Original Research Article

PARTIAL DISTRIBUTION OF TRACE METALS BETWEEN WATER AND SEDIMENTIN QUA IBOE RIVER, ORUK ANAM, NIGERIA

Abstract:
Environment which man lives needs to be sustained for life continuity. Environmental sustainability should be understood as a responsibility for all humans living within the environment. Some people erroneously believe that environmental sustainability is solely the responsibility of government. It is the responsibility of both government and individuals as a sustained environment is beneficial to both inhabitants and the government. This calls for the need for education of inhabitants of the impacts of human activities and indiscriminate wastes disposal on humans and the environment. It is worthy of note of a positive relationship between concentrations of contaminants in water bodies and sediment lying beneath. This is because some pollutants in water bodies are naturally adsorbed onto sediment lying beneath. In this study, trace metals (Cd, Cr, Ni, Cu, V, Pb and Sn) in water and sediment were determined using ASS. A significant positive relationship was established between the trace metals in water and sediment in the studied river. Correlation analysis revealed positive relationships between Cd with Cr, Ni, Cu, V and Pb in the water and sediment in both seasons. In wet season, results revealed that there was a significant positive relationship between Cd in water and that in sediment ($r = .925$, $p<0.01$). In dry season, there was a significant positive relationship between Cd in water and that in sediment ($r = .973$, $p<0.01$). The partial distribution revealed that as the concentration of the metals in water increased, there was corresponding increase in concentration of the metals in sediment. This condition is capable of causing bioaccumulation of the metals in commercial fishes especially bottom feeders with potential consequences on man through food
Keywords: trace metals, water, sediment, analysis, ASS, and statistical.

Introduction

The environment and its compartments have been severely polluted by trace metals andother chemicals through anthropogenic activities. Although pollution occurs naturally, it is the anthropogenic activities that create more problems (Akpan, *et al.*2024; Etuk *et al.*, 2020). Researchers have revealed that the levels of pollution in different environmental media depend on levels of anthropogenic activities among other factors within these media. Variation in levels of pollution across geographical regions is a function of variation in 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 (Akpan *et al.* (2024). Trace metals are known to be naturally occurring contaminants, but anthropogenic activities introduced them in large quantities in different environmental compartments. This resulted in a reduced ability of the environment to support life effectively, thereby threateninglives of humans, animals and plants. This occurs due to their bioaccumulation in the food chain as a result of their non-degradable state. Environmental pollutants continue to be a worldwide concern and it is one of the greatest challenges faced by the global society. Among all the pollutants, trace metals have received significant attention to environmental chemist due to their non-biodegradabilityin the environment (El-Zeing*et al.* (2018). Trace metals are toxic even at low concentration and they include arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium among others (Ogri*et al.* (2011). Increasing levels of trace 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 withoutadequate treatment (Udosen *et al.* 2016).

Trace 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 activities 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 significantly through indiscriminate discharge of excessive wastes than what the environment can handle

Some important anthropogenic sources which significantly contribute to the trace metal 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 release nickel, vanadium, mercury, selenium and tin among other activities (Amirah *et al.,* 2013; Emara *et al.,* 2015). Researchers have found out that human activities contribute significantly to environmental pollution due to everyday manufacturing of goods to meet the demands of the escalatingpopulation.

2. Methods

2.1 Study Area

The study area, Qua Iboe River as shown in Figure 1 is located between latitude 04^{o}28'31. and 07^{o}10'12.4''0''North of the equator and between 06^{o}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 NsitUbium local government area before flowing into Alantic Ocean via Beight of Bonny.

