

Assessment of Seasonal Variations of Some Heavy Metals between Water and Sediment in Qua Iboe River, OrukAnam, Nigeria

Abstract:

Environment which man lives requires sustainability for life continuity. This is because human activities release enormous amounts of diverse contaminants into aquatic ecosystem are continually increasing. It is worthy of note of some relationship between concentrations of contaminants in water bodies and sediment lying beneath through desorption of some contaminants from the water. In this study, heavy metals (Cd, Cr, Ni, Cu, V, Pb and Sn) in water and sediment were determined using atomic absorption spectrophotometer. The results were subjected to statistical analysis using statistical package for social sciences. A significant positive relationship was established between the heavy metals in water and sediment in the studied river. A significant positive relationship between Cd in water and that in sediment was established at ($r = .973$, $p < 0.01$), between Cu in water and that in sediment ($r = .844$, $p < 0.01$) in dry season. In wet season, results revealed that there was a significant positive relationship between Cd in water and that in sediment ($r = .925$, $p < 0.01$), Cr in water and sediment ($r = .991$, $p < 0.01$), Cu in water and sediment ($r = .937$, $p < 0.01$). The results also revealed that the levels of the metals in both water and sediment were higher in dry season than wet season due to concentration and dilution effects respectively. The distribution revealed that as the concentration of the metals in water increased, there was a corresponding increase in concentration of the metals in sediment. This condition is capable of causing bioaccumulation of the metals in commercial fish especially bottom feeders with potential consequences on man through food chain.

Keywords: Analysis, ASS, heavy metals, sediment, statistical, and water.

Introduction

“The environment and its compartments have been severely polluted by heavy metals and other chemicals through anthropogenic activities. Although pollution occurs naturally, it is the anthropogenic activities that create more problems” (Akpan, *et al.*, 2024). “Researchers have revealed that levels of pollution in different environmental media depends significantly on unregulated levels of anthropogenic activities among other factors within these media”. “Variation in levels of pollution across geographical regions is a function of variation in levels of anthropogenic activities across such regions. In an environment, pollution affects both the biotic and the abiotic components of the environment. In aquatic environment, there is a correlation between the levels of pollution in water and sediment lying underneath and fish that live in the water as well as human that depend on the water and fish for consumption” (Ido *et al.*, 2023). Heavy metals are known to be naturally occurring contaminants which exist within background levels, but anthropogenic activities introduce them in large quantities into environment. This resulted in a reduced ability of the environment to support life thereby threatening life of humans, animals and plants. This occurs due to bioaccumulation in the food chain as a result of the non-degradable nature of the trace metals. “Environmental pollution will continue to be a worldwide concern and one of the great challenges faced by the global society. Among all the pollutants, heavy metals have received significant attention to environmental chemist due to their non- biodegradability” (El-Zeinger *et al.*, 2018). “Some heavy metals are toxic even at low concentrations. Metals such as arsenic, lead, cadmium, nickel, mercury, chromium,

cobalt, zinc and selenium are highly toxic even in minor quantity” (Ogriet *et al.*, 2011). “Increasing levels of heavy metals in our resources is currently an area of greater concern, especially since a large number of industries are discharging their metal containing effluents into fresh water without adequate treatment” (Udosenet *et al.*, 2016).

“Heavy metals become toxic when they are not metabolised by the body and accumulate in the soft tissues. They may enter the human body through food, water, air or absorption through the skin when they come in contact with humans in agriculture, manufacturing, pharmaceutical, industrial or residential settings” (Alinnor, I. and Alagoa, A. 2014). Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children. Natural and human activities are contaminating the environment and its resources, they are discharging more than what the environment can handle. “Some important anthropogenic sources which significantly contribute to the heavy metals contamination in the environment include automobile exhaust which releases lead, smelting which releases arsenic, copper and zinc; insecticides which release arsenic and burning of fossil fuels which releases nickel, vanadium, mercury, selenium and tin” (Amirah *et al.*, 2013; Emarat *et al.*, 2015; Edemet *et al.* 2020). “Researchers have found out that human activities contribute significantly to environmental pollution due to the everyday manufacturing of goods to meet the demands of the increasing population in our nation. Over the years, OrukAnam has witnessed tremendous anthropogenic activities culminating in the overall development of the area. These activities include roads construction, industrialisation and all kinds of agricultural practices. The end products of these activities are usually washed into the aquatic environment when it rains thereby polluting the ecosystem with all kinds of heavy metals” (Amirah *et al.*, 2013). There is recent data of the levels of these metals in the study area hence, the needs for assessment of the levels of the metals and seasonal variations in water and sediment in both wet and dry seasons.

