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Ecological and Health Risk Assessment of Heavy Metals in Sediments, Surface Waters and Oysters (*Crassostrea Gasar*) from Eastern Obolo Marine Ecosystems, Akwa Ibom State, Nigeria

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Abstract: *The contamination of the environment by heavy metals is significant because of the non-biodegradable and persistent nature of these sets of metals. Reports on the contamination of water by heavy metals can be regarded as uncertain if the levels of these metals in sediment are not taken into consideration. Sediments, surface waters and oysters (Crassostrea gasar) from the Atlantic coastline, Iko river, Obolo river, Amadaka river and Emeremen river were analyzed for the levels of the concentrations of Co, Tl, Th, U, Se, Tl and Ag using inductively coupled plasma-optical emission spectroscopy method. Seasonal and spatial distribution of the metals were determined as the bases for ecological and health risk assessment of the environment. The distribution of the analyzed metals in the sediment followed te following order ((mg/kg dw) Th (38.05) > U (22.70) > As (11.06) > Tl (0.56) > Se (0.45) > Co and Ag (below detection limit). In the oysters were Th (46.67) > U (9.20) > As (7.11) > Se (5.05) > Tl (0.63) > Co and Ag (below detection limits). The water had far lower concentrations of the metals (0.01 – 0.19 mg/l). The results obtained indicate no statistically significant variation between the seasonal sediment data sets at $P \leq 0.05$. A strong correlation (0.50 – 0.99) between the metals was revealed indicating a common source (mainly anthropogenic) for the metals. Of the five study sites, only the Atlantic coastline and Iko river were contaminated by some of the metals studied; Se, Th, U, As and Tl, with Iko river found to be more polluted. Co and Ag were below the detection limit in all the study sites in sediments, water and oysters in both seasons. All the metals were below the detection limit along Obolo River, Amadaka River and EmeremeEastern River during both seasons, thus indicating the sites were relatively uncontaminated by the heavy metals studied. The metal contamination status was significantly bio-indicated by the oysters at all the study sites in both seasons. The ecological risk indices revealed no contamination status for Obolo river, Amadaka river and Emeremen river, but low to moderate pollution status for the Atlantic coastline and Iko river, especially for As, Th and U. Based on bioconcentration data of the oysters, the health risk indices (daily intake of metal, health index, target hazard quotient and total target hazard quotient, etc) have revealed that As in the oysters from Iko river and the Atlantic coastline of Eastern Obolo may pose a significant health risk to consumers. Adequate regulation and remediation of the ecosystems to safeguard ecological and human health is therefore recommended.*

Keywords: *Sediments, Heavy metals , Health index, Surface water, Pollution Hazard quotient*

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1.0 Introduction

Crude oil and gas exploration and production within the Eastern Obolo marine ecosystems, in Akwa Ibom State in the Niger Delta, Nigeria, has been on for over six decades and is still ongoing given the current new investments in oil and gas within the Oil Mining License Field 13 (OML 13). Coupled with some rapid urbanization and industrialization activities, there are reported cases of significant contaminations of Eastern Obolo marine and other aquatic environments by several several organic and inorganic pollutants, including heavy metals and polycyclic aromatic hydrocarbons (PAHs), etc (Enemugwem, 2009; Etesin *et al*. 2013; Akpan *et al.*, 2019; Udoidiong, 2010; Nwaichi and Ntorgbo, 2016; Ubong *et al.*, 2020; Yawo and Akpan, 2001).

The concerns are the implications for the health and wellbeing of humans and resident biota species which interact regularly with various pollutants in the aquatic ecosystems of the area (Enemugwem, 2009; Chijioke *et al.*, 2018). This is so, given the fact that over 70% of inhabitants of Eastern Obolo are traditionally engaged in inland and deep-sea fisheries, thus leaving a small percentage of the population in farming and fish-drying racket craft (Akasi - local) for their livelihood (Olujide, 2006; Enemugwem, 2009; Igbemi *et al.*, 2019). The locals are mostly engaged in artisanal inland and deep-sea pelagic and benthic fisheries for their livelihood, a situation which brings them regularly in contact with the various components of the marine ecosystems such as seafood, sediments, water and air (Enemugwem, 2009; Georg *et al.*, 2014; Udotong *et al.*, 2017; Raghukumar, 2017). These and other activities have been potential anthropogenic causes of pollution of the ecosystems in the area (Igbemi *et al.*, 2019; EIA, 2020). Studies have shown that activities which disturb the sea bed such as trawling, dredging, digging, piling or drilling, etc. may and often expose sediment-trapped heavy metals and other contaminants from the sea bed and thereby lead to their redistribution and recontamination among components of affected ecosystems, either temporarily or for the longer term (Ohimain *et al.*, 2008; Fennel *et al.*, 2019).

Rezaei *et al*. (2021), reported an increase in contamination of the north coast of the Persian Gulf, Iran, by some heavy metals and attributed it to effluents from a nearby petrochemical industry. Studies have also shown that desalination processes are a source of pollution in marine/aquatic ecosystems (Hosseini *et al*., 2021). Some recent studies, including a report by the United Nations Environmental Programme (UNEP) in 2011, have found the Eastern Obolo area as being highly polluted, or as having a potentially high risk of being significantly contaminated by several point and non-point sources, especially those related to the petroleum industries operating in the area and the Niger Delta region of Nigeria (Benson and Etesin, 2007; Udoidiong, 2010; Udoh and Ekanem, 2011; Chijioke *et al.*, 2018; Igbemi *et al.*, 2019; Ubong *et al.*, 2020; Yawo and Akpan, 2021).

Much of the pollution problems of the area also derive from its location along the

Niger Delta coastline. This has predisposed the area to several intra and trans-boundary contaminations from other parts of the Niger Delta region. Eastern Obolo area is contaminated through the atmosphere, the interlinked inland waterways, as well as the Atlantic Ocean (Enemugwem, 2009; Udotong *et al.,* 2017). Specific reference is often made to the spread of oil sleeks and dead aquatic organisms in 1998 to Eastern Obolo coastline and the Lagos lagoon within few days of a major crude oil spill from oil producing facility located along Ibeno coastline (Enemugwem, 2009; Udotong *et al.*, 2017). The significance of this is underscored by the current ranking of the Niger Delta as one of the five most petroleum polluted deltas in the world (Nnaji and Uzoekwe, 2018).

There have been several episodic oil spills within the Niger Delta over the years, and most of these have affected Eastern Obolo environments directly or indirectly (Enemugwem, 2009; Udotong *et al.*, 2017; Chijioke *et al.*, 2018). Such incidences have been well documented and there are some reported data giving quantitative estimates of crude oil spilled in the Niger Delta on yearly bases from 1976 (Udotong *et al.*, 2017; Chinedu and Chukwuemeka, 2018). Generally, well over 9 – 13 million barrels of crude oil has been spilled in the Niger Delta over the past 50 years (Nnaji and Uzoekwe, 2018).

Heavy metals contaminations of the environment may cause different kinds of stress, including death and disruption of the delicate balance in marine and terrestrial ecosystems' biodiversity due to their toxicity (Weissmannova *et al.*, 2019). Lead (Pb) exposure alone is reported to be causing about 3% of cardiovascular diseases and 2% of the ischæmic heart disease burden worldwide (WHO, 2010). Presently, Nigeria is ranked fifth, with an annual pollution-related death toll of 257,093, among the ten countries with the highest pollution-related deaths worldwide (Weiss, 2017).

This study was inspired by the need to ascertain the current heavy metals contamination status of marine ecosystems in Eastern Obolo**.** Although several studies have been conducted on Iko river, there has been a dearth of pollution information/data on other rivers along Eastern Obolo coastline. This study therefore aimed at determining the levels of seven selected heavy metals in five study sites along Eastern Oboo coastline, evaluating the variation of the heavy metals' concentration in both rainy and dry seasons and determines the possible ecological and health hazards associated. The environmental components of interest in this study are sediments, surface water, and oysters (*Crassostrea gasar*).

