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Seasonal Assessment of Heavy Metals Concentrations in Sediment of the Sapele River, Nigeria

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Abstract

The concentrations of heavy metals in the environment of Sapele Local Government Area, Delta State, Nigeria, were examined. This study employed an experimental design methodology. A total of fifteen composite sediment samples were gathered in December 2024 and June 2025. The sediment was collected using a corer and clean plastic bottles. The samples were air-dried, mechanically ground with a mortar and pestle, and sieved through a 2 mm mesh for subsequent analysis. A weight of 1.0 g of each sediment sample was placed into Kjeldahl flasks. Aqua regia (15 cm^3) was introduced, mixed thoroughly, and allowed to sit overnight. The flasks were then heated on a hot plate at 50 °C for 30 minutes, after which the temperature was increased to 120 °C and maintained for 2 hours.

Following cooling, 0.2 M HNO_3 (10 cm^3) was added to the mixture. The resultant solution was filtered using Whatman no. 541 filter paper. The filtrate was then transferred to a 50 cm^3 standard flask and diluted to the mark with 0.2 M HNO_3. The concentrations of heavy metals were analyzed using the AAS Unicam 939 model. The heavy metal concentrations (mg kg-1) recorded during the dry season were as follows: sediment: Fe (22.18 ± 14.82), Mn (9.67 ± 2.75), V (3.39 ± 3.30), Ni (2.18 ± 0.78), Cd (0.48 ± 0.75), while during the wet season, the values were: Fe (23.28 ± 0.24), Mn (9.45 ± 2.63), V (3.31 ± 3.34), Ni (1.94 ± 1.48), Cd (0.48 ± 0.74). The total average concentrations of heavy metals for both dry and wet seasons were: V (3.319), Ni (2.061), Cd (0.477), Pb (0.039), Mn (9.557), Co (0.117), Zn (0.042), Fe (22.833). The concentrations of heavy metals varied between the wet and dry seasons. The average concentrations of Ni, V, Cd, Pb, and Mn exceeded WHO standards in both seasons. Conversely, the average concentrations of Co in the sediment fell within the WHO recommended limits for both dry and wet seasons. Notably, Fe concentrations were the highest across all seasons.

Keywords: Seasonal Variation, Niger Delta, Environmental Pollution, Heavy Metals, Sediment, Public Health.

Introduction

Heavy metals are naturally found in small amounts in soil, although they rarely reach toxic levels (Obruche et al., 2018). However, human activities have significantly elevated these levels at numerous contaminated land and water sites (Ozpinar & Polart 2020). Soil plays a vital role in both rural and urban settings, where effective land management is essential for maintaining soil quality. Human activities, including technology, industrialization, agriculture, transportation, education, construction, trade, and nutrition, have transformed the entire environmental system into what can be described as a 'throwing society.' This characterization arises from the indiscriminate disposal of wastewater, which, combined with a growing global population and urbanization, has exacerbated the issue (Itodo et al., 2021). The application of synthetic products, such as pesticides, paints, batteries, industrial waste, and the land application of both industrial and domestic sludge, can lead to the contamination of urban and agricultural soils with heavy metals. Water pollution occurs when chemical, physical, or biological substances exceed the capacity of a water body to assimilate or decompose these substances, potentially harming the aquatic ecosystem. Precipitation that reaches the Earth's surface follows two primary pathways: it either flows over the surface or infiltrates the soil (Ogwuche & Obruche, 2020). Water that flows over the ground is commonly referred to as runoff. Surface water encompasses water that flows in streams and rivers, as well as water stored in natural or artificial lakes. It includes any water that flows or rests on land and is exposed to the atmosphere; this includes

lakes, ponds, lagoons, rivers, streams, oceans, ditches, and man-made impoundments (Miao et al., 2015). An analysis of soil samples from Uyo town conducted by Akaeze revealed the presence of heavy metals such as lead, copper, and iron in the soil, which may contaminate soil water, a primary source of drinking water. Oil spills and the dumping of petroleum effluents on land are prevalent occurrences (Obruche et al., 2019). Gas flaring significantly contributes to the contamination of soil with heavy metals. The distribution of heavy metals in aquatic ecosystems, particularly those affected by human activities, has emerged as a critical environmental issue (Hassabo et al., 2022).

In the Sapele River, elevated levels of trace metals, especially in sediments, serve as a reliable indicator of pollution caused by human actions. The presence of high concentrations of heavy metals is frequently linked to anthropogenic factors rather than the natural enrichment of sediments through geological weathering. In the Sapele river, sediments accumulate contaminants over time and are in a continuous exchange with the overlying water column. Analyzing heavy metals in sediments allows for the identification of pollutants that may be absent or present in low concentrations in coastal waters (Gao, 2016).