2. Material and Methods

2.1 Study Area

The study area Qua Iboe River as shown in Figure 1 is located between latitude 04°28'31. and 07°10'12.4''0'' North of the equator and between 06°65'41.2'' East of Greenwich Meridian. “It is the main river that drains across Akwa Ibom State. It flows in a southern direction through EtimEkpo, Ikot Okoro in OrukAnam via Ibagwa in Abak to EkpeneObom and EkpeneUkpa in Etinan Local Government Area, then through Ndiya in NsitUbiom local government area before flowing into Atlantic Ocean via Beight of Bonny” (Akpan *et al.*, 2024).

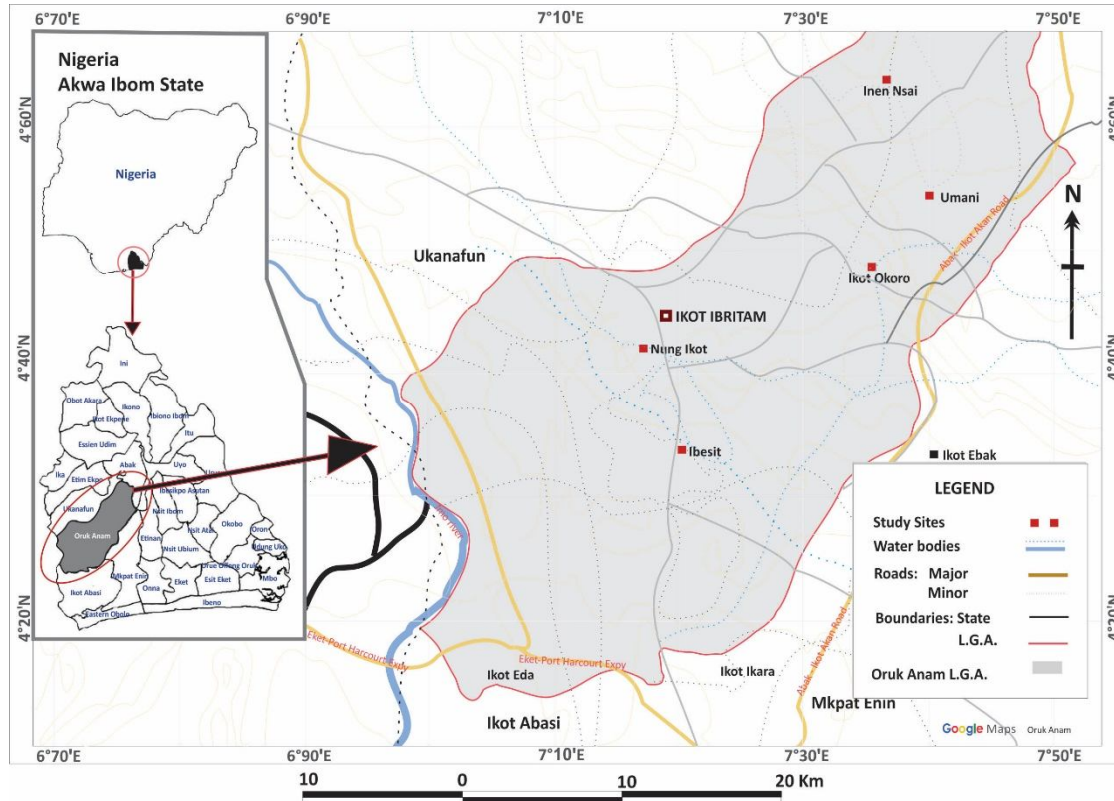


Figure 1: Map of the study area.

Predominant human activities in the study area include agriculture, roads construction, fishing and boating.

2.2 Samples Collection and Analysis

Samples were collected between November and October covering wet and dry seasons from five sampling locations namely: InenNsai (upstream), Umani, Ikot Okoro (downstream), Nung Ikot and Ibesit (downstream).

Determination of Heavy Metals in Water: “The concentrations of heavy metals were determined using UNICAM solar 969 Atomic Absorption Spectrophotometer (AAS). The water samples (100 mL each) were filtered using filter paper No.1. The filtrate was acidified with HNO₃ (10 mL) and 50% HCl solution (10 mL). It was evaporated to near dryness on an electric hot plate. The solution was transferred to a 100 mL volumetric flask and made up to mark with deionised water” (Edemet *al.* 2020). A blank was also prepared the same way with the omission of the sample using deionised water. The samples were aspirated into the air/acetylene flame.

Determination of Heavy Metals in Sediment

Sediment samples (1.0 g) were weighed into 250 mL Pyrex conical flasks. Mixed perchloric acid, nitric acid and sulphuric acid in the ratio of 1:2:2 (15 mL) were added and the samples were digested on a hot plate in a fume chamber at until dense white fumes appeared, signaling the end of digestion. The contents were cooled and filtered using filter paper (Whatman No.42) into 50 mL volumetric flasks and made up to mark with distilled water. A blank was also prepared similarly with the omission of the sample. The digested samples were aspirated into the AAS.