2.0 Materials and Methods

2.1 The Study area

This study was conducted along Eastern Obolo marine ecosystems; precisely some of the rivers and Atlantic coastline. Eastern Obolo is located on the continental fringe of the Atlantic coast, presently in Eastern Obolo Local Government Area (L. G A.), Akwa State, Niger Delta, Nigeria (Figure 1). Eastern Obolo L.G. A, lies between latitudes $4^0$26” and $4^0$50” North and longitude $7^0$30” and $7^0$55” East; that is, within the equatorial region as well as the tropical mangrove belt and the Gulf of Guinea, and is bound to the North by Mkpat Enin and Ikot Abasi LGAs, the South-East by Onna L.G.A, the West by the Andoni L.G.A. (Rivers State). and the south by the Atlantic Ocean (Enemugwem, 2009; Bassey *et al*, 2019; Igbemi *et al.*, 2019).

The geological and physiographic information of the Eastern Obolo area and coastline indicates that the area belongs to the lithostratigraphic unit known as the Benin Formation. That is, the topmost stratigraphic layer of the Niger Delta region is characterized by alternating sequences of gravel, sand, silt, clay and alluvium. The Benin formation which this area belongs is about 200 m thick and lies over the Agbada Formation and Akata Formation at the base (in that order) (George *et al*., 2014; Harry *et al*., 2017; Nwawuike and Ishiga, 2018; Bassey *et al*., 2019; Igbemi *et al*., 2019). The coastal marine vegetation of the area is characterized by mangroves, Nypa palms, grasses, etc. clustered on the mangrove marsh planes along river banks and sand beaches (Etesin *et al*., 2013; Geoge *et al*., 2014; Juhl, 2018; Harry *et al*., 2017). Eastern Obolo area has two main seasons; the rainy (April - October) and dry (November - March) seasons each year. It has an average temperature of 26 ^{0}C to 28 ^{0}C and an average annual rainfall estimated between 2000 mm to 3000 mm (Igbemi *et al*., 2019; Bassey *et al*., 2019). Some slight variations in the climatic conditions, duration of the seasons, temperature and rainfall have been reported for the area due to the global climate change phenomenon (Bassey *et al*., 2019). The hydrology of the area includes many rivers, creeks and the Atlantic Ocean, among which are Iko River, Obolo River, Obianga River and Imo River estuaries (Enemugwem, 2009).

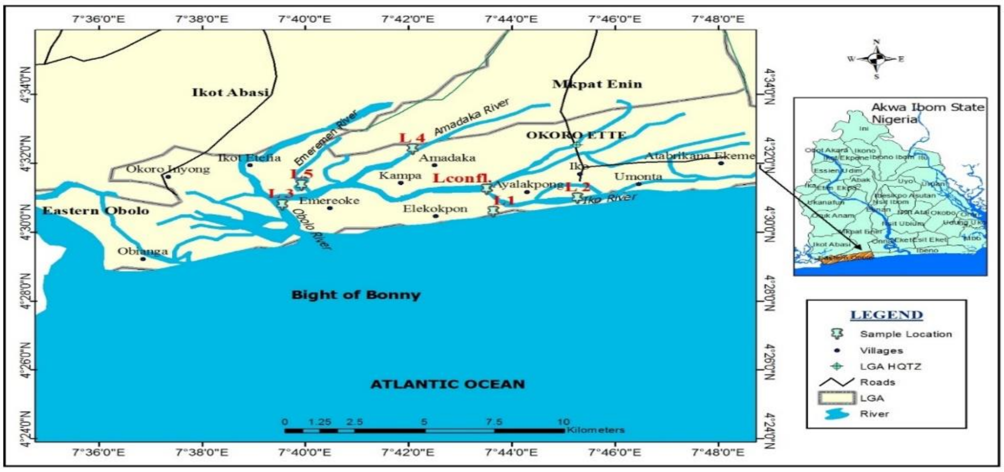

Fig 1: Map showing Eastern Obolo coastline and sampling locations

2.2 Sampling Locations

Five sampling sites were selected and marked out for the present study. (Table 1 and Figure 1). As earlier noted, Eastern Obolo has four main estuaries with their mouths along the Atlantic Ocean coastline at the Bight of Bonny (Enemugwem, 2009; Udoidiong, 2010; Etesin *et al.*, 2013; Harry *et al.*, 2017). The geographic coordinates of each of the study sites were obtained with a Global Positioning System (GPS) (Garmin GPS Map 785) and presented in Table 1.

Table 1: The sampling locations and their geographic coordinates

		Coordinates	
Location No	**Name of Location and Sediment type**	**Latitude**	**Longitude**
L 1	Atlantic Ocean beach** (white sand)	04^{0}30’.405”N	007^{0}43’.663”E
L 2	Iko river (at Umonta) (mud)	04^{0}30’.734”N	007^0 45’.199”E
L 3	Obolo river (mud)	04^{0}30’.705”N	007^0 39’.354”E
L 4	Amadaka river* (at Amadaka beach) (mud)	04^{0}32’.227”N	007^{0}42’.159”E
L 5	Emeremen river* (mud)	04^{0}31’.154”N	007^{0}39’.808”E

****The sediments along L1 were ocean beach sand, but mangrove mud at all the other locations.**

Amadaka and Emeremen Rivers are located farther downstream of Eastern Obolo River which feeds and empties them from and into the Atlantic Ocean.

2.3 Sample collection

Seasonal samples were collected at each study site in July (rainy season) and February (dry season) of 2021 in line with procedures described by Onjefu *et al*. (2016, 2020) and Tuo *et al*. (2019). Three replicate samples of each of the sediments, overlying river water and oyster clusters were collected within 10 m radius of each geographic coordinates (Bassey *et al*, 2019; Tuo *et al.*, 2019). This enabled mature oysters to be carefully collected as described by Benson *et al*. (2016), Chariton *et al.* (2016). All the samples were collected during the low tide as recommended by the United States Environmental Protection Agency (US EPA), to ensure the samples were exposed to the same conditions during the time of collection (US EPA, 2002).

2.3.1 Sediments collection and preparation

Triplicate 5-10 kg sediment samples were collected at each sampling site at depths of 0 - 10 cm from the surface. This was done with the help of a Van Veen grab sampler. The sediments were collected at the intertidal, backwash or littoral zone, which is also the zone where clusters of oysters were found (Benson *et al*, 2016; Kiin-Kabari *et al*, 2017; Nwawuike and Ishiga, 2018; Tuo *et al*, 2019). Each collected sediment sample was immediately transferred into a black polythene bag which was pre-washed and rinsed with dilute (20%) nitric acid to ensure the metals were not adsorbed on the walls of the bags. Each bag of the sample was immediately labelled, stored in a closed ice-cooled box and taken to the laboratory for analysis (Batley and Simpson, 2016 a; Benson *et al*., 2016; Simpson *et al.*, 2016).

Sediment samples from each sampling site were immediately homogenized when moist and a portion of the homogenized sediments were air-dried for over 48 hours. The dry sediment samples were then ground with porcelain pestle and mortar and then sieved to less than 2 mm. A 2 g portion of the sieved sediments was taken and acid-digested to solubilize their metal content, according to the modified method by Simpson and Batley (2016).

2.3.2 Water collection and preparation

The overlying river and ocean water samples were collected at the sampling sites, along with the sediments and oysters. The water samples were collected with plastic bottles (pre-rinsed and washed with dilute nitric acid) held below the surface at about 10 - 25 cm depth and towards the water current. Few drops of analytical-grade nitric acid were added to each water sample in the bottle to attain pH < 2. The acid was added to minimize loss of the heavy metals content through adsorption, sorption and/or precipitation on the walls of the bottles (APHA, 2012; Rice *et al.*, 2012; Benson *et al.*, 2016; US EPA, 2023). Then the sample bottles were immediately covered and labeled, placed in an ice cooled box, and transported to the laboratory for analysis.