While heavy metal concentrations in the Sapele water column can be relatively low, sediment concentrations may be significantly higher. It is estimated that approximately 90% of particulate matter transported by rivers settles in estuaries and coastal regions. The accumulation of metals from the overlying water into the sediment is influenced by factors such as pH, ionic strength, anthropogenic contributions, the type and concentration of organic and inorganic ligands, and the available surface area for adsorption, which is affected by variations in grain size distribution (Ogawara, 2020). The impact of heavy metal contaminants in sediments can be either acute or chronic (cumulative) on benthic organisms. The sediment in the study area, Qua Iboe Estuary, similar to other estuaries in the Niger Delta region of Nigeria, experiences significant salinity fluctuations between wet and dry seasons, which are further influenced by petroleum exploration activities and the use of iethyocides by local fish farmers. The estuarine ecosystem in the Niger Delta region has also faced a third-tier oil spill that occurred on November 22, 2003, due to a leak from an oil company facility in the area (Wang & Hu, 2014). Metals can persist in the environment and accumulate in the food chain, leading to elevated levels in the liver and muscle tissues of fish. Consequently, the quality of water and sediment within an aquatic ecosystem can influence both the quantitative and qualitative distribution of its fauna and flora.

Assessing the relative concentrations of pollutants, including heavy metals and both organic and inorganic substances, in the Sapele River is crucial for evaluating the eco-toxicological implications of specific contaminant loads (Ostadhossein et al., 2015). In aquatic environments, sediments and biota typically serve as reservoirs for metals. Research has demonstrated that nearly all metal content in aquatic ecosystems is found within water sediments. Sediments act as the primary storage sites for metals, sometimes containing over 99% of the total metal present in the system. Heavy metals may exist in concentrations significantly exceeding their natural background levels, thereby contaminating marine

sediments in coastal areas adjacent to industrial and urban developments. The significance of sediments as indicators of metal pollution in aquatic environments has been underscored (Obruche et al., 2022). The levels of harmful and toxic substances tend to be greater in sediments and biological tissues compared to water. One sensitive method for identifying areas contaminated with heavy metals involves analyzing the concentration ratios of cadmium, copper, and zinc in oysters. It was observed that the concentrations of heavy metals in oysters are inversely related to salinity. The progress in utilizing sediments and biological indicators for pollution monitoring is attributed to the fact that concentrations measured in water bodies do not always accurately represent the extent of pollution. Information regarding accumulation in biota is heavily influenced by the chemical properties of the metals, their propensity to bind to specific materials, and the lipid content and composition of the biological tissues (Li et al., 2016). The assessment of harmful and toxic substances in water sediments and biota provides direct insights into the pollution levels present in aquatic environments. The findings regarding the accumulation of heavy metals in aquatic ecosystems indicate that these metals are present either within aquatic organisms or within sediments (Abu et al., 2020). Sediments act as a repository for the majority of metals found in the aqueous phase. The monitoring of sediments, alongside the assessment of heavy metal concentrations, is crucial for identifying toxic pollutants within river sediments (Bullon et al.,2022). According to Ho et al., the linear correlation coefficients for Ni, Cr, Cu, Pb, and Zn exceeded 0.81 in the sediments of the Yenshi River during the dry season. Furthermore, the linear correlation coefficients for Fe and Mn, along with trace metals (Ni, Cr, Co, Pb, and Zn), were greater than 0.60, suggesting that Fe, Mn, and the fractions of trace heavy metals originate from a common pollution source in the Yenshi River. Notably, the concentration of metals diminished with increasing sediment depth in rivers heavily polluted with heavy metals. This research was conducted to assess the seasonal concentrations of heavy metals in the sediments of the Sapele River, located in Delta State, Nigeria.

MATERIALS AND METHOD

Description of Study Area

The area under investigation is situated in the Sapele region of Delta State, Nigeria Ou, S. F., (Zheng et al., 2021). This region is positioned between longitudes 3°E-9°E and latitudes 4°30'N-5°21'N, within the southern oil-rich Niger Delta. Delta State is characterized by frequent annual rainfall, which ranges from 3000 to 4500 mm. The combination of high rainfall, humidity, and river discharge during the rainy season, along with the low, flat terrain and poorly drained soils, leads to significant flooding (Obruche et al., 2019). The climate of the study area is typical, comprising a rainy season from May to November and a dry season from December to March. The average monthly temperature during these two seasons varies between 26.10 °C and 28.2 °C, with relatively lower temperatures, below 26 °C, occurring in January and July. Local winds observed in coastal regions during the dry season include the subdued continental air mass known as Harmattan, characterized by an average wind speed

ranging from 0 to 4 m/sec. Sapele, recognized as a significant socio-economic city in Delta State, has attracted considerable attention from researchers over the past few decades for various reasons (Obruche et al., 2025). The site chosen for these analyses is the Sapele River, located in Delta State.

Samples Collection Procedures for Sediment

A random sampling method was utilized for the sediment collection (APHA, 2005; WHO, 2010; Obruche et al., 2025). A total of fifteen (15) sampling sites, as indicated in the sampling program design, were selected. Fifteen sampling sites were used in other to cover the whole study area. Surface sediment samples were extracted using a corer with a diameter of 6.5 m to a depth of 10 cm. Between each sampling location, the corer was rinsed with de-ionized water. The sediment samples were extruded from the corer into a tray and subsequently stored in clean plastic plates within a cold container, which was then transported to the laboratory for pretreatment and analysis. Systematic triplicate samples were collected at intervals of 2 km apart at each location. These three samples were combined to create a single composite sample, resulting in a total of 15 samples from the study area. Each sample bottle was labeled at its respective location, packed into a cooler, and transported to the laboratory for analysis.