Quality Control

Quality control of the analytical data was guaranteed through the implementation of laboratory quality assurance and laboratory methods as well as the use of standard operating procedures, calibration with standards and analysis with reagent blanks.

Statistical Analyses

The generated data were subjected to descriptive statistics analysis using statistical package for social sciences (SPSS).

3. Results and Discussion

3.1 Levels of Heavy Metals in Water and Sediment Samples

The results of the levels of investigated heavy metals in water and sediment samples analysed in this study were presented in Tables 1 and 2.

Table 1: Levels (mg/L) of heavy metals in water samples in wet and dry seasons

Trace								
Metals		Cd	Cr	Ni	Cu	V	Pb	Sn
IN	Wet	0.02±0.01	0.01±0.01	0.01±0.01	0.02±0.01	0.01±0.01	0.00±0.00	0.02±0.01
	Dry	0.03±0.01	0.01 ±0.01	0.02±0.01	0.03±0.01	0.02±0.01	0.00±0.00	0.00±0.01
UM	Wet	0.02±0.01	0.01 ±0.01	0.02±0.01	0.05±0.01	0.02±0.01	0.00±0.00	0.01±0.01
	Dry	0.04±0.01	0.0 ±0.01	0.03±0.01	0.07±0.01	0.03±0.01	0.00±0.00	0.02±0.01
IO	Wet	0.0±0.00	0.03 0.01	0.0±0.00	0.07±0.01	0.0 ±0.00	0.00±0.00	0.02±0.00
	Dry	0.06±0.01	0.04 ±0.01	0.01±0.01	0.08±0.01	0.04±0.01	0.01±0.00	0.02±0.01
NI	Wet	0.05±0.01	0.0±0.01	0.02±0.01	0.08±0.01	0.03±0.01	0.00±0.01	0.02±0.01
	Dry	0.07±0.00	0.08±0.00	0.04±0.01	0.10±0.00	0.04±0.01	0.01±0.00	0.03±0.00
IB	Wet	0.05±0.01	0.06±0.01	0.03±0.01	0.08±0.01	0.03±0.01	0.01±0.01	0.02±0.01
	Dry	0.08±0.00	0.09±0.00	0.04±0.00	0.10 ±0.01	0.04±0.01	0.01±0.00	0.03±0.01

IN = InenNsai, UM = Umani, IO = Ikot Okoro, NI = Nung Ikot, IB = Ibesit, STD = Standard deviation.

Table 2: Levels (mg/kg) of heavy metals in sediment for wet and dry seasons

Trace								
Metals		Cd	Cr	Ni	Cu	V	Pb	Sn
IN	Wet	0.02±0.01	0.02±0.01	0.02±0.01	0.05±0.01	0.03±0.01	0.01±0.01	0.02±0.01
	Dry	0.03±0.01	0.03±0.01	0.03±0.01	0.06±0.01	0.03±0.01	0.01±0.01	0.02±0.01
UM	Wet	0.06±0.01	0.04±0.00	0.04±0.01	0.07±0.01	0.04±0.01	0.01±0.01	0.04±0.01
	Dry	0.10±0.08	0.15±0.01	0.05±0.01	0.08±0.00	0.05±0.00	0.02±0.01	0.05±0.01
IO	Wet	0.08±0.01	0.05±0.01	0.07±0.01	0.11±0.01	0.06±0.01	0.03±0.01	0.05±0.00
	Dry	0.13±0.01	0.11±0.00	0.10±0.00	0.21±0.01	0.07±0.01	0.03±0.00	0.08±0.00
NI	Wet	0.10±0.01	0.11±0.01	0.08±0.01	0.15±0.01	0.06±0.01	0.03±0.01	0.07±0.01
	Dry	0.21±0.01	0.20±0.00	0.10±0.00	0.17±0.00	0.08±0.00	0.03±0.00	0.08±0.00
IB	Wet	0.10±0.01	0.11±0.01	0.08±0.01	0.10±0.01	0.03±0.01	0.01±0.01	0.07±0.01
	Dry	0.21±0.01	0.21±0.00	0.17±0.00	0.18±0.01	0.08±0.01	0.03±0.00	0.08±0.01

IN = InenNsai, UM = Umani, IO = Ikot Okoro, NI = Nung Ikot, IB = Ibesit, STD = Standard deviation.

Levels of Heavy Metals in Water: Table 1 shows the levels of heavy metals in water in both wet and dry seasons. The distribution pattern of the levels of heavy metals in the water indicated $Cu > Cd > Cr > V > Ni > Sn > Pb$.

