

**Toxic Metal Concentration and Ecological Risk Assessment in Surface Water, Soil Sediment, and Atmosphere in two Selected Creeks in Rivers State**

**<sup>1</sup>Iyaye David, <sup>2</sup>Aseminaso Tubonemi O., <sup>3</sup>Dagogo-Brown Igirigi Deinabobo, <sup>4</sup>Digitemie Esther Ingonabo**

<sup>1,2</sup>Africa Centre of Excellence Public Health and Toxicological Research, University of Port Harcourt, Nigeria

<sup>3</sup>Department of Medical/Surgical Nursing Faculty of Nursing Sciences, Federal University, Otuoke, Nigeria

<sup>4</sup>Department of Maternal and Child Health Nursing, Faculty of Nursing Sciences, Federal University, Otuoke, Nigeria

**Corresponding Author: aseminaso\_omineokuma@uniport.edu.ng**

**Abstract**

Pollution puts the balance of the earth's support systems at risk, and it threatens the existence of the marine ecosystem: air, surface water, and soil sediment. Samples were collected at three points within the creeks of Isaka and Marine Base for toxic metals analysis. Five toxic metals (As, Cd, Hg, Mn, and Pb) were analyzed using Atomic Absorption Spectrophotometer. The analyses of Isaka creek revealed As and Hg to be of the same concentration of  $0.002 \pm 0.00$  mg/l in surface water, and  $0.001 \pm 0.00$  mg/kg apiece in both soil sediment and air. Cd was found to be  $0.032 \pm 0.001$  mg/l concentration in surface water,  $0.064 \pm 0.003$  mg/kg in soil sediment and  $0.002 \pm 0.00$  ppm in air. The concentration of Mn was found to be  $0.055 \pm 0.004$  mg/l in surface water,  $2.406 \pm 0.34$  mg/kg in soil sediment and  $0.005 \pm 0.00$  ppm in the air analysis. For Pb, a concentration of  $0.232 \pm 0.10$  mg/l was found in surface water,  $0.704 \pm 0.043$  mg/kg in soil sediment and  $0.002 \pm 0.00$  ppm in air. The result of Marine Base creek showed As to be of a concentration. of  $0.007 \pm 0.00$  mg/l in surface water,  $0.002 \pm 0.00$  mg/kg in soil sediment and  $0.001 \pm 0.00$  ppm in the air. The concentrations of Cd were  $0.023 \pm 0.001$  mg/l,  $0.041 \pm 0.001$  mg/kg, and  $0.001 \pm 0.00$  ppm in surface water, soil sediment and air respectively. Hg has mean concentrations of  $0.0005 \pm 0.00$  mg/l in surface water,  $0.002 \pm 0.00$  mg/kg in soil sediment and  $0.0005 \pm 0.00$  ppm in air, while that of Mn was observed to be  $0.067 \pm 0.001$  mg/l in surface water,  $37.632 \pm 0.064$  mg/kg in soil sediment and  $0.011 \pm 0.002$  ppm in the air. Concentration for Pb metal was observed to be  $0.166 \pm 0.001$  mg/l in surface water,  $1.407 \pm 0.188$  mg/kg in soil sediment and  $0.002 \pm 0.00$  ppm in the air. Also, the contamination factor revealed that the water and soil samples from both creeks fell within low contamination factor ( $CF < 1$ ), indicating no pollution. The Ecological Risk Index ( $E_r^i$ ) for all the deleterious elements in the surface water and sediments were  $< 30$ , indicating trivial effect from ingestion of surface water or dermal source for intake of sediment from both creeks as they pose no ecological threat to human lives. The sum Risk Index ( $RI = \sum E_r^i$ ) for all the toxic metals in the surroundings of both creeks is to be tagged slight as the values are very low below 40. However, the particulate matter concentration of the toxic metals As, Cd, and Pb contained in the atmosphere is higher than the acceptable limits of USEPA. There should therefore be control over the sources of these pollutants to prevent ecological problems.