2.3.3 Oysters collection and preparation

The oysters (*C. gasar*) samples were collected from the natural field population at each sampling site, and at low tide. The low tide exposed the oyster spats and clusters and made it easy to assess and collect the mature samples (4 - 8 cm long) (Santhanam, 2018; Tuo *et al*., 2019). With their shells intact, the oysters were scraped or cut from their mangrove root or Nypa palm substrate with a sharp knife.

The oyster samples from each sampling site were put in a pre-rinsed plastic bag, labelled and transported in an ice-cooled box to the laboratory. The composite oyster meat or tissues, oven-dried at 105 ^{0}C for about 48 hours; oven model DHG-9070A) were ground with porcelain mortar and pestle, and then sieved to obtain < 2 mm size powdered tissue samples (Benson *et al.*, 2016; US EPA, 2007, 2023). Precisely, 2 g size of each sieved oyster meat was put into a digestion flask for acid digestion (Benson *et al*, 2016; Tuo *et al.*, 2019).

2.3.4 Temperature and pH

The pH and temperature of the water samples were determined in situ. The pH was determined directly with a pH meter (Ohaus Starter 2100). Temperature was also determined directly with a digital thermometer (Model: Digi-thermo Quartz, range: -55 - 148 ^{0}C).

2.3.5 Digestion of Samples

The sediments, water and oyster samples were digested to obtain the total recoverable metals (TRM) from each as described by Simpson *et al.* (2016). The US EPA method 3052, as well as standard methods described by APHA (2012), Rice *et al.* (2012), Simpson *et al.* (2016), Tuo *et al* (2019), Onjefu *et al.* (2016, 2020) and US EPA (2007, 2023) using mixed acids of HCl: HNO_3 (3: 1) to solubilize the content of the metal before the use of inductively coupled plasma-optical emission spectrophotometer (ICP-OES) to determine the metals.

2.3.6 ICP-OES analysis

Inductively coupled plasma-optical emission spectrophotometer (Model: Agilent 720 ICP-OES) was used to analyze the total metal content in the digest. Prior to the ICP-OES analysis the samples of the environmental matrices (sediments, water and oyster tissues) had been prepared as described above.

2.3.7 Statistical Analyses of results

Statistical analysis on whole sediment concentrations of the heavy metals was performed using Minitab 17 statistical software. A two-tailed t-test ($P \leq 0.05$; hypothesized means difference = 0) was used to evaluate the significance of variability between the dry and rainy seasons' heavy metals data sets obtained
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from the five study locations as described by APHA (2016) and Tuo (2019). The Pearson's correlations between the metals were also determined for sediment data from the five sampling sites for the dry and rainy seasons, respectively (Tables 5 and 6).

3.0 Results and Discussion

3.1 Distribution and Concentrations of the Heavy Metals along the Sampling Locations

The sediments, waters and oysters (*C. gasar*) tissue concentrations of heavy metals measured in this study (Co, Ag, Tl, As, Se, Th and U) along the five sampling locations are presented in Tables 2–3. In the Tables are the temporal {dry (D) and rainy (R) seasons} as well as spatial (locations L1, L2, L3, L4 and L5) distributions of the heavy metals under study.

3.3 Heavy metals in sediment

Heavy metal concentrations in the sediments were used to screen the sediments for ecotoxicological quality. This was carried out as a first-tier risk assessment approach established within the framework for heavy metals' hazard characterization It involved the comparison of measured metals concentrations with their world average reference background values reported by Turekian and Wedepohl (FDEP, 1994; WHO, 2010; Onjefu, *et al.*, 2016, 2020; El-Alfy *et al*., 2020; US EPA, 2007, 2023). Sediment was the preferred media for this assessment owing to its role as the major repository of contaminants, including heavy metals in aquatic environments (FDEP, 1994; Benson *et al.*, 2016; El-Alfy *et al*., 2020; Onjefu *et al*., 2016, 2020).

Table 2: The seasonal sediments concentration (mg/kg dw $\pm$ s. d, n = 3) of some heavy metals along the Atlantic coastline and Rivers in Eastern Obolo L.G.A and reference shales and WHO values.

Heavy Metal	L1		L2		L3		L4		L5		Shales*	WHO *
	D	R	D	R	D	R	D	R	D	R		
Co	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	19.00	___
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL	LDL	BDL	BDL	0.07	___
Tl	BDL	BDL	BDL	0.56±1.00	BDL	BDL	BDL	BDL	BDL	BDL	1.40	___
As	8.48±1.00	3.61±0.99	11.06±2.50	9.63±1.00	BDL	BDL	BDL	BDL	BDL	BDL	13.00	20.00
Se	BDL	0.45±1.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.60	___
Th	19.10±4.50	16.85 ±6.90	38.05±9.00	27.24±11.50	BDL	BDL	BDL	BDL	BDL	BDL	12.00	___
U	6.48±0.50	0.97±0.99	22.70±5.50	15.82±3.50	BDL	BDL	BDL	BDL	BDL	BDL	3.70	___

***Sources: Onjefu *et al.* (2016, 2020) and Turekian and Wedepohl (1961), BDL=below detection limit; s.d. = standard deviation, dw = dry weight**.

Table 3: The seasonal water concentrations (mg/l, mean $\pm$ s. d, n = 3) of some heavy metals along the Atlantic coastline and inland rivers of Eastern Obolo L.G. A.

Heavy metals	**L1**		**L2**		**L3**		**L4**		**L5**	
	D	**R**	**D**	**R**	**D**	**R**	**D**	**R**	**D**	**R**
Co	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tl	0.02±0.00	0.01±0.03	0.02±0.04	BDL	BDL	BDL	BDL	BDL	BDL	BDL
As	0.03±0.01	0.002±0.01	0.04±0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	BDL	BDL	BDL	0.02±0.02	BDL	BDL	BDL	BDL	BDL	BDL
Th	0.19±0.15	0.16±0.10	0.12±0.14	0.27±0.15	BDL	BDL	BDL	BDL	BDL	BDL
U	0.03±0.04	0.13±0.02	0.08±0.03	0.13±0.04	BDL	BDL	BDL	BDL	BDL	BDL

Table 4: The seasonal concentrations (mg/kg dw, mean ± s d, n = 3) of heavy metals in oyster tissues from Eastern Obolo L.G.A. coastline

Heavy metal	L1		L2		L3		L4		L5	
	D	R	D	R	D	R	D	R	D	R
Co	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Tl	BDL	BDL	BDL	0.63±6.67	BDL	BDL	BDL	BDL	BDL	BDL
As	5.28±1.98	5.42±1.48	7.11±0.49	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	4.50±1.98	3.99±1.48	5.05±0.49	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Th	0,08±2.97	11.40±4.93	11.85±4.39	46.67±10.00	BDL	BDL	BDL	BDL	BDL	BDL
U	4.70±1.48	0.45±2.96	9.20±4.87	8.04±33.33	BDL	BDL	BDL	BDL	BDL	BDL

Table 5 Heavy Metals correlation data obtained for sediments in the dry season

	Co	*Ag*	*Tl*	*As*	*Se*	*Th*	*U*
Co	1						
Ag	-	1					
Tl	-	-	1				
As	-	-	-	1			
Se	-	-	-	-	1		
Th	-	-	-	0.972367	-	1	
U	-	-	-	0.898869	-	0.976336	1

Table 6 Heavy metals correlation data obtained for sediments in the rainy season

	Co	*Ag*	*Tl*	*As*	*Se*	*Th*	*U*
Co	1						
Ag	-	1					
Tl	-	-	1				
As	-	-	0.928319	1			
Se	-	-	-0.25	0.1279	1		
Th	-	-	0.815962	0.972404	0.355758	1	
U	-	-	0.998188	0.949009	-0.19128	0.849272	1