Levels of Cadmium in Surface Water: The levels of cadmium in water samples across sampling locations during wet season ranged between 0.02 ± 0.01 and 0.05 ± 0.01 mg/L and between 0.03 ± 0.01 and 0.080 ± 0.01 mg/L. The results obtained in this study were consistent with

levels obtained by Udosenet *et al.* (2014) and were higher than maximum permissible limits of 0.003 and 0.005 mg/L recommended for aquatic medium by Nigeria Industrial Standard and World Health Organisation respectively. Higher levels of cadmium are usually obtained in liver and kidney and lowest concentration in pancreas and spleen (Akpan *et al.* 2024). Effects of higher levels in man include kidney damage, diarrhea, stomach pains, and bone fracture among others.

Levels of Chromium in Surface Water: The levels of Cr in surface water ranged between 0.01 ± 0.01 and 0.068 ± 0.01 mg/L in wet season and during dry season, the levels ranged between 0.02 ± 0.09 and 0.087 ± 0.004 mg/L. Chromium is essential nutrient for humans and shortage may cause heart disease, disruption of metabolisms and diabetes. Excessive intake may cause real danger to human health such as skin rashes, stomach upset and ulcer, respiratory problems etc.

Levels of Nickel in Surface Water: The levels of Ni recorded across sampling locations ranged between 0.01 ± 0.01 and 0.03 ± 0.01 mg/L in wet season and between 0.02 ± 0.01 and 0.04 ± 0.00 mg/L during dry season nickel. Levels recorded in study were consistent with maximum permissible limits of 0.02 and 0.07 mg/L for aquatic ecosystem recommended by NIS and WHO respectively. Nickel is relatively toxic and widespread in the environment. The effects of nickel exposures range from skin irritation, lungs and nervous system damage etc. Sources of Ni to the environment include weathering of minerals and rocks and geochemical emission and anthropogenic activities.

Levels of Copper in Surface Water: The mean levels of Cu obtained in surface water across sampling locations during wet season ranged between 0.02 ± 0.01 and 0.08 ± 0.01 mg/L in wet season and between 0.03 ± 0.01 and 0.10 ± 0.01 mg/L during dry season. In both seasons, levels obtained were with result reported by Idoet *et al.* (2023) and below maximum permissible limit of 2.0 mg/L for aquatic environment recommended by NIS. Cu is essential to metabolism. Higher levels are toxic and cause liver damage. Long term exposure can result in nose, mouth and eyes irritation. Other effects include headache, dizziness, vomiting etc. (Udosenet *et al.* 2016).

Levels of Vanadium in Surface Water: The mean levels of V in surface water across all sampling locations during wet season ranged from 0.01 ± 0.01 to 0.03 ± 0.01 mg/L and from 0.02 ± 0.01 to 0.04 ± 0.01 mg/L. In both seasons, the levels recorded in some locations were above permissible limits of 0.02 mg/L for aquatic ecosystems recommended by NIS and USEPA. Higher levels in man can result lung disease and stomach problems.

Levels of Lead in Surface Water: From Table 3, the levels of Pb in water across the sampling locations ranged between 0.00 ± 0.00 and 0.01 ± 0.00 mg/L in wet season and between 0.00 ± 0.00 and 0.01 ± 0.00 mg/L during dry season. The results obtained were below limits of 0.01 mg/L and 0.05 mg/L for surface water according to USEPA and NIS standards respectively. Higher concentration in man can result in brain and kidney damage, reproduction failure. Other effects include hearing loss, anemia, hypertension, kidney impairment, immune system dysfunction etc.

Levels of Tin in Surface Water: The mean levels of Sn in water across sampling locations ranged between 0.00 ± 0.01 and 0.02 ± 0.01 mg/L in wet season and during dry season levels obtained range between 0.02 ± 0.00 to 0.03 ± 0.01 mg/L. The levels of tin obtained in this study in both seasons were consistent with 1.0 and 2.0 mg/L standards given by NIS and WHO respectively.

On the whole, the levels of all the heavy metals determined in this study were higher in downstream than upstream due to increase in levels of anthropogenic activities downstream and downstream movement of contaminants in the studied river. "Comparatively, levels of

heavy metals recorded in dry season were higher than levels obtained in wet season due to concentration and dilution effects in dry and wet seasons respectively” (Uwahet *al.* 2021).

Levels of Heavy Metals in Sediment: Table 2 shows the results of mean levels of heavy metals in sediment across the sampling locations. The distribution pattern is shown below: Cu > Cd > Cr > Ni > V > Sn > Pb.

