely monitored considering the dangerous effect of lead when assessed by humans. Lower range values of 0.025±0.000 – 1.424±0.002 mg/kg contrary to the findings of this report was recorded by Wokoma and Friday (2017), 0.09 – 2.30 mg/kg mentioned by Vincent-Akpu et al., (2015), 0.42±0.60 – 1.44±0.69 recorded by Onajite and Ovie (2022) while higher values of 43.64±4.80 – 53.61±15.8 mg/kg was reported Sani et al., (2022). The dry season recorded higher values than the wet season in this study, aligning with the findings of Edokpayi et al. (2017). Seasons and stations varied significantly during the period of this study at $p<0.05$. Edokpayi et al., (2017) reported not finding any significant variations between the seasons while Sani et al., (2022) recorded that there was no significant difference across stations but was silent on seasons.

The mean concentration of nickel observed in this study ranged from 0.06 ± 0.01 to 9.17 ± 0.28 mg/kg, which is below the WHO's recommended limit of 20 mg/kg for unpolluted sediments. Comparable values have been reported by other researchers: Vincent-Akpu et al., (2015) recorded 0.4–2.3 mg/kg, Wokoma and Friday, (2017) found 0.067 ± 0.001-3.957 ± 0.002 mg/kg, Ebong and John, (2021) reported 7.63–9.21 mg/kg, and Onajite and Ovie, (2022) noted a range of 0.99 ± 0.50-2.32 ± 0.61 mg/kg. All these fall within the range identified in the present study.

This research found higher mean concentrations of nickel in the wet season compared to the dry season, which contrasts with the findings of Nwadinigwe et al., (2014), who reported higher levels in the dry season. Significant variations were observed across both seasons and stations. Onajite and Ovie, (2022) also reported significant station-based differences, while Maurya et al., (2018) observed no significant seasonal variation.

Concentration of chromium was investigated and ranged between 5.19±0.03 – 10.56±0.47 mg/kg. A range of 0.307±0.003 – 7.353±0.008 reported by Wokoma and Friday (2017) can be likened to that reported in this study. Higher range of 1.9 – 13.6 mg/kg and mean value of 48.74±13.22 were recorded by Vincent-Akpu et al., (2015) and Maurya et al., (2018) respectively whereas a lower range of 1.36±0.68 – 2.90±0.91 mg/kg was found by Onajite and Ovie (2022). The dry season had more mean concentration compared to the wet season in this report but the contrary was found by Edokpayi et al., (2017) which reported higher values in the wet season than in the dry season. The seasons and stations significantly varied at $p<0.05$. While Maurya et al., (2018) conformed to the findings of this report, Edokpayi et al., (2017) found that the seasonal variations were not significantly different.

Table 2: Mean Concentration (±SD) of Select Heavy Metals of Sediment from Rumuolumeni Axis of New Calabar River

S/No	Parameter	Range of Concentration (Unit)
1	Zinc	4.08±0.04 – 11.89±0.17 mg/kg
2	Copper	3.79±2.22 – 9.61±0.34 mg/kg
3	Cadmium	0±0 – 0.43±0.37 mg/kg
4	Lead	3.61±0.33 – 7.21±0.16 mg/kg
5	Nickel	0.06±0.01 – 9.17±0.28 mg/kg
6	Chromium	5.19±0.03 – 10.56±0.47 mg/kg

Conclusion

It was observed that the sediment in the Rumuolumeni section of the New Calabar River is polluted as conductivity, THC and sulphate were higher than WHO permissible limits for an unpolluted sediment. The high concentration of THC could be responsible for the fast deterioration of mangroves and other marine plants in some parts of the river. It however had some concentrations of organic carbon and matter.

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