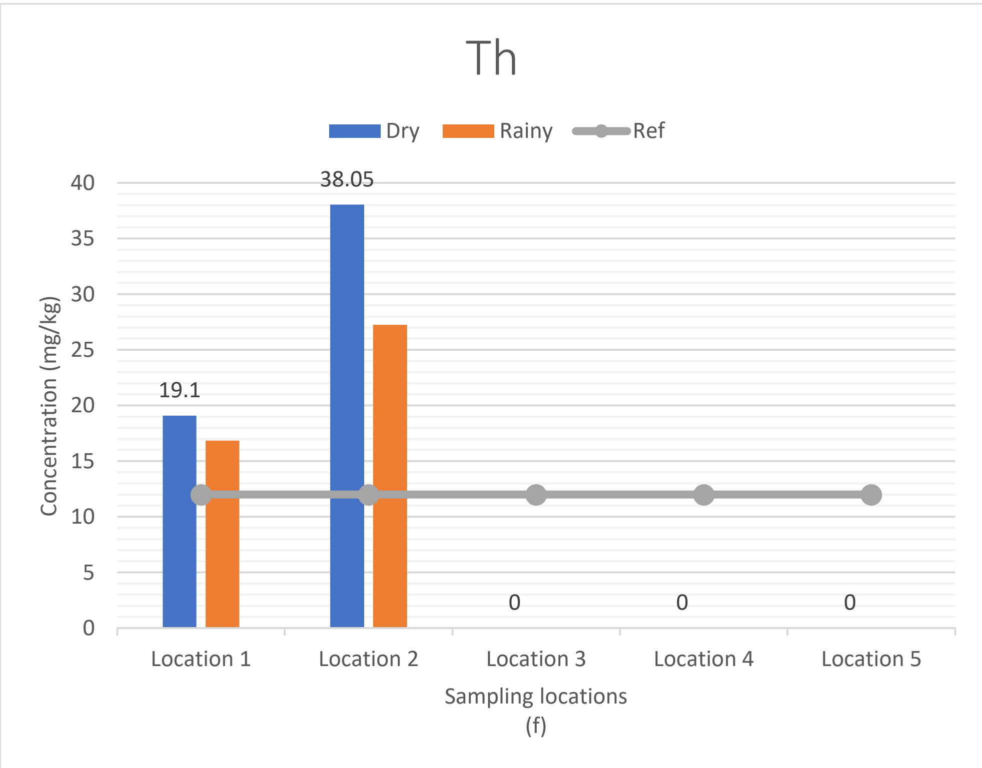

Fig 2: Concentrations of thorium in sediments with reference background values

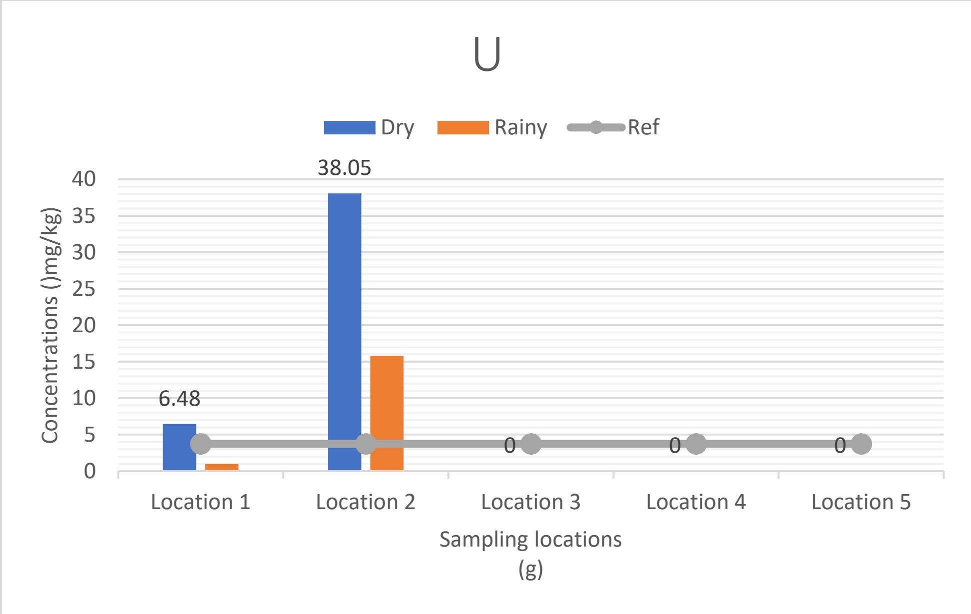

Fig 3: Concentrations of uranium with reference background values

3.4. 1 Heavy metals in sediments from the study locations

The results in Table 2 showed that the sediments generally contained higher concentrations of the detected heavy metals than the water and oysters. This is in line with previous studies which have established sediments as the major repository of contaminants, including heavy metals in aquatic environments (Onjefu *et al.*, 2016, 2020). The strong correlation (0.5-0.99) in Tables 5 and 6 between the metals in the sediments (Tables 5 and 6) revealed they share a common origin. Also, the two-tailed t-test results indicated no statistically significant variations between the seasonal data sets ($P < 0.05$). All the metals were below the detection limit (BDL) along L3 (Obolo River), L4 (Amadaka River) and L5 (Emeremen river). Co and Ag were also below the detection limit along L1 (the Atlantic coastline) and L2 (Iko River). These results are slightly similar to results from other studies in the Niger Delta, Nigeria.

Even though heavy metals are usually associated with crude oil spills, Owamah (2013) determined Pb, Fe, Co, Cd, Ni, Cu and Cr, and found Co with the lowest concentration in sediments from some petroleum-impacted rivers in the Niger Delta region of Nigeria. More so, Ogwugwa *et al.* (2018) found Co at 0.92 mg/kg-dw and Ag at 1.04 mg/kg-dw in sediments from Ogoniland, Niger Delta, a region highly impacted by crude oil spills.

The metal Tl was found at 0.56 mg/kg dw at L2 only during the rainy season along L2, and Se was found at 0.45 mg/kg dw only during the rainy season along L1. Their singular occurrence may be associated with precipitation from the atmosphere or runoff by rainfall. Burning of fossil fuels and vegetation or sediment dredging along L2 may therefore be some of its possible sources (Lavenir *et al.*, 2020; McMaster *et al.*, 2020; Doulgeridou *et al.*, 2020).

Th, As and U were found only along L1 and L2 during both seasons at levels between 0.97 and 38.05 mg/kg dw. However, only Th and U were present at levels above their reference background values (Figures 2 and 3), thus indicating some significant contamination by both metals The results show that L2 was the most contaminated in this study followed by L1. Petroleum-related anthropogenic sources such as drilling and dredging along L2 were possibly the other sources of contamination of both sites. L2 was dredged in 2021. Location L1 which lies in the direction of the flow of water from L2 during low tide was probably contaminated by materials from L2. Sampling site L1 having lower heavy metals concentrations may have been due to higher sandy grain sizes, low organic matter and binding sites at L1 (Simpson and Batley, 2016; Juhl, 2018; Hamid *et al.*, 2022). The higher concentrations obtained during the dry season may be due to less solubilization of the metals due to water acidification as a result of acid rain associated with petroleum gas flaring (Attah, 2012; Fennel *et al.*, 2019). Studies have shown that lower pH favours the solubility of heavy metals and vice versa (Onjefu *et al*., 2016, 2020; US EPA 2023).

3.4.2 Heavy metals in water from study locations

The surface water at the five sampling sites had the lowest concentrations of heavy metals (0.01 – 0.19 mg/l). Generally, a distribution pattern very similar to the sediments was observed for the heavy metals in water at the five sampling sites (Table 3). As in the sediments and oysters both Co and Ag were below the detection limit at all the sites in both seasons. Also, as in the other environmental matrices all the heavy metals studied were below detection limit along L3 (Obolo river), L4 (Amadaka river) and L5 (Emeremen river). The metals were present only along L1 (the Atlantic coastline) and L2 (Iko river) during both seasons.