Levels of Cadmium in Sediment: The levels of Cd in sediment samples across sampling locations ranged between 0.02±0.01 and 0.10±0.01 mg/kg in wet season and between 0.03±0.01 and 0.21±0.01 mg/kg in the dry season. The results were similar to levels reported by Gu *et al.* (2018). Levels recorded in all locations in both seasons were consistent with permissible limits of 0.03 – 3.0 mg/kg in sediment recommended by department of petroleum resources.

Levels of Chromium in Sediment: The levels of Cr in sediment across all the sampling locations ranged between 0.02±0.01 and 0.11±0.01 mg/kg in wet season while it ranged between 0.03±0.01 and 0.21±0.00 mg/kg during dry season. These levels were consistent with levels recorded by Uwahet *al.* (2021) and below 0.5 mg/L permissible limit in sediment recommended by Department of petroleum Resources (DPR).

Levels of Nickel in Sediment: The levels of Ni in this study ranged between 0.02±0.01 and 0.08±0.01 mg/kg in wet season while during dry season the levels ranged between 0.03±0.01 and 0.17±0.00 mg/kg. Levels were higher in dry season than wet season across the sampling locations reflecting concentration and dilution effects in dry and wet season respectively (Edemet *al.* 2020).

Levels of Copper in Sediment: The level of Cu in this study across the sampling locations ranged between 0.05±0.01 and 0.15 0.01 mg/kg in wet season and between 0.06±0.01 and 0.18±0.01 mg/kg in dry season. The levels of Cu recorded in sediment samples in this study were higher than levels reported by Uwahet *al.* (2013) and lower than permissible limit of 1.0 mg/kg recommended by NIS.

Levels of Vanadium in Sediment: The levels of vanadium in sediment obtained in this study across all the locations ranged between 0.03±0.01 and 0.06±0.01 mg/kg in wet season and between 0.03±0.01 and 0.08±0.01 mg/kg during dry season. Levels recorded were higher in dry season than wet season due to concentration and dilution effects in dry and wet season respectively, Etuket *al.* (2020). Levels recorded in some sampling locations were higher than permissible limit of 0.002 mg/kg in sediment given by NIS. The study area requires routine monitoring of the metals through research to prevent escalation.

Levels of Lead in Sediment: The level of Pb in sediment samples across the sampling locations ranged between 0.01±0.01 and 0.03±0.01 mg/kg in wet season and between 0.01±0.01 and 0.03±0.00 mg/kg during dry season. These levels were consistent with levels reported by Akpan *et al.*, 2024; Idoet *al.* 2023 and below permissible limit of 2,2 mg/kg in sediment given by DPR.

Levels of Tin in Sediment: The levels of Sn across the sampling locations during wet season ranged between 0.02±0.01 and 0.07 mg/kg and between 0.02±0.00 and 0.08±0.01 mg/kg in the dry season. As indicated in Table 2, the results showed that there were significant differences in levels obtained between Umani and InenNsai locations ($p < 0.05$) in wet season. Levels obtained in all sampling locations in both seasons were below permissible of 0.5 mg/kg in sediment in aquatic ecosystems given by WHO and DPR.

Table 3: Correlation between heavymetals in water for wet season

	Cd	Cr	Ni	Cu	V	Pb	Sn
Cd	1						
Cr	.954**	1					
Ni	.891**	.780**	1				
Cu	.910**	.840**	.925**	1			
V	.938**	.854**	.937**	.955**	1		
Pb	.929**	.922**	.875**	.912**	.919**	1	
Sn	.390	.392	.431*	.497*	.476*	.488*	1

. **. Correlation is significant at the 0.01 level (2-tailed). *.Correlation is significant at the 0.05 level (2-tailed).

Table 4: Correlation between heavy metals in water for dry season

	Cd	Cr	Ni	Cu	V	Pb	Sn
Cd	1						
Cr	.966**	1					
Ni	.934**	.906**	1				
Cu	.936**	.893**	.986**	1			
V	.880**	.805**	.967**	.967**	1		
Pb	.917**	.864**	.908**	.931**	.915**	1	
Sn	.881**	.842**	.874**	.844**	.880**	.862**	1

** . Correlation is significant at the 0.01 level (2-tailed). *.Correlation is significant at the 0.05 level (2-tailed).

Results in Tables 3 and 4 present correlations between heavy metals in water across all the sampling locations for wet and dry season respectively. Results presented in Table 3 showed that Cd had significant positive relationship with Cr ($r = .954$, $p < 0.01$), Ni ($r = .891$, $p < 0.01$), Cu ($r = .910$, $p < 0.01$), V ($r = .938$, $p < 0.01$), Pb ($r = .929$, $p < 0.01$). Cu showed significant positive relationship with V ($r = .937$, $p < 0.01$), Pb ($r = .875$, $p < 0.01$) while Pb showed correlation with Sn ($r = .488$, $p < 0.05$).