*Keywords:* toxic metals, soil sediments, surface water, atmosphere, contamination, ecological risk.

## **1. Introduction**

On a daily basis, a large number of chemical compounds derived from industrial activities are continuously introduced into the marine ecosystem (Iyama & Edori, 2014). As a result, the marine habitats include intricate combinations of potentially harmful substances known as contaminants. These pollutants are significantly linked to human activity because they include sewage, toxic metals and metalloids, persistent organic compounds, harmful dinoflagellates, bacteria, and viruses, as well as more recently, newly emerging new chemicals from medicinal products as well as personal care products. Moreover, as industrialization and urbanization spread throughout emerging nations like Nigeria, the degradation and contamination of the natural ecosystems are more severe than ever. This is demonstrated by observations of hypoxia in coastal oceans, a decline in biodiversity, the extinction of aquatic life, and many other phenomena (Gu & Wang, 2015).

Substances invasion into the marine ecosystem, either deliberately or incidentally by humans, can have detrimental effects on the environment, including risks to human healthiness, complications to aquatic activities, deterioration of sea water quality for various uses, and a reduction in sea products. Toxic or heavy metal is any steel chemical element with a comparatively high density and toxic at minimal amount. Due to their toxicity even at low concentrations, capacity to enter food chains, and ability to be concentrated by aquatic animals, toxic metals are considered to be major contaminants of aquatic bio-systems. They are regarded as the most precarious ecosystem contaminants considering their propensity for bioaccumulation and toxicity. Their contamination may have catastrophic impacts on the recipient environment's ecological balance as well as a variety of aquatic creatures.

Most recently, there has been an increasing ecological and global public health issues that has to do with pollution of the environment by these metals. Besides, human exposure has increased due to their use in a good number of industrial, agricultural, domestic, and technological applications (Bernhoft, 2012). Reported sources of heavy or toxic metals in the environment include geogenic and anthropogenic sources like oil exploration and combustion, agricultural activities, pharmaceutical wastes, domestic effluents, mining, smelting operations etc (He et al., 2005)

## **2. Materials and Methods**

The study was conducted in Isaka and Marine Base creeks in Okrika and Port Harcourt LGAs, Rivers State. Isaka creek is a salty H<sub>2</sub>O body located in Isaka, Okrika L.G.A of Rivers State, Nigeria. It is an armlet of the National Ports Authorities highway-sea that lies between Latitude 4°73 North and Longitude 6°99 East. The river is decked by mangrove vegetation by the sides. However, wastes originating from dumped boats, open bathrooms, municipal trashes, and spills emanating from oil thefts have escalated the unhealthy status of the creek. Marine base is situated in Port Harcourt at Latitudes 04° 43' and 04° 57' North of the Equator and between Longitudes 06° 53' and 07° 58' East of the Greenwich Meridian and is bounded by the Dockyard creek, Bonny River and Amadi creek, of the Niger Delta, at an elevation of about 12m above sea level. It is roughly 60km from the crest up stream of the Bonny River. Marine base is in the coastal area of Port Harcourt, where loading and off-loading of crude oil and other petroleum products by ships, cargo oil tankers occur. The marine base surrounding is not free from contaminants from petrol products, effluents from industries and garbage migrating via drains from hinterland. Thus, has a direct impact on the inhabitant H<sub>2</sub>O organisms such as mudskippers, periwinkles, oysters, and crabs as well as the consumers.



Figure 1: Generalized geological map showing the study areas.