Analytical Procedure for Sediment

Experimental

The sample was sun-dried, pulverized, and sieved to pass through a mesh size of 2 mm. One gram (1.0 g) of the sediment samples was measured into a Kjeldahl flask. Fifteen (15 cm3) of aqua regia was added and stirred to moisten the sample. The sample was allowed to sit overnight. The following day, the flask was placed on a hot plate and heated to 50°C for 30 minutes. The temperature was then increased to 120°C, and heating continued until the white fume completely disappeared. The sample was subjected to cooling, followed by the addition of 10 cm^3 of 0.2 M HNO_3. The resultant mixture underwent filtration using Whatman no 541 filter paper. Subsequently, both the flask and the filter paper were rinsed with small aliquots of 0.2 M HNO_3. The filtrate was then transferred into a 50 cm^3 flask and adjusted to the mark with 0.2 M HNO_3. A blank sample was prepared using identical methods, excluding the sediment. The concentrations of Ni, V, Cd, Pb, Co, Fe, Mn, and Zn were quantified utilizing a Flame Atomic Absorption Spectrophotometer (AAS).

Statistical Analysis

The correlation coefficients (r) among extractable heavy metals in sediment were assessed through Pearson's Product Moment Correlation Coefficient (r), employing the Statistical Package for Social Science (SPSS).

RESULTS AND DISCUSSION

The concentrations of the eight heavy metals (Ni, V, Cd, Pb, Mn, Fe, Co, and Zn) in sediment samples collected from 15 sampling locations within the study area, along with control samples, are detailed in Tables 1 - 3, corresponding to the dry and wet seasons, respectively. The results are expressed as mean±SD, coefficient of variance, % coefficient of variance (CV%), and standard deviation (SD).

Table 1: Concentrations (mg/kg) of heavy metals in sediment during the dry season.

Heavy Metal	HSD_1	HS_2	HS_3	HSD_4	HS_5	HSD_6	HSD_7	HS_8	HS_9	HSD_{10}	HSD_{11}	HSD_{12}	HSD_{13}	HSD_{14}	HSD_{15}	HSDC	CV	%CV	Mean±SD
Ni	2.12	0.04	0.02	4.20	2.02	2.80	4.20	2.10	0.38	1.10	0.08	1.17	4.00	4.78	3.75	0.01	0.7758	77.58	2.18±0.78
V	4.28	2.28	10.00	5.33	11.13	2.95	3.42	0.66	0.73	2.95	0.35	0.21	1.23	1.28	3.28	0.02	0.989	98.9	3.34±3.30
Cd	1.02	0.03	0.25	0.18	0.33	0.35	0.20	0.23	0.30	0.05	0.03	0.66	0.20	3.04	0.30	0.38	1.575	157.5	0.48±0.75
Pb	0.16	0.02	0.02	0.02	0.02	0.01	0.07	0.03	0.03	0.04	0.27	0.02	0.02	0.02	0.02	0.02	1.385	138.5	0.05±0.07
Mn	8.03	9.50	9.06	8.310	8.31	9.51	11.26	7.20	3.09	9.95	11.95	12.02	9.07	13.25	14.50	13.17	0.284	23.4	9.67±2.75
Fe	24.02	8.90	9.98	10.92	49.47	49.47	8.99	7.80	11.09	18.72	19.09	21.09	25.52	24.27	46.42	30.10	0.661	66.1	22.82±14.82
Co	0.08	0.08	0.08	0.08	0.08	0.06	0.05	0.05	0.07	0.02	0.02	0.22	0.24	0.22	0.22	0.24	0.7595	75.95	0.10±0.08
Zn	0.03	0.04	0.04	0.03	0.02	0.06	0.05	0.05	0.05	0.06	0.07	0.07	0.06	0.06	0.05	0.05	0.304	30.4	0.05±0.02

HSD = Heavy metals in sediment samples, HSD C = Heavy metals in control sediment samples

Table 2: Concentrations (mg/kg) of heavy metals in sediment during wet season.

Heavy metal	HSD1	HSD2	HSD3	HSD4	HSD5	HSD6	HSD7	HSD8	HSD9	HSD10	HSD11	HSD12	HSD13	HSD14	HSD15	HSDc	CV	%CV	Mean±SD
Ni	2.00	0.10	0.01	3.99	2.00	2.02	3.89	2.09	0.30	1.08	0.05	1.07	3.08	4.00	3.39	0.90	0.762	76.23	1.94±1.48
V	4.19	2.00	10.20	5.55	10.99	3.00	3.30	0.60	0.70	2.90	0.28	0.20	1.18	1.29	3.27	0.06	1.008	100.8	3.31±3.34
Cd	1.00	0.13	0.33	0.18	0.30	0.32	0.09	0.19	0.28	0.10	0.03	0.69	0.20	3.30	0.30	0.32	1.342	134.2	0.48±0.74
Pb	0.15	0.01	0.02	0.01	ND	ND	0.06	0.02	0.03	0.03	0.03	0.02	0.01	0.01	0.02	0.06	1.342	143.2	0.03±0.04
Mn	8.00	9.50	9.00	7.99	8.310	8.98	11.19	7.07	3.00	9.89	10.85	12.00	9.00	13.0	13.90	12.99	0.279	27.9	9.45±2.64
Fe	25.69	10.05	9.99	11.90	50.50	49.49	9.00	8.00	12.00	20.2	21.01	23.00	25.40	25.01	48.00	28.09	0.640	64.0	23.28±0.25
Co	0.07	0.08	0.07	0.07	0.08	0.04	0.03	0.03	0.0	0.02	ND	0.02	0.99	0.19	0.22	1.00	1.867	186.7	0.13±0.25
Zn	0.02	ND	0.04	0.01	0.01	0.02	0.04	0.05	0.05	0.02	0.04	0.07	0.06	0.05	0.04	0.10	0.582	58.17	0.04±0.20