In dry season, results in Table 4 showed correlation between heavy metals in water. It shows that Cd had significant positive correlation with Cr ($r = .966, p < 0.01$), Ni ($r = .934, p < 0.01$), Cu ($r = .936, p < 0.01$), V ($r = .880, p < 0.01$), Pb ($r = .917, p < 0.01$) and Sn ($r = .881, p < 0.01$). Cu showed significant positive correlation with V ($r = .967, p < 0.01$), Pb ($r = .908, p < 0.01$), Sn ($r = .874, p < 0.01$) while between Pb and Sn, a significant positive correlation was established at ($r = .862, p < 0.01$). The results indicated that as the concentration of Cd in water increased, there was a corresponding increase in the concentrations of other trace metals studied in the water. Similar pattern was observed during wet season. That means as the concentration of one metal in water increased, there was also a corresponding increase in the concentrations of other metals in the water. By extension, it implies that all the metals determined, had similar source of contamination of the river. Hence for sustainability of the river under study for use by present and future generations, routine monitoring of the metals is strongly advocated.

Table 5: Correlation between heavy metals in sediment during wet season

	Cd	Cr	Ni	Cu	V	Pb	Sn
Cd	1						
Cr	.901**	1					
Ni	.963**	.859**	1				
Cu	.933**	.967**	.948**	1			
V	.965**	.880**	.992**	.960**	1		
Pb	.953**	.801**	.973**	.893**	.971**	1	
Sn	.991**	.912**	.982**	.960**	.983**	.962**	1

** . Correlation is significant at the 0.01 level (2-tailed). * .Correlation is significant at the 0.05 level (2-tailed).

Table 6: Correlation between heavy metals in sediment during dry season

	Cd	Cr	Ni	Cu	V	Pb	Sn
Cd	1						
Cr	.928**	1					
Ni	.844**	.823**	1				
Cu	.752**	.773**	.985**	1			
V	.912**	.833**	.978**	.928**	1		
Pb	.891**	.756**	.933**	.870**	.976**	1	
Sn	.923**	.852**	.969**	.918**	.994**	.970**	1

** . Correlation is significant at the 0.01 level (2-tailed). *.Correlation is significant at the 0.05 level (2-tailed).

Results in Tables 5 and 6 present correlation of heavymetals between heavy metals in sediment for wet and dry seasons respectively. For wet season (Table 5), results show that Cd had significant positive correlation with Cr ($r = .901$, $p < 0.01$), Ni ($r = .963$, $p < 0.01$), Cu ($r = .933$, $p < 0.01$), V ($r = .965$, $p < 0.01$), Sn ($r = .991$, $p < 0.01$). Ni had a significant positive correlation with Cu ($r = .967$, $p < 0.01$), V ($r = .880$, $p < 0.01$), Pb ($r = .801$, $p < 0.01$) and between Pb and Sn a positive correlation was established at ($r = .962$, $p < 0.01$) Table 4. During dry season (Table 6), Cd showed a significant positive relationship with Cr ($r = .928$, $p < 0.01$), Ni ($r = .844$, $p < 0.01$), Cu ($r = .752$, $p < 0.01$), V ($r = .912$, $p < 0.01$), Pb ($r = .891$, $p < 0.01$) and Sn ($r = .923$, $p < 0.01$). Cu also showed significant positive correlation with V ($r = .978$, $p < 0.01$), Pb ($r = .933$, $p < 0.01$) and Sn ($r = .969$, $p < 0.01$) while between Pb and Sn, a significant positive relationship was established at ($r = .970$, $p < 0.01$). The results revealed that as the concentration of Cd in sediment increased, there was corresponding increase in concentrations of other trace metals in sediment in both seasons. It implies that an increase in the concentration of one trace metal in sediment resulted in a corresponding increase in the concentrations of other metals in sediment as reported by Iwegbue (*et al.* 2012). By extension, it implies that all the trace metals studied had similar source of contamination to the studied river and hence the need for routine monitoring to prevent escalation.

Table 7: Spatial distribution between heavy metals in water and sediment in wet season

		Sediment						
		Cd	Cr	Ni	Cu	V	Pb	Sb
Water	Cd	.925**	.941**	.922**	.963**	.939**	.907**	.936**
	Cr	.869**	.991**	.850**	.968**	.875**	.790**	.887**
	Ni	.908**	.780**	.926**	.859**	.935**	.940**	.912**
	Cu	.983**	.864**	.989**	.937**	.987**	.974**	.992**
	V	.970**	.869**	.947**	.907**	.950**	.964**	.963**
	Pb	.922**	.929**	.911**	.944**	.926**	.870**	.934**
	Sn	.477*	.408*	.473*	.455*	.464*	.458*	.494*

** . Correlation is significant at the 0.01 level (2- tailed). * .Correlation is significant at the 0.05 level (2-tailed).