Again, like the sediments Se occurred only at L2 during the rainy season. Similar results found by other researchers elsewhere were attributed to precipitation and/or solubility of the heavy metals due to high pH and the ambient temperature of surface water (Onjefu *et al.*, 2016, 2020; Benson *et al.*, 2016; US EPA, 2007, 2022, 2023). The present results also confirmed that sediments were the major reservoir of the metals detected, which possibly have the same anthropogenic sources as those in the sediments. In comparison with the results in Table 4, another factor suggested for the lowest levels of the metals in the water would be the significant bioaccumulation of the detected heavy metals by aquatic organisms, including oysters. The oysters had higher concentrations of the metals than the water (Table 4).

Oysters have been reported as good bioindicators of heavy metals contamination due to their ability to bioaccumulate and tolerate high levels of metals in their tissues (Kiin-Kabari *et al.*, 2017; Tuo *et al.*, 2019; Maher *et al.*, 2016; Manickavasagam *et al.*, 2019). The present results are in line with findings reported by Onjefu *et al.* (2016, 2020), Benson *et al.* (2016), Maher *et al.* (2016), McMaster *et al.* (2020), Tuo *et al.* (2019) and Hamid *et al. (*2022). As already noted, higher pH favours metals precipitation from water, while higher temperatures favour solubility of metals (Simpson and Batley, 2016; Pobi *et al.*, 2019; Hamid *et al.*, 2022). The range of pH and temperature measured were pH 5.75- 7.37 and 27- 33 ^{0}C, respectively.

3.4.3 Heavy metals in Oysters from study locations

The results in Table 4 indicate that the oysters had levels of the metals at L1 and L2 between those in the sediments and surface water (0.08 – 46.67 mg/kg dw). Similar distribution patterns to those in water and sediments were again observed in the oysters, which significantly reflected the occurrence and relative abundance of the metals at the five sampling sites. All the metals were found below the detection limit in the oysters from L3 (Obolo River), L4 (Amadaka river) and L5 (Emeremen River) in both seasons. Also, Co and Ag were below the detection limit at L1 and L2 in both seasons. Th and U had the highest concentration values as in the sediments. The present bioaccumulation results have confirmed previous findings that oysters are good bioindicators of heavy metal contaminants in marine environments (Maher *et al.*, 2016; Manickavasagam *et al.*, 2019; Tuo *et al.*, 2019).

3.5 Ecological risk assessment

3.5.1 Geoaccumulation Index (lgeo)

The accumulation index (lgeo) predicts the degree of contamination of sediments by heavy metals. The lgeo determination for each metal was based on the equation developed by Muller which is widely used by researchers (Benson *et al*., 2016; Abdullah *et al*., 2020):

$$\text{Igeo} = \log 2 \frac{Cn}{1.5Bn} \quad (1)$$

where log2 = 0.3010, Cn is the measured concentration of the metal/element in the sediment or soil sample, and Bn represents the standard reference background level for the metal (generally considered as the pristine, preindustrial or uncontaminated level or concentration of the metal). The factor 1.5 is the constant introduced to normalize possible natural (lithogenic) variations in the sediments or soils (Abrahim and Parker, 2008; Romano *et al.*, 2015; Benson *et al*., 2016; Abdullah *et al*., 2020).

The geoaccumulation index classifies sediments into seven (7) grades as originally proposed by Muller for the assessment of sediment or soil quality. They are:

i. Class 0 – lgeo value < 0 – implying that the sample is practically unpolluted;
ii. Class 1 – lgeo valaue > 0 – 1, rated as unpolluted to moderately polluted;
iii. Class 2 – lgeo > 1 – 2, moderately contaminated/polluted;
iv. Class 3 – lgeo > 2 – 3, moderately to slightly polluted;
v. Class 4 – lgeo > 3 – 4, moderately to strongly polluted;
vi. Class 5 – lgeo > 4 – 5, strongly to extremely polluted; and
vii. Class 6 – lgeo > 5, very strongly to extremely polluted (Abrahim and Parker, 2008).

The lgeo results for the sediments are presented in Table 7. The Igeo index results (Table 4.2) indicated unpolluted to moderately polluted status for the sediments concerning the metals determined along L1 and L2. Having all the metals below the detection limit along L3, L4 and L5 suggested that those sites were relatively unpolluted concerning the metals under study. The foregoing lgeo index results suggested a strong anthropogenic input of heavy metals along the coastline of Eastern Obolo.

Table 7 Geoaccumulation index (lgeo) for sediments along Eastern Obolo coastline

	lgeo index									
Metal	L1		L2		L3		L4		L5	
	D	R	D	R	D	R	D	R	D	R
Co	-	-	-	-	-	-	-	-	-	-
Ag	-	-	-	-	-	-	-	-	-	-
Tl	-	-	-	0.08	-	-	-	-	-	-
As	0.13	0.06	0.17	0.15	-	-	-	-	-	-
Se	-	0.15	-	-	-	-	-	-	-	-
Th	0.32	0.28	0.64	0.46	-	-	-	-	-	-
U	0.35	0.05	1.23	0.86	-	-	-	-	-	-

The major source of contamination may be linked to the residual effect of past and/or present oil and gas production and exploration activities along Iko River (L2), Obolo River (L3) and offshore which often involve drilling oil wells, dredging of the river, oil spill incidences, gas flaring, discharge of well-completion chemicals etc (Ohimain *et al.*, 2008; Chijioke *et al.*, 2018; Fennel *et al*., 2019; WHO, 2000; Tulcan *et al.*, 2021). Ogwugwa *et al*. (2018) found high levels of Ba (42.39 mg/kg dw) in sediments from Ogoniland, Niger Delta, Nigeria and attributed its sources to the use of $BaSO_4$ (barium sulphate) to increase the density of drilling fluid during drilling operations. Studies have established that drilling, dredging or any activity which disturb the sea/river bed may expose sediment-trapped metals to the surface water and sediments and cause further pollution in the affected ecosystems (Ohimain *et al*., 2008; Fennel *et al*., 2019).

3.5.2 Contamination Factor (CF)

The contamination factor (CF) is an index method for determining the degree of contamination by a contaminant (for example, a heavy metal) relative to the average world/continental or crustal background composition of the contaminant (metal) concerned. The reference composition could otherwise be a measured local or regional background concentration from a geologically similar, but uncontaminated area (Pandey *et al.*, 2015; Benson *et al.*, 2016; Onjefu *et al.*, 2016, 2020).

The equation for contamination factor (CF) is:

$$CF_i = \frac{Ci}{Cni} \qquad (2)$$

where Ci is the measured concentration of a given heavy metal in a sediment sample, and Cni is the standard preindustrial (uncontaminated) reference level of the metal in mg/kg. The contamination factor categorizes sediment quality into four classes namely:

CF < 1 – indicates low contamination status: 1 < CF < 3 – moderate contamination status; 3 < CF< 5 – considerable contamination status; and 6 < CF - very high contamination status (Benson *et al.*, 2016; Onjefu *et al.*, 2016, 2020). The world average background values for shales (Table 2) reported by Turekian and Wedepohl (1961) was used (Benson *et al.*, 2016; Pobi *et al.*, 2019; Onjefu *et al.*, 2016, 2020; Tulcan *et al.*, 2021; Saha *et al.*, 2022).

The CF results are presented in Table 8. The contamination factor, CF, indicated class 1; low contamination status for Co, Ag, Tl, As, and Se along L1, L2, L3, L4 and L5 (CF < 1 and BDL). However, the contamination status for Th and U were moderate contamination along L1, and moderate to very highly contaminated (1 < CF > 6) along L2. All the metals occurred at below detection limit along L3, L4 and L5. The highest CF (6.14) was recorded for U during the dry season at L2.

Table 8: The contamination factor, CF, for the sampling sites (L1 – L5)

Metal	L1		L2	
	D	R	D	R
Co	-	-	-	-
Ag	-	-	-	-
Tl	-	0.24	0.40	0.71
As	0.65	0.28	0.85	0.74
Se	0	0.75	1	
Th	1.59	1.40	3.17	2.27
U	1.75	0.26	6.14	4.27

*** All the metals were below the detection limit for L3 to L5**

Some seasonal and spatial variations were observed in the CF results. Drilling, dredging and other petroleum activities may be responsible for the high CF values at L1 and L2 for Th and U (Etesin *et al*., 2013; Benson *et al.*, 2016; Ohimain, 2008; EIA, 2020; Udo *et al*., 2020).