Table 3: Average concentrations (mg/kg) of heavy metals in sediment for wet and dry seasons

Heavy metal	dry season	wet season	Average concentrations for dry and wet seasons	WHO standard
Ni	2.18	1.938	2.061	0.02
V	3.34	3.300	3.319	0.1
Cd	0.48	0.476	0.477	0.003
Pb	0.05	0.027	0.039	0.01
Mn	9.668	9.445	9.557	0.1-0.5
Fe	22.383	23.283	22.833	0.3
Co	0.103	0.131	0.117	0.1-0.5
Zn	0.049	0.035	0.042	3.0

The concentrations of heavy metals (Ni, V, Cd, Pb, Mn, Fe, Co, and Zn) measured in mg/kg at fifteen (15) geo-referenced points in sediment samples from the study area during both dry and wet seasons are detailed in Tables 1-3. The findings revealed that the mean concentrations of heavy metals in mg/kg in the sediment samples for the dry and wet seasons were as follows:

Fe (22.18 ± 14.82), Mn (9.67±2.75), V (3.39±3.30), Ni (2.18±0.78), Cd (0.48 ± 0.75), Co (0.10±0.01), Zn (0.49 ± 0.08), Pb (0.05±0.07) for the dry season, and Fe (23.28±0.24), Mn (9.45±2.63), V (3.31±3.34), Ni (1.94±1.48), Cd (0.48±0.74), Pb (0.03±0.03) for the wet season. All heavy metals were detected in every sediment sample. The mean concentrations of all heavy metals exceeded those of the control sediment in both dry and wet seasons, yet remained below the standards set by the World Health Organization. The mean concentrations of Mn, Ni, Pb, and Zn during the dry season were greater compared to those in the wet season, with the exception of Fe, V, and Co. This discrepancy may be attributed to the slow movement of water within the sediment and the potential for high absorption of heavy metals by the sediment. The concentrations of Cd remained consistent across both dry and wet seasons. This may be due to the low amount of Cd in the area. The most significant anthropogenic impact was noted at location 5, this may be due to high anthropogenic activities in that area. (Li et al., 2011) confirmed a yearly increase in average metal concentrations in its research work carried out in another river in Sapele. The concentration of most metals was observed to be higher in the dry season than in the wet season. Among all metals analyzed, iron was identified as the most prevalent in sediment for both seasons. The results indicate that metal concentrations varied across different sampling locations, likely due to the geological distribution of minerals that differs from one site to another. Among the metals identified, lead (Pb) exhibited the lowest concentration, which was notably higher during the dry season. This phenomenon may be attributed to effective sedimentation, as the water is primarily influenced by tidal currents during this period. Ekpo et al. (2023) in his research work indicated that the average concentrations of metals in sediment across both seasons in the study area followed this order: Pb (25.73 µg g-1) > Cu (18.48 µg g-1) > Ni (2.91 µg g-1) > Cd (1.35 µg g-1). The heavy metals that are potentially bio-available include those that can be ingested by humans and are typically regarded as having anthropogenic origins.

Seasonal Dynamics of Individual Element in Study Area

Nickel (Ni)

The nickel levels in sediment samples analyzed from the study area showed a mean ± SD of (2.18 ± 1.69 mg/kg) and a % CV of (77.58%) for the dry season (refer to Table 1). In a similar manner, the mean ± SD of (1.94 ± 1.477 mg/kg) and % CV of (76.23%) for nickel were recorded in the sediment during the wet season (see Table 2 and Figure 1). The overall average concentration of nickel in the sediment of the study area was determined to be 2.06 mg/kg, as illustrated in Table 3. The maximum concentration of 4.78 mg/kg was observed at location 14 (Table 1), while the minimum concentration of 0.04 mg/kg was noted at location 2 (Table 1). This work is in agreement with the research conducted by Chindah et al., nickel concentrations varied between 3.50 ± 2.4 mg/kg and 3.50 ± 2.5 mg/kg for the dry and wet seasons, respectively. Furthermore, the research work is in line with the research work of Obruche et al., (2022) which indicated that nickel (Ni) exhibited elevated concentrations during the dry seasons in comparison to the rainy seasons, with average concentrations recorded at 14.33

mg/kg for dry seasons and 9.75 mg/kg for wet seasons. Asia et al. documented a nickel range of 2 – 33 µg/g. In a related investigation, Obasohan reported a nickel range of (0.020 - 0.35) mg/kg. Additionally, Howard et al. noted a mean concentration of 0.08 mg/kg of nickel in the sediment of the study area. Nickel is recognized as highly toxic to aquatic organisms and is relatively accessible to these organisms. Petroleum waste is known to contain significant concentrations of nickel. Continuous discharge of such waste into aquatic ecosystems may lead to the accumulation of this metal in the environment. Potentially bioavailable heavy metals are those that can be ingested by humans and are typically regarded as anthropogenic in origin.