Table 8: Spatial distribution between heavy metals in water and sediment in dry season

		Sediment						
		Cd	Cr	Ni	Cu	V	Pb	Sn
Water	Cd	.973**	.980**	.891**	.828**	.918**	.861**	.929**
	Cr	.975**	.959**	.762**	.670**	.825**	.787**	.838**
	Ni	.967**	.856**	.885**	.797**	.953**	.953**	.958**
	Cu	.966**	.853**	.922**	.844**	.977**	.975**	.977**
	V	.897**	.778**	.925**	.855**	.977**	.973**	.973**
	Pb	.904**	.866**	.912**	.862**	.939**	.917**	.934**
	Sn	.854**	.848**	.792**	.730**	.843**	.787**	.860**

** . Correlation is significant at the 0.01 level (2-tailed). * .Correlation is significant at the 0.05 level (2-tailed).

Correlation analysis between heavy metals in water and sediment showed significant positive correlations both at $p < 0.05$ and $p < 0.01$. In wet season, results in Table 7 revealed that there was a significant positive relationship between Cd in water and that in sediment ($r = .925$, $p < 0.01$), Cr in water and sediment ($r = .991$, $p < 0.01$), Ni in water and sediment ($r = .926$, $p < 0.01$), Cu in water and sediment ($r = .937$, $p < 0.01$) and Sn in water and sediment ($r = .494$, $p < 0.05$). Results in Table 8 shows that during dry season, there was a significant positive relationship between Cd in water and that in sediment ($r = .973$, $p < 0.01$), Cr in water and in sediment ($r = .959$, $p < 0.01$), Ni in water and sediment ($r = .885$, $p < 0.01$), Cu in water and sediment ($r = .844$, $p < 0.01$), V in water and sediment ($r = .977$, $p < 0.01$), Pb in water and that of the sediment ($r = .917$, $p < 0.01$), Sn in water and sediment ($r = .860$, $p < 0.01$). These results of spatial distribution of trace metals between water and sediment for both seasons implies that there was a significant positive relationship between concentration of trace metals in water and the metals in sediment (Mohiuddin *et al.* 1012). This indicated that as the concentrations of trace metals in water increased significantly, there was a corresponding significant increase in the concentrations of the metals in sediment in both seasons. This positive relationship in levels of trace metals between water and sediment could be ascribed to desorption (deposition) of these chemicals on the sediment from overlying water. The rate of desorption of these chemicals from

the overlying water onto the sediment depends on the flow rate of the river, time frame, gravitational force, time, among other factors. Summarily, the heavier the load of these chemicals in the river, the greater they were enriched in sediment lying underneath reported by Iwegbue (*et al.* 2012). There were also some correlations ($r > 0.01$), which suggested some levels of relationship even though not significant (Tables 7 and 8).

4. CONCLUSION

The following conclusions were drawn based on the objective and statistical analyses of the results.

The results of the analysis indicated variations in levels of Cd, Cr, Ni, Cu, V, Pb and Sn analysed in water and sediment samples across the sampling locations of Qua Iboe River. Higher levels of the metals determined were recorded in dry season than wet season due to concentration and dilution effects of the metals in water and sediment in dry and wet seasons respectively. There was a significant positive relationship in the distribution between concentrations of heavy metals in water and sediment in the two seasons. It implied that as the concentrations of the metals in river water were increased, there were also corresponding increases in concentrations of the metals in the sediment. By extension, it implies that there is a positive correlation between the level water pollution and level of sediment pollution in aquatic ecosystem. It therefore means that the control of water pollution is directly a control of sediment pollution as well as aquatic organisms which live in the water. The levels of trace metals in aquatic ecosystem are attributed significantly to levels of anthropogenic activities other than natural sources since these activities introduce them in large amounts into the environment. Therefore to maintain safe limits of the metals determined in water and sediment in this research as recommended by WHO, NIS, USEPA in aquatic ecosystem, human activities in our environment must be carried out in compliance to regulatory framework by government.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

Disclaimer (Artificial intelligence)

Option 1:

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

Option 2:

Author(s) hereby declare that generative AI technologies such as Large Language Models, etc. have been used during the writing or editing of manuscripts. This explanation will include the name, version, model, and source of the generative AI technology and as well as all input prompts provided to the generative AI technology

Details of the AI usage are given below:

1.

2.

3.