3.5.3 Enrichment Factor (EF)

The enrichment factor (EF) (Table 9) enables the assessment of the intensity of anthropogenic activities contributing to a site's contamination (Weissmannova *et al.*, 2019). It is given by the ratio of a metal/element concentration in a sample to a reference value of an element or metal of interest (Pandey *et al.*, 2015; Onjefu *et al*., 2016, 2020). Fe with reference background value of 47200 mg/kg dw and EF equation described by Onjefu *et al.* (2016, 2020), Weissmannova *et al.* (2019) and Abdullah *et al*. (2020) were used.

Table 9 The enrichment factor (EF) for the heavy metals at the study sites

Metals	EF				
	L1	L2	L3	L4	L5
Co	0.00	0.00	0.00	0.00	0.00
Ag	0.00	0.00	0.00	0.00	0.00
Tl	0.00	1.44	0.00	0.00	0.00
As	2.76	2.86	0.00	0.00	0.00
Se	4.41	0.00	0.00	0.00	0.00
Th	8.88	9.76	0.00	0.00	0.00
U	11.15	18.68	0.00	0.00	0.00

The EF values close to 1.0 indicates a natural (lithogenic) origin for the element being assessed, less than 1.0 indicates a probable mobilization or reduction of the element, and values above 1.0 probably indicate that the element has anthropogenic origin in the environment. More so, the EF values of more than 10.0 strongly suggest an anthropogenic origin for the metal concerned (Pandey *e al.*, 2015; Benson *et al.*, 2016; Aljahdali and Alhassan, 2020).

The EF results in Table 9 suggested a natural enrichment of Tl at L2. Tl was below the detection limit at L1 (EF = 0.00). In contrast, the enrichment factors obtained for Th, As, U and Se were values above 1 along L1 and L2, respectively, thus indicating probable anthropogenic sources for the enrichment of these metals at the two sites. The probable anthropogenic sources may be oil and gas exploration and production activities as well as construction and dredging along L2 and offshore of L1. Rapid urbanization, burning of vegetation during farming or fossil fuels, as well as contaminants from agricultural fields may also be factors in the enrichment of these heavy metals along L1 and L2 (Ogwugwa *et al.*, 2018; Chinedu and Chukwuemeka, 2018; Igbemi *et al.*, 2019; Ohimain *et al.*, 2008; EIA, 2020; Abudawood *et al.*, 2023; Fortoul *et al.*, 2014; WHO, 2000; Lavenir *et al.*, 2020). Sampling sites L3, L4 and L5 are outside the tidal influence of L2 and this may be a factor in the non-detection of the metals at those sites (Honda *et al.*, 1987; Enemugwem, 2009; US EPA, 2002, 2022, 2023; Rezaei *et al.*, 2021).

3.5.4 The Pollution Load Index (PLI)

The pollution load index (PLI) provides an assessment of the overall integrity of a study site {which is the intertidal coastal ecosystem in Eastern Obolo concerning heavy metals (contaminants) measured in the sediment samples (Benson *et al.*, 2016; Onjefu *et al.*, 2016, 2020; Aljahdali and Alhassan, 2020). The PLI is used to determine the degree of anthropogenic heavy metals or contaminants accumulation in aquatic sediments.

The PLI is derived from the contamination factor (CF) and is given by the equation

$$PLI = \sqrt[n]{(CF1xCF2xCF3 \ldots .CFn)} \qquad (3)$$

where CF is the contamination factor of a metal, i, and n is the number of metals or contaminants measured at a site (Benson *et al.*, 2016; Aljahdali and Alhassan, 2020).

The PLI classifies sediments' environmental pollution status as follows: Class 1: < 0 – 0, no pollution, Class 2: 0 – 1, low degree of pollution, Class 3: 1 – 2, moderate degree of pollution, Class 4: 2 – 4 high degree of pollution; Class 5: 4 – 8 very high degree of pollution; and Class 6: 6 – 18, extremely high degree of pollution (Aljahdali and Alhassan, 2020). Table 10 contains the pollution load index (PLI) results for L1- L5 from this study.

The PLI results indicated that the study locations/sites L3, L4 and L5 were relatively unpolluted during both seasons (PLI = 0.00). Those sites are outside the tidal influence of L2. However, with an average PLI of 0.84 for both seasons L1 had a low degree of pollution by Th, U, As, Se and Tl. Moreso, an average PLI of 1.55 indicated that L2 was moderately polluted with respect to Tl, As, Th and U. Given the surface hydrology of the area characterized by semidiurnal flow pattern of the ocean and rivers, also petroleum activities and dredging along L2, the

Table 10: The pollution load index (PLI) of the study sites

Location/site	**Dry season**	**Rainy season**	**Average (PLI)**
L1	1.22	0.45	0.84
L2	1.60	1.50	1.55

L3	0.00	0.00	0.00
L4	0.00	0.00	0.00
L5	0.00	0.00	0.00

PLI also suggested that L1 which lies along the flow direction of water from L2 during low tide was probably contaminated by materials from L2. That is in addition to the sandy texture of sediments at L1 which reduces the site's capacity to bind metals. Studies have shown that locations in the direction of flow of water and wind are usually more polluted than those in the opposite direction (Honda *et al.*, 1987; Rezaei *et al.*, 2021). Sandy sediments are also known to have low organic matter and larger grain sizes, hence low binding sites and retention capacity for heavy metals and other contaminants (Zhang *et al.*, 2021). These factors could account in part for the lower pollution status at L1. The abandoned artisanal refinery site operated about ten years ago in the watershed of L5 did not seem to have significant effect on the contamination of L3, L4 and L5 with respect to the metals studied (PLI = 0.00). The long residence time (over ten years) of metals from the artisanal refining of petroleum may have resulted in some natural remediation of the metals (Juhl, 2018; Simpson and Kumar, 2016; US EPA, 2007, 2022, 2023). According to US EPA (2023), a residence time of six months could result in some significant natural reduction of contaminants (example, heavy metals) concentration.

3.5.5 The Modified Degree of Contamination Index (mCd)

The modified degree of contamination index, mC_d, in sediment (Table 11) is known to offer practically verifiable and generalized means of estimating the overall level of contamination at a given sampling site. It was first proposed by Lars Hakanson, a Swedish scientist, and is based on the equation:

$$mC_d = \frac{\sum_{i=1}^{i=n} CFi}{n} \qquad (4)$$

where CFi = the contamination factor of a metal, i, and n = the number of contamination factors at each site. Using mC_d the classification of contamination status is given as follows (Benson *et al*., 2016; Aljahdali and Alhassan, 2020): $mC_d < 1.5$ - indicates no to very low degree of contamination, $1.5 \leq mC_d < 2$ - low degree of contamination, $2 \leq mC_d < 4$ - moderate degree of contamination, $4 \leq mC_d < 8$ - a high degree of contamination, $8 \leq mC_d < 16$ - a very high degree of contamination, $16 \leq mC_d < 32$ - extremely high degree of contamination, and $mC_d \geq 32$ - refers to an exceedingly high degree of contamination.

Table 11: The modified degree of contamination index, mC_d, for the sampling sites

Location/site	Dry season (D)	Rainy season ®	Mean
L1	1.33	0.61	0.97
L2	2.61	2.00	2.31
L3	0.00	0.00	0.00
L4	0.00	0.00	0.00
L5	0.00	0.00	0.00
Cumulative mean			1.64

The mCd index obtained revealed no to very low degree of contamination (mean mCd = 0.97) along L1 (Table 11) . The results also indicated a moderate degree of contamination with a mean mCd value of 2.31 at L2. Slight variations were obtained for the dry and rainy seasons' mCd, the dry season generally having higher values at L1 and L2. This trend may be associated with less solubilization of the metals during the dry season due to the absence of acid rain, hence less ocean/river acidification (Attah, 2012; Fennel *et al.*, 2019; Barrera and Ariza, 2017). With all the metals found below detection limit (BDL) L3, L4 and L5 had generally no degree of contamination (mCd = 0.00). This classification is similar to and confirms the status revealed by the PLI, CF, lgeo, etc.