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

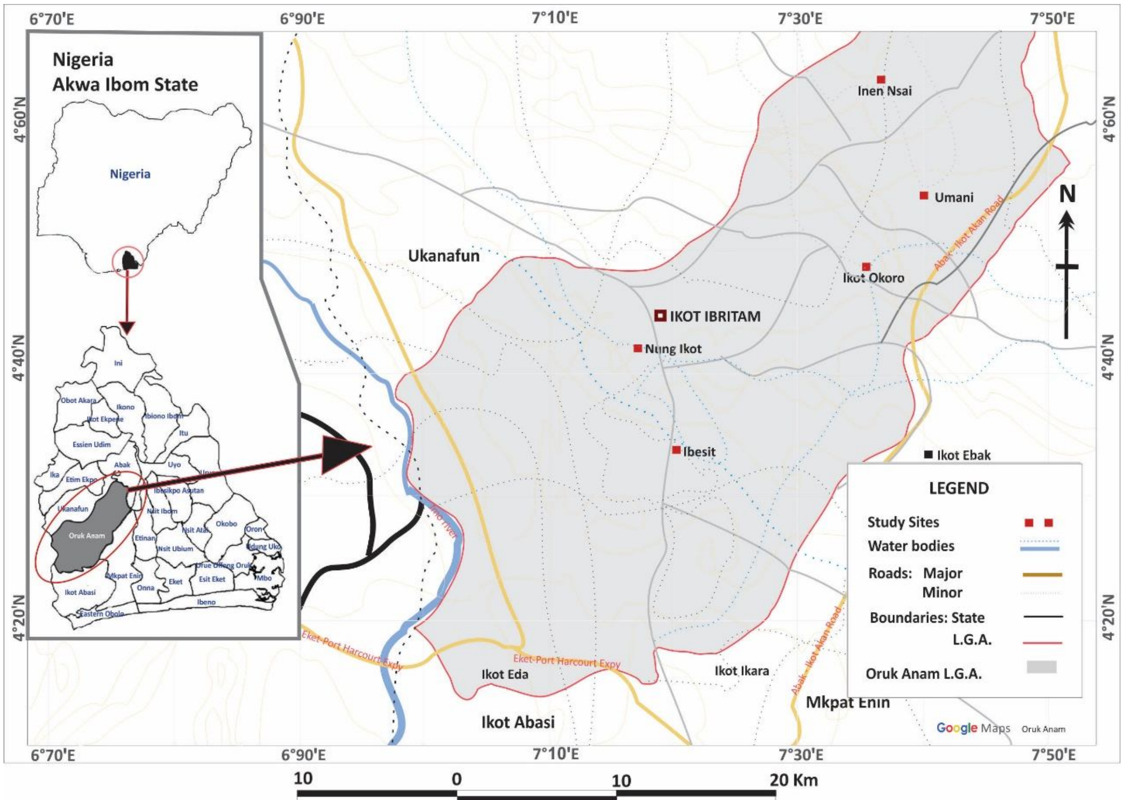

Fig 1 :Map showingthe study location

2.2 Samples Collection and Analysis

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

Determination of Trace Metals in Water: The concentrations of trace metals in water 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 HNO_3 (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. 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 Trace 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 (15mL) were added and the samples were digested on a hot plate in a fume chamber until dense white fumes appeared, signaling the end of digestion. The contents were cooled and filtered using filter paper (Whatman No.42) into 50mL volumetric flasks and made up to mark with distilled water. A blank was also prepared similarly with the omission of the sample (Ido *et al.*, 2023; Qu *et al.*, 2018). The digested samples were aspirated intothe AAS.

Quality Control

Quality control of the analytical data was guaranteed through the implementation of laboratory operating procedures, quality assurance and laboratory methods as well as the use of standard 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

3.1 Levels of Trace Metals in Water and Sediment Samples

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

Table 1: Levels (mg/L) of trace 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±a0.01	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 trace 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 Trace Metals in Water:

Table 1 shows the levelsof trace metals in water in both wet and dry seasons. The partial distribution of the trace metals in the water indicated Cu > Cd > Cr > V > Ni > Sn > P

Levels of Cadmium in Surface Water: The levels of cadmuim 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 in dry season. The results obtained in this study were consistent with levels obtained by Udosen*et al.*(2014)

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 in the dry season, the levels ranged between 0.02±0.09 and 0.087±0.004 mg/L. Higher levels were obtained in dry season than in wet season.