REFERENCES

Akpan NA, Udombeh RB. and Mfon BU. Investigation of the Quality of Physicochemical Parameters in Water Samples from Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom State, Nigeria. *Asian Journal of Geological Research*. 2024;7(1): 31 – 40.

Akpan NA, Udombeh RB, Ukpong MB. and Iboroakam EU. Effects of Human Activities on Trace Metals in Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom State, Nigeria. *International Journal of Science Research Archive*. 2024;11 (01): 2120 - 2128.

Akpan NA, Udombeh RB. and Ekaete JA. Comparasion of Investigated levels of Physicochemicals Parameters in Qua Iboe River, OrukAnam Stretch, Nigeria with Portable water standards. *Asian Journal of Chemical Sciences*. 2024;14(03) 52 – 62.

Alinnor I. and AlagoaA. Trace Metals Distribution in Fish, Sediment and Water Samples from Nkisa River Nigeria. *British Journal of Applied Science and Technology*, 2014;4 (20): 2901 - 2913.

Amirah M, Afiza A, Faizal W, Nurliyana M. and Laili S. Human Health Risk Assessment of Metals Contamination through Consumption of Fish. *Journal of Environmental pollution*, 2013;(1): 1 - 5.

El-Zeiny M, El-Hamid H. and El-Alfy M. Anthropogenic impacts on water quality of River Nile and marine environment, Rosetta branch using geospatial analyses. *Journal of Environmental Science*. 2018;47: 89 – 101.

Emara M, Frank K, Dawuh A and Faith Assessment of heavy metals concentration in water and edible tissue of Nile tilapia (*Oreochromis niloticus*) from two fish farm irrigated with different water sources, Egypt. *International Journal of Environment*, M. 2015;4(1) 121-150.

Etuk BA, Udiong DS. and Akpakpan AE. Human Health Risk Assessment of Trace Metals in Water from Cross River Estuary, Niger Delta, Nigeria. *Asian Journal of Chemical Sciences*. 2020;7(3): 1 – 11.

Ido UH, Akpan NA, Udombeh RB. and Udoidiong OM. Bioaccumulation of Trace Metals in fish from Issiet River, Uruan, Nigeria. *Science Journal of Analytical Chemistry*. 2023;11(4): 40 – 48.

Iwegbue CM, Alimoro FO, Nwajei GE, Eguavoen OI. Concentrations and distribution of trace metals in water and streambed sediment of Orogodo River, Southern Nigeria. *Soil and sediment contamination: An international Journal*. 2012 Apr 1: 21(3): 382 – 406.

- Mohiuddin CM, Otomo K, Ogawa Y, Shikazono N. Seasonal and spatial distribution of trace metals in the water and sediment of the Tsurami River in Japan. *Environmental monitoring and assessment*. 2012 Jan,184: 265 – 79.
- Ogri OR, Eja ME. and Malu SP. Seasonal variations of heavy metals in surface sediment from Great Kwa River Estuary South Eastern coast of Nigeria. *International Journal of Environmental Science*. 2011;6(2): 78 – 85.
- Qu L, Huang H, Xia F, Liu Y, Dahlgren RM, Zhang M. and Mei K. Risk analysis of heavy metals concentration in surface water across the rural – urban interface of the Wen-Rui Tang River, China, Nigeria. *Journal of Environmental Pollution*. 2018;237: 630 -649.
- Udosen ED, Offiong NO. and Alade IG. Human health risk assessment of trace metals due to dietary intake of some edible fish species collected from Enyong Creek, Itu. Book of proceedings of 37th Annual International Conference, workshop and Exhibition, Akwa Ibom State. 2014;1224-1231.
- Udosen ED, Offiong NO, Edem S. and Edet JB. Distribution of trace metals in surface water and sediments of Imo River Estuary (Nigeria): Health risk assessment, seasonal and physicochemical variability, *Journal of Environmental Chemistry and Ecotoxicology*. 2016;8 (1): 22 – 25.
- Uwah IE, Solomon FD, Rebecca A.Etiuma, P. and Unyime EE. Evaluation of status of heavy metals pollution of sediments in Qua Iboe river estuary and associated creeks South – Eastern, Nigeria. *Journal of Environmental Pollution*. 2013;2(4):120 - 132.
- UwahEI, Edem EM, Udosen IE, Udosen ED. and Udoidiong OM. Quantification of Pollutants levels in water, sediment and winkles in Akani Obio, Uruan River, Nigeria. *Science Journal of Analytical Chemistry*. 20208;(2): 45 – 47.
- Uwah EI, Rapheal UO, Essien DU. and Okon MU. Atomic absorption spectrophotometric determination of elements in water, fish and sediment of Ataobong River, Nigeria. *Science Journal of Analytical Chemical Chemistry*. 2021;9(4): 68-69