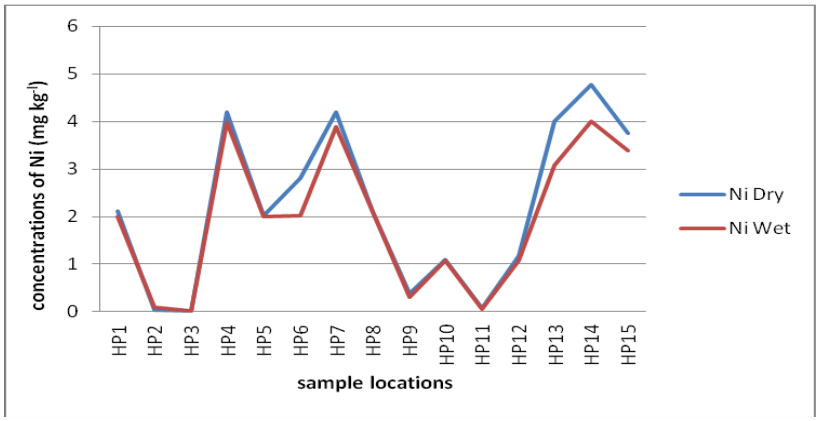


Figure 1. Seasonal Variations of Ni in sediment

Vanadium (V)

The analysis of sediment samples from the study area indicated a vanadium concentration of 3.34±3.30 mg/kg, with a coefficient of variation (% CV) of 77.130 % during the dry season, as detailed in Table 15 and illustrated in Figure 12. In contrast, the wet season revealed a concentration of 0.0379±0.0349 mg/kg and a % CV of 100.8 %, as presented in Table 2 and Figure 2. The overall average concentration of vanadium in the sediment samples from the study area was determined to be 3.319 mg/kg, as shown in Table 3. This average concentration of 3.319 mg/kg is significantly higher than the control sediment sample, which exhibited a vanadium concentration of 0.002 mg/kg. The maximum concentration of vanadium, recorded at 11.13 mg/kg, was found at location 5 during the dry season, while the minimum concentration of 0.03 mg/kg was noted at location 9 during the wet season, as indicated in Table 2. Essien and Benson4 reported a mean vanadium concentration of 16.23 mg/kg in the sediment of the study area. Chindah et al. noted that vanadium concentrations were relatively elevated in both seasons, with minor variations between the dry (0.04 mg/kg) and wet (0.13 mg/kg) seasons. The elevated levels of vanadium found in the sediment may be attributed to crude petroleum oil spillages, which are prevalent in the region. The vanadium levels identified in this study, particularly in Ukpenekang, pose a significant environmental threat,

indicating pollution. It is imperative to address this issue, as there is a considerable risk of heavy metal accumulation in the environment. This gives excellent agreement with those in literatures previously reported by Obruche et al. (2018) in their findings.

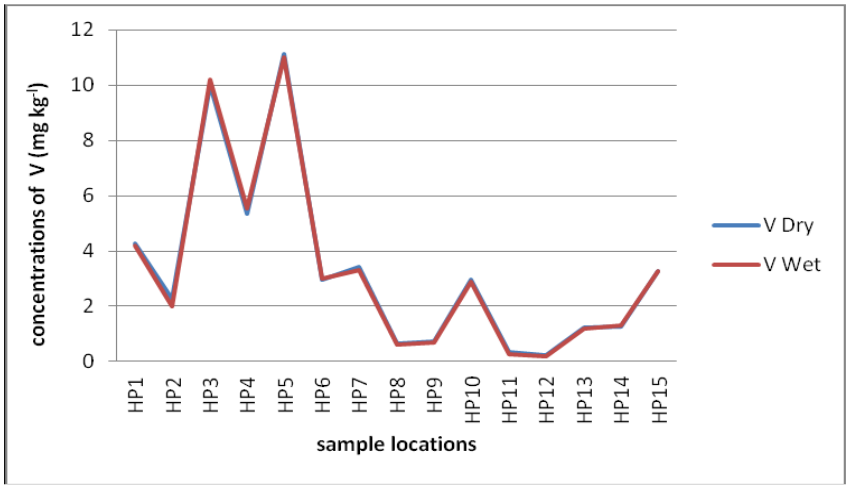


Figure 2: Seasonal Fluctuations of V in Sediment

Cadmium (Cd)

The average ± SD concentration of Cd in surface sediment samples was (0.477 ± 0.752 mg/kg) with a % CV of (157.54 %) during the dry season (refer to Table 1 and Figure 3). In a similar manner, the mean ± SD (0.476 ± 0.741 mg/kg) and CV % (155.71 %) were noted in the surface sediment samples from the study area throughout the wet season (see Table 2 and Figure 3). The overall average concentration of Cd in sediment for both dry and wet seasons was 0.477 mg/kg (as shown in Table 3). The maximum concentration of 3.04 mg/kg was observed at location 14, as indicated in Table 1 during the dry season, while the minimum concentration of 0.03 mg/kg was recorded at location 11 during the wet season (refer to Table 2). The mean concentration of Cd exceeded that of the control sediment sample (0.38 mg/kg). Olatunji and Osibanjo148 noted that "the concentration of Cd in sediment varied between 0.17 - 0.51 mg/kg with a mean concentration of 0.40±0.26 mg/kg during the dry season and 0.17 - 0.32 mg/kg with a mean of 0.24±0.12 mg/kg during the dry seasons of the 2024 and 2025 study periods. The concentration of cadmium during wet seasons ranged from 0.16-0.32 mg/kg with a mean of 0.25±0.05 mg/kg in the 2024 and 2025 study periods. In the wet seasons of 2024 and 2025 study periods, the concentration varied between (0.18-0.42) mg/kg with a mean value of 0.30±0.08 mg/kg.