3.5.6 The potential ecological risk index (PERI)

This index which was first proposed by the Swedish geochemist, Lars Hakanson was used to characterize the potential ecological hazard posed by the heavy metals in the sediments (Benson *et al*., 2016; Ma and Han, 2020). PERI measures the probable degree of contamination of metals in marine/aquatic environments (or soil) about the relative toxicity of the overall metals as well as the probable environmental responses in the short- and long-term (Benson *et al.*, 2016; Ma and Han, 2020).

The following equation was used to estimate the risk index (Ri):

$$R_i = \sum E_f^i \quad (5)$$

$$\text{And } E_f^i = \sum T_r^i \frac{C_s^i}{C_n^i} = \sum T_r^i \mathrm{CF_i} \quad (6)$$

where R_i = the sum of the risk factor index (E^i_f) of the heavy metals in the sediment sample. The E_f^i, the ecological risk factor, is otherwise referred by researchers to as the monomial PERI for a single metal. The C_s^i is the observed concentration of the metal in the sediment sample, while C_r^i is the reference geochemical background value for the heavy metal. CF_i is the contamination factor of metal, i. The factor T_r^i is the toxic response factor for the given metal. The determined values of T_r^i obtained from the literature are Cd (30), Cr (2), Ni (5), Hg (40), Pb (5), Zn (1), As (10), Mn (1), V (2), Cu (5) and Ti (1) (Benson *et al.*, 2016; Hamid *et al.*, 2022; Weissmannova *et al.*, 2019; Ma and Han, 2020).

The PERI classifications are as follows. E_f^i < 40, low risk; 40 ≤ E_f^i < 80, moderate risk; 80 ≤ E_f^i < 160, considerable risk; E_f^i ≥ 320, very high risk. Similarly, the R_i < 150, indicates low risk; 150 ≤ R_i < 300, moderate risk; 300 ≤ R_i< 600, high risk; R_i ≥ 600, very high risk (Benson *et al.*, 2016; Ma and Han, 2020).

Of all the heavy metals studied only As has its toxic response factor (T^i_r) available in the literature. The PERI assessment was therefore based on the As content of the sediments. The calculated ecological risk factor (E^i_f) and risk factor (Ri) based on As indicated a low potential ecological risk status (E^i_f < 40, and Ri < 150) at all the sampling sites in both seasons (maximum Ri = 7.76 at L2). Precisely, the E^i_f results were L1 (4.65), L2 (7.76); L3, L4 and L5 had As below the detection limit and therefore zero E^i_f. In this study, and based on As only, the Ri had the same value as the E^i_f at each site (both had minimum value = 4.65, maximum = 7.76, and mean = 2.21). The present results for PERI are consistent with several previous research findings and reported case studies (Ma and Han, 2020). The PERI is often spiked by the presence of heavy metal(s) with high T^i_r such as Cd and Hg (Ma and Han, 2020; see Appendix).

The PERI method has some relative advantages when compared with other index approaches or methods. For instance, the toxic response factor, T^i_r, enables the PERI to distinguish the difference among contaminants' contribution to the toxicity at the site(s). The PERI also provides a means of assessing ecological threats to an aquatic ecosystem and humans (Ma and Han, 2020).

3.5.7 Health risk assessment

Exposure route for the heavy metals under study (Co, Ag, Tl, Se, Th, U, and As) through ingestion of oysters (*C. gasar*) was explored for this health risk assessment. The bioaccumulation data of the oysters obtained from this study are presented in Table 4. The oysters met the major criteria for good bioindicators or biomonitors described by Maher *et al.* (2016). Remarkably, the oysters significantly reflected the heavy metals distribution and accumulation pattern in the sediments and water samples, including their abundance or non-detection of Ag and Co, etc (they were below the detection limit) in the sediments and water from each of the sampling sites during both seasons. The bioconcentration factor (BCF) data obtained are contained in Table 12 below.

$$\text{Bioconcentration Factor (BCF)} = \frac{Conc.\ of\ a\ metal\ in\ organism\ tissue}{Concentration\ of\ the\ Metal\ in\ Water} \quad (7)$$

$$BCF = C_b/C_w \quad (8)$$

where C_b represents the concentration in the biota, and C_w that of the surrounding water it is in contact with (Maher *et al*., 2016; Tuo *et al.*, 2019; US EPA, 2023).

The BCF provides better representative data for suspension- or filter-feeding aquatic organisms than the biota-sediment accumulation factor (BSAF) which is best for sediment-feeding or dwelling organisms (US EPA, 2023). Oysters are suspension or filter feeders (Santhanam, 2018; Maher *et al.*, 2016; Juhl, 2018; Tuo *et al.*, 2019).

Table 12: The bioconcentration factor (BCF) of oysters from the coastline of Eastern Obolo

Metal	BCF									
	L1		L2		L3		L4		L5	
	D	R	D	R	D	R	D	R	D	R
Co	BDL	-	-	-	-	-	-	-	-	-
Ag	BDL	-	-	-	-	-	-	-	-	-
Tl	BDL	-*	-**	-*	-	-	-	-	-	-
As	180.67	2710.00	177.75	-	-	-	-	-	-	-
Se	-	-	-	-**	-	-	-	-	-	-
Th	0.42	71.25	98.75	172.85	-	-	-	-	-	-
U	156.67	3.46	115.00	61.85	-	-	-	-	-	-

***The metal is present in the oysters but below the detection limit in water; ** the metal is detected in water, but below the detection limit in oysters; - below the detection limit in both water and oyster tissues.**

The BCF values ranged from 0.42 (Th at L1, D) to 2710 (As at L1, R). the present results are in tandem with values obtained elsewhere by Kiin-Kabari *et al.* (2017), Tuo *et al.* (2019) and review by Manickavasagam *et al.* (2019). Generally, from Table 12 the order of magnitude of BCF in this study was As > Th > U > Co, Ag, Tl and Se (which were either below the detection limit in the oyster tissues or water. This trend has confirmed some earlier studies which found that oysters and other bivalve molluscs can accumulate high concentrations of Zn and Cu, etc and still function effectively (exhibit high tolerance) by storing the metals in sub-cellular, non-toxic forms while leaving only very small amounts of the metal in metal-sensitive cell components (Ansari *et al.*, 2004; Maher *et al.*, 2016; Juhl, 2018).

The BCF data obtained were interpreted based on the established ecological risk assessment criteria for BCF and BSAF which are (US EPA, 2023): BCF or BSAF < 250 – indicate low concern; ≥ 250 – medium concern; ≥ 1000 – considered as high concern; and ≥ 5000 – indicate contaminants that are of high-risk concern.

Using these quality guidelines ranking scheme and the BCF data in Table 12, the present study has indicated that Th, U, As, Tl, Co, Se, and Ag have low concerns at the five sampling sites (BCF < 250). Also, arsenic (As) showed a high-risk concern at L1 (rainy season), but a low concern at L2, L3, L4 and L5. The BCF data predicts the contamination status of the ecosystem concerning the heavy metals measured, but do not necessarily indicate their toxicity to the oysters due to the high tolerance capacity of oysters (US EPA, 2007, 2022, 2023; Maher *et al.*, 2016). Many impaired oysters (evidenced by dead and empty shells on substrates) were found at L5 during sample collection. However, the specific contribution of the metals studied to the observed oysters' impairment is not exactly clear as the sampling site is in the drain basin of an abandoned artisanal crude oil refining site. Notwithstanding, Garcia *et al.* (2009) had reported among others the development of histopathological lesions in oysters in Mandinga Lagoon, Mexico due to Heavy metals (Cr, Cd, Pb, etc.) contamination.