Levels of Nickel in Surface Water: The levels of Ni 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.

Levels of Copper in Surface Water: The mean levels of Cu 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. This result is consistent with result reported by (Uwah*et.*, (2020).

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

Levels of Lead in Surface Water: From Table 1, the levels of Pb in water across 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.

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 obtain ranged between 0.02±0.00 to 0.03±0.01

On the whole, the levels of all the trace metals determined in this study were higher in downstream than upstream due to increase in levels of anthropogenic activities downstream as well as naturally downstream flow of contaminants in the studied river. Levels of trace 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.

Levels of Trace Metals in Sediment: Table 2 shows the results of mean levels of trace 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.

Levels of Chromium in Sediment: The levels of Cr in sediment across all 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 (Uwah*et al*. (2021).

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 of Copper in Sediment: The level of Cu in sediment 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±0.01mg/kg in dry season. The levels of Cu recorded in sediment samples in this study were similar to levels recorded in other portions of the river by Uwah*et al.* (2013).

Levels of Vanadium in Sediment: The levels of vanadium in sediment in this study across all the sampling locations ranged between 0.03±0.01 and0.06±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 both dry and wet season respectively.

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).

Levels of Tin in Sediment: The levels of Sn in sediment 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 InenNsailocations ($p<0.05$) in wet season.

Table 3: Correlation between trace metals 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 trace 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 trace metals in water for wet and dry season respectively across all the sampling locations. Results presented in Table 3 show 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 trace 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. Similar pattern of correlation of the metals across the sampling locations was observed during wet season. That means as the concentration of one metal in water increased, there was a corresponding increase in the concentrations of other trace metals in the water.

Table 5: Correlation between trace 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 trace 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 trace metals between trace metals in sediment for wet and dry seasons respectively. For wet season (Table 5), results showed 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 ($r = .962$, $p<0.01$). 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 increase in the concentration of one trace metal in sediment resulted in a corresponding increase in the concentrations of other metals in sediment. By extension, it implies that all the trace metals studied had similar source of contamination to the studied river

Table 7: Correlation between trace 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: Correlation between trace metals in water and sediment in dry season

	Sediment						
	Cd	**Cr**	**Ni**	**Cu**	**V**	**Pb**	**Sn**
Cd	.973**	.980**	.891**	.828**	.918**	.861**	.929**
Cr	.975**	.959**	.762**	.670**	.825**	.787**	.838**
Ni	.967**	.856**	.885**	.797**	.953**	.953**	.958**
Water 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)

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Discussion

Partial distribution of the trace 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 ($r = .860$, $p<0.01$). The partial distribution of the trace metals between water and sediment for both seasons implied that there was a significant positive relationship between concentration of trace metals in water and the metals in sediment. 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 for 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 among other factors. Summarily, the heavier the load of these chemicals in the river, the greater they were enriched in sediment lying underneath. There were also some correlations at ($r > 0.01$), which suggested some levels of relationship even though not significant (Tables 7 and 8).

Conclusion

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

The water and sediment samples obtained from Qua Iboe River contained variable levels of the investigated trace metals (Cd, Cr, Ni, Cu, V, Pb and Sn).The investigated trace metals showed seasonal variations in the samples across all the sampling locations. Correlation analyses revealed positive relationships between Cd with Cr, Ni, Cu, V and Pb in the water and sediment in both seasons. There was also significant positive relationship between concentrations of trace metals in water and sediment in the two seasons. The partial distribution revealed that as the concentrations of the trace metals in river water increased, there was also a corresponding increase in concentrations of the metals in sediment beneath the river. By extension, it therefore means that control of the levels of contaminants in water implies control of contaminants levels in sediment also.

Availability of data and materials

Data were generated during statistical analysis.

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