The relative standard deviation for cadmium (Cd) concentration fluctuated from 6% during the wet season to 26% in the dry season. The average concentration of Cd in sediment observed in this study exceeded the values reported by Howard et al., which was 0.09 mg/kg, and Udosen and Awakama, who recorded 0.04 mg/kg in the same study area. During the dry season, Ideriah et al. documented the percentage composition of heavy metals in sediment

samples as follows: 22.27% lead (Pb), 25.41% copper (Cu), 37.78% cadmium (Cd), 22.24% chromium (Cr), 24.84% nickel (Ni), 21.43% manganese (Mn), and 22.43% zinc (Zn). Chinda et al. reported that Cd concentration varied between 0.030 and 0.014 mg/kg during the wet season, while a consistent concentration of 0.0005 mg/kg was noted in the dry season. Ikpee et al. indicated cadmium concentrations of 1.5 ± 1.0 µg/g and 1.8 ± 1.2 µg/g in sediment samples from the study area for the dry and wet seasons, respectively, with a mean concentration of 1.2 µg/g to 1.5 µg/g. Cadmium is a non-essential element, and once it enters a biological system, it can persist for extended periods; its excretion is notably slow, and at certain concentrations, it can be harmful to humans and other living organisms, particularly when present as cadmium chloride ($CdCl_2$) in aqueous environments. There have been documented instances of fatalities in humans due to the consumption of aquatic resources contaminated with elevated levels of cadmium (Festus-Amadi et al., 2021).

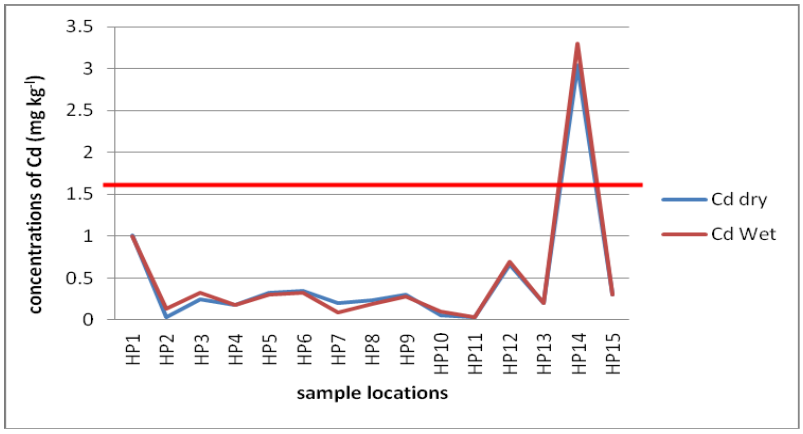


Figure 3: Seasonal variations of Cd in sediment with DPR standard

Lead (Pb)

The mean±SD concentration and % CV of lead (Pb) in surface sediment samples from the study area were recorded as 0.05±0.07 mg/kg and 138.53 %, respectively, during the dry season (refer to Table 1 and Figure 4). Conversely, during the wet season, sediment samples indicated a mean±SD of 0.03±0.04 mg/kg and a % CV of 134.20 % for Pb in the study area, as illustrated in Tables 1 and 2, along with Figure 4. The overall average concentration of Pb in surface sediment samples across both dry and wet seasons was determined to be 0.039 mg/kg (see Table 3). A study conducted by Ikpee1 in the same area found that the mean Pb concentration in sediment samples varied between 42.0±20.0 µg/g during the dry season and 25.54 ± 22.56 µg/g during the wet season. The findings indicated that the average concentrations of metals in sediment samples for both seasons followed the order Pb > Cu > Ni > Cd, with respective values of 25.73 µg/g, 18.48 µg/g, 2.91 µg/g, and 1.35 µg/g. Olatunji and Osibanjo reported Pb concentrations in sediment ranging from 13.67 to 18.11 mg/kg, with mean levels of 15.75 ± 1.49 mg/kg during the dry season, and from 14.92 to 19.08 mg/kg,

with a mean Pb level of 16.96 ± 1.45 mg/kg during the wet season. Additionally, the work is in agreement with Obruche et al., (2019) which documented a mean concentration of 2.94 mg/kg in the sediment of the study area. According to (Murphy., 2021), lead concentrations in sediment were found to be higher during the wet season (0.003 - 0.027 mg/kg) compared to the dry season (0.01 mg/kg). The detection of Pb in the sediment of the study area may be linked to Pb-laden effluents discharged into the ecosystem. The utilization of lead in various industrial processes and consumer products (such as batteries, gasoline additives, rolled and extruded products, cable sheathing, paints, alloys, and pigments) may also contribute to this presence. The existence of lead poses significant risks to aquatic life, as fish and other aquatic organisms are particularly susceptible to Pb and often retain a substantial percentage of ingested lead, which can subsequently enter the human food chain. The apparent increase in Pb levels within the study area indicates a gradual pollution trend attributed to Pb.