3.5.8 Human health risk evaluation of heavy metals content of oysters

The human health risk assessment approaches developed by the US EPA (1991, 2013) were used for this assessment. As earlier noted, only the exposure pathway through ingestion of the oysters were considered for this risk evaluation since oysters are only ingested as food by adults and children.

The daily intake of each metal (DIM) from oral ingestion of the oysters in this study was estimated using the equation:

$$DIM = \frac{Cmetal\ x\ DNI\ x\ Cf}{Bw} \qquad (9)$$

where, DIM (mg/kg-day) = the estimated daily intake rate of the metal through ingestion of the seafood/food item concerned (in this case the oysters). C_{metal} = the measured metal concentration in the oysters/seafood tissue(s) consumed (mg/kg dw). DNI = the estimated average rate of daily nutritional intake of seafood (in this case oysters) (g/day), which was estimated in 2011 by the United Nations Food and Agriculture Organization (FAO) as being 62.62 and 60.0 g capita^{-1} day^{-1} for adults and children, respectively, for Nigeria (Abubakar *et al.*, 2015; Benson *et al.,* 2016). C_f = the conversion factor of the fresh (wet) food item (seafood/oyster) to dry constant weight. It was estimated as reported by Abubakar *et al.* (2015) and Benson *et al.* (2016):

$$C_f = IR_{ww} – IR_{dw} \qquad (11)$$

$$IR_{ww} = IR_{dw} \left(\frac{100-W}{100}\right) \qquad (12)$$

where IR_{ww} and IR_{dw} are the wet weight intake rate and dry weight intake rate of the food (oyster), respectively, and W is the percent moisture (water) content of the food concerned (oyster). In this study, the average moisture content of the oyster tissues was 80.62%, which gave a C_f value of 0.1938. Bw is the average body weight of a person. The average body weight of adults (> 18 years) and children (6-18 years) in Nigeria is 70 kg and 48 kg, respectively, according to Benson *et al.* (2016).

Table 13 presents the DIM for the metal arsenic (As) based on its concentrations in the oyster tissues in both seasons.

Table 13 Estimated daily intake of the heavy metals in the oysters (mg/kg-day) (DIM)

Metal		L1	L2	L3	L4	L5	Cumulative Average
As*	Adult	0.93	1.23	-	-	-	0.43
	Children	1.29	1.72	-	-	-	1.29

:* **Only arsenic (As) was evaluated for DIM given the fact that no RfD for the other metals studied was available in the literature, and Co and Ag were below the detection limit at all the sites in both seasons.**

Based on the DIM results obtained (Table 12), the health index (HI) was used to estimate the possible human health risk associated with the consumption of oysters from the study sites in Eastern Obolo (Khan *et al.*, 2009; Abubakar *et al.*, 2015; Benson, *et al.*, 2016; Weissmannova *et al.*, 2019).

$$HI = \frac{DIM}{RfD} \qquad (10)$$

where R_fD = recommended daily reference intake dose (mg/kg-day) of each metal through ingestion which (see Appendix).

The following assessment criteria were used:

HI ≤ 1 – indicates there are no potential risks associated with the DIM from the food.

HI > 1 – indicates significant health risk associated with the intake of the metal through daily ingestion of the food.

From the results obtained (Table 13), As which showed low and high-risk concern from the BCF results at L1 and L2, (Co and Ag were found below detection limit) has DIM from the oysters at all the study sites above the R_fD limit (that is, HI > 1) for adults and children. It therefore follows that intake of the metal (As) by adults and children through ingestion of oysters from the present study sites L1 and L2 may pose significant health risk to adults and children. The present result compares favorably with the earlier finding reported by Benson *et al*. (2016). They reported similar health risk for the metals which were determined in crabs from Douglas creek, Ibeno, Nigeria, except Cr which had DIM below its R_fD.

3.5.9 The Target hazard quotients (THQ AND THQ_{tot})

The target hazard quotient (THQ) is given by a ratio of the determined concentration of a contaminant to the reference daily tolerable intake dose (R_fD), below which the contaminant would normally be expected to pose no appreciable health risk from the contaminant/heavy metal to the individual consumer of the food. The THQ values above 1 generally indicate that health risk is possible from the level of contaminant concentration in the food (oysters). The THQ is estimated and used to predict either non-carcinogenic or carcinogenic risks to the consumer. It was estimated in this study based on the US EPA specifications (US EPA, 2013; WHO, 2010):

$$THQ = \frac{EF \ X \ ED \ X \ FIR \ X \ Cmetal}{RfD \ X \ Bw \ x \ AT} \ x \ 10^{-3} \qquad (13)$$

The total hazard quotient (THQ_{tot}) or hazard index (HI) is the sum of all the estimated THQ at each site: $THQ_{tot} = \sum_{i=1}^{i=n} THQ$ (14)

(Note: The THQ_{tot} or hazard index gives the overall risk due to exposure to toxic heavy metals at a site).

where EF = The exposure frequency to the contaminant for an individual (365 days/year);

ED = The exposure duration, which is 52.5 years and 6 years, for Nigerian adults and children respectively, based on the 2013 world Bank's estimate of average life expectancy in Nigeria (Benson *et al.*, 2016; Abubakar *et al*., 2015). It is 70 years for adults and 6 years for children based on the US EPA estimates (US EPA, 2013: WHO, 2010; Benson *et al*., 2016; Kortei *et al*., 2020). FIR = the daily seafood ingestion rate capita^{-1} day^{-1} for adults and children, respectively. For Nigeria, based on the FAO estimates of 2011, these are 62.6 g and 60.0 g per day for individual adults and children, respectively (Abubakar *et al*., 2015; Benson *et al*., 2016). C_{metal} is the measured concentration of the contaminant (heavy metal) (mg/kg dw) in the food (oysters). Bw is the average body weight of an individual which in Nigeria is 70 kg and 48 kg for adults (> 18 years) and children (6-18 years), respectively (Benson *et al.,* 2016). The AT is the exposure time for either non-carcinogenic (AT_n) or carcinogenic (AT_c) risks and is estimated as 365 days year^{-1} x ED. The 10^{-3} is a unit conversion factor (Kortei *et al*., 2020). The THQ and THQ_{tot} estimated for As, were well above 1, indicating that consumption of the Oysters from L1 and L2 may pose significant carcinogenic and/or noncarcinogenic risks to individual adults and children (Mok *et al*., 2015; Benson *et al.*, 2016; Kormoker *et al*., 2020; Tuo *et al*., 2019; Fang *et al.*, 2003; Weissmannova *et al.*, 2019), and Kortei *et al*. 2020; Kiin-Kabari *et al.*, 2017; WHO, 2010; US EPA, 2023). The present findings are consistent with results reported by Benson *et al*. (2016), Khan *et al*. (2009), Kormoker *et al.* (2020), Tuo *et al*. (2019), and Kortei *et al*. (2020) for some heavy metals.

4.0 Conclusion

The ecological and health risk assessment results obtained for sediments, surface water and oysters have revealed a moderate contamination status for Iko River and the Atlantic Ocean coastline in Eastern Obolo with respect to Th, U and As. Iko River was more contaminated and probably the major source of contamination for the Atlantic Ocean coastline due mainly to dredging and crude oil and gas related anthropogenic activities. In contrast, Obolo River, Amadaka River, and Emeremen River had uncontaminated status with respect to Th, U, As, Co, Ag, Se and Tl as these metals were below detection limits in the sediments and surface waters studied along the three rivers. However, the THQ and THQ_{tot} estimated for As, were well above 1, indicating that consumption of the Oysters from L1 and L2 study sites may pose significant carcinogenic and/or non-carcinogenic risks to individual adults and children. Hence, adequate remediation interventions are recommended for Iko River and the Atlantic coastline.

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Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable.

Availability of data and materials

The publisher has the right to make the data public.

Competing interests

The authors declared no conflict of interest

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Authors' contribution

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