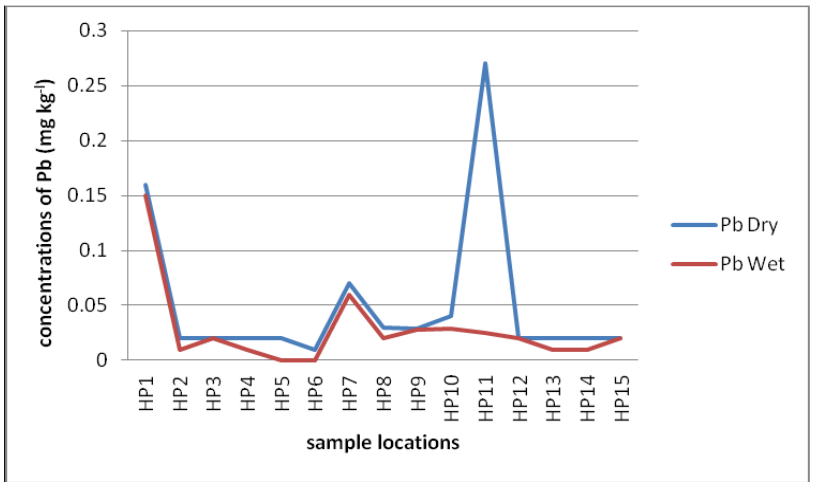


Figure 4: Seasonal Fluctuations of Pb in Sediment

Manganese (Mn)

The concentration of Mn in the surface sediment of the study area was measured at (9.67 ± 2.75 mg/kg) with a coefficient of variation (% CV) of (28.47 %) during the dry season (refer to Table 1 and Figure 5). For the wet season, the mean concentration was (9.45 ± 2.6 mg/kg) with a % CV of (27.942 %) as indicated in the sediment samples from the study area (see Table 2, Figure 5). The overall average concentration of Mn in the sediment samples from the study area was determined to be 9.557 mg/kg (as shown in Table 3). These concentrations were found to be lower than the control sediment samples, which exhibited a Mn concentration of 13.17 mg/kg. The maximum concentration recorded was 14.50 mg/kg at location 15, as detailed in Table 1, while the minimum concentration of 3.09 mg/kg was observed at location 9, as presented in Table 2.

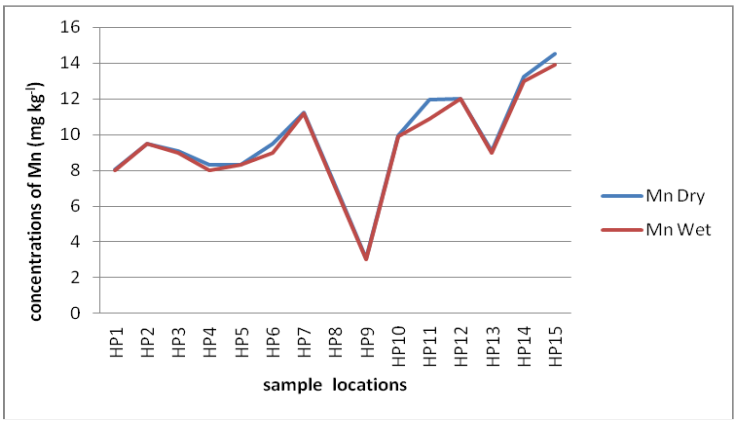


Figure 5: Seasonal Variations of Mn in Sediment

Iron (Fe)

The average ± standard deviation (SD) concentration and percentage coefficient of variation (% CV) of Fe in surface sediment samples from the study area were recorded as 22.38 ± 14.81 mg kg-1 and 66.198 %, respectively, during the dry season (Table 1, Figure 6). In the wet season, the mean ± SD was noted as 23.28 ± 14.91 mg/kg, with a CV % of 64.043 % (Table 2, Figure 6). The overall average concentration of Fe across both dry and wet seasons was determined to be 22.833 mg/kg (Table 3). The maximum concentration of 49.47 mg/kg was observed at location 6, while the minimum concentration of 7.80 mg/kg was found at location 8 (Figure 6). A related study conducted by Murphy et al., (2021) reported a mean concentration of 35.40 mg/kg of Fe in sediment samples from the same area. The elevated levels of Fe in the sediment samples from the study area may be linked to the discharge of waste containing iron and effluents rich in corroded iron pipes, containers, and scraps into the aquatic environment. The consistently high concentration of Fe in all analyzed samples in this research indicates its abundance in the study area, although industrial activities may also play a role in this phenomenon. Furthermore, the significant concentration of Fe in sediment samples may imply potential contamination of the sediment in the study area by iron.

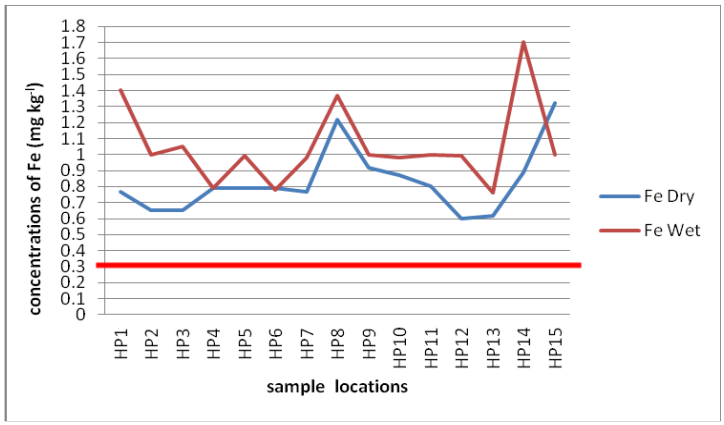


Figure 6: Seasonal Fluctuations of Fe in Sediment

Zinc (Zn)

The study also identified an average concentration of 0.03± 0.01 mg kg-1 and a coefficient of variation (CV) of 30.44% for Zn in surface sediment samples, as illustrated in (Table 1, Figure 7) during the dry season. In comparison, the average concentration recorded during the wet season was (0.03 ± 0.02 mg/kg) with a CV of (58.166%) for Zn in sediment samples (Table 2, Figure 7). The overall average concentration of Zn from sediment samples in the study area for both dry and wet seasons was determined to be 0.042 mg/kg (Table 3). The maximum concentration of 0.07 mg/kg Zn was observed at location 11 (Enua Eyet Ikot), while the minimum concentration of 0.02 mg kg-1 was found at location 5 (Figure 7). According to the findings of Chindah and Braide, the concentrations of Zn in sediment samples from the study area were greater during the dry season (1.03 - 2.04 mg/kg) compared to the wet season (0.063 - 0.277 mg/kg). Obruche et al., 2018 reported an average concentration of 5.68 mg kg-1 in sediment samples collected from the Tributary of Qua Iboe River Estuary. Overall, the concentration of Zinc in sediment samples was relatively low across all investigated locations. Although zinc is not classified as a human carcinogen, the ingestion of substantial amounts (390 mg kg-1 per day for (3 – 13) days or approximately 27 mg/kg of Zn daily) can be fatal. Symptoms such as vomiting, diarrhea, abdominal cramps, and in some instances, intestinal hemorrhage may arise from prolonged exposure to elevated levels of zinc (Zhu et al., 2022).



Figure 7: Seasonal Fluctuations of Zn in Sediment

Cobalt (Co)

The mean concentration of cobalt in the sediment of the study area during the dry season was recorded at 0.10 ± 0.07 mg/kg, with a coefficient of variation (% CV) of 75.95 % (Table 1, Figure 8). In contrast, during the wet season, the mean concentration was found to be 0.13 ± 0.24 mg/kg, with a % CV of 186.72 % for surface sediment samples from the same area (Table 2, Figure 8). The overall average concentration for both dry and wet seasons was noted to be 0.117 mg/kg (Table 3). In a related investigation, Essien and Benson documented mean concentrations of 0.09 mg/kg and 0.27 mg/kg of Co in surface water and sediment samples, respectively. Cobalt is a vital element that is anthropogenically introduced into aquatic

environments through runoff resulting from fertilizer application. The toxicity of cobalt is relatively low when compared to numerous other heavy metals, although exposure to significantly elevated levels may lead to adverse health effects (Ekpo et al., 2024).

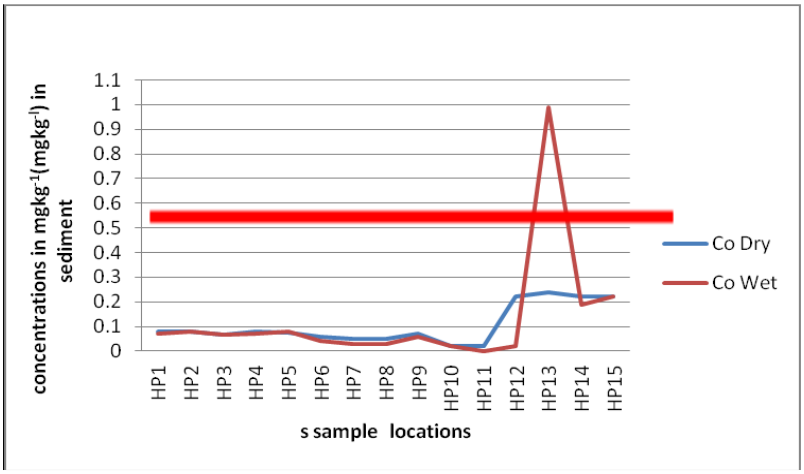


Figure 8: Seasonal fluctuations of Co in sediment

CONCLUSION

Based on the findings of this study, it can be inferred that the levels of all examined heavy metals, specifically Mn, Ni, Pb, and Zn, in sediment were elevated during the dry season compared to the wet season, with the exception of Fe, V, and Co. Fe was consistently the most prevalent metal across all seasons, with sediment exhibiting the highest levels of pollutants. The mean concentrations of heavy metals such as Ni, V, Cd, Pb, and Mn exceeded WHO standards during both dry and wet seasons. Conversely, the average levels of Co in the sediment remained within the WHO recommended limits for both seasons. Concentrations of Fe were the highest across all seasons. This work is a novelty because it has not be reported that it has been carried out before today. The findings indicate a pressing need for closer environmental monitoring in the area under investigation, alongside the implementation of suitable proactive measures to safeguard community health, given the bio-accumulative nature of heavy metals. Furthermore, due to the health risks and potential effects of these metallic pollutants on community well-being, the State Environmental Health Agency, along with other pertinent regulatory bodies, should establish regular monitoring programs to assess the levels of heavy metal contaminants in the sediment samples from the study region.

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