### **Sampling method and procedure**

9. Three water samples of 10 litres each, at a depth of 0.5 meters were collected using a manual pump from each of the creeks, at the beginning, middle, and tail points.
10. The digest was then taken for Atomic Absorption Spectrophotometer (AAS) analysis for the quantitative assay of toxic metals (As, Cd, Hg, Mn, Pb) present in the water samples respectively.
11. Three soil samples were collected at the beginning, middle, and tail points from the surrounding of the creeks at a depth of 0cm – 10cm. The soils were stored in sterile bags and air dried at room temperature, and then screened for toxic metals.
12. Three air samples were equally taken at the beginning, middle, and tail points from the surrounding of the creeks for quality assessment with the use of high-volume samplers and glass fiber filters.
13. The specimens were assayed for toxic metals with the use of AAS.

### **Materials and Reagents**

#### **For Surface Water Analysis**

5. Atomic absorption spectrophotometer (AAS), burner, conical flask, funnel, filter paper, measuring cylinder, volumetric flask.
6. Deionized-distilled water, Conc.  $\text{HNO}_3$ , Stock metal solutions, Standard metal solution, fuel, and oxidant.

#### **For Soil Sediment Analysis**

7. Atomic absorption spectrophotometer (AAS), burner, conical flask, funnel, filter paper, measuring cylinder, volumetric flask, weighing balance.
8. Deionized-distilled water, Conc.  $\text{HNO}_3$ , Hydrogen peroxide, Stock metal solutions, Standard metal solution, fuel, and oxidant.

#### **For Air quality analysis**

9. Atomic absorption spectrophotometer (AAS), burner, conical flask, funnel, filter paper, measuring cylinder, volumetric flask, weighing balance.

10. Deionized-distilled water, Conc. HNO<sub>3</sub>, Hydrogen peroxide, Stock metal solutions, Standard metal solution, Fuel, and oxidant.

### **Digestion procedure of the collected samples**

#### **Extraction of toxic metal in surface water for analysis**

A 100ml of well mixed acidified specimen was transferred into a brittle container for digestion. 5ml of HNO<sub>3</sub> was added to the sample in fumehood. Little heat was afterwards applied with a fire plate to induce evaporation before precipitation. Continuous heating and addition of conc. HNO<sub>3</sub> was done until digestion is completely indicated by a bright light-colored solution. Used fragile container were washed with metal free H<sub>2</sub>O and then filtered. The filtrate was then relocated to a 100ml volumetric vessel and diluted to mark. A portion of this solution was later taken for required metal determination.

#### **Extraction of toxic metal in sediment for analysis**

1g of well mixed sediment was transferred into 100ml conical flask for digestion. 10ml 1:1 of HNO<sub>3</sub> and peroxide was added to the sample in fumehood. It was then brought to a slow boiling by heating at 95<sup>0</sup>C on a hot plate. Additional 2ml of water and 3ml of hydrogen peroxide was introduced, covered, and heated until effervescence subsides, after which it was cooled and filtered into a measuring container and make up 100ml. A portion of this solution is afterward taken for required metal and cations determination.

#### **Extraction of toxic metals in air for analysis**

The aerodynamic filter of 2.5um were pre-weighted in a weighing balance before proceeding to the field for air particulate matter trapping; and deposited filter paper reweighed after sampling. It was then placed in 100ml breakable vessel for digestion; after which 10ml 1:1 of HNO<sub>3</sub> and peroxide acid was added to the sample in fume hood sufficient to completely submerge the filter paper. Next was to gently reflux in watch glass at 95<sup>0</sup>C on a hot plate. Additional 2ml of H<sub>2</sub>O and 3ml of hydrogen peroxide was later introduced, covered, and heated until effervescence subsides. It was cooled then filtered into a measuring vessel and make up to 100ml. Portion of this solution was taken for required metal and cations determination.

### **Data interpretation**

Descriptive statistics was adopted to depict the average, range, mean and standard deviations (SD) of the assayed noxious elements in the air, surface water, and soil sediment specimens. The test of significance and one-way ANOVA were also employed to depict the causes of toxic metals in the studied site, the contamination dynamics and potential linkage among established variables. Statistical analysis was done using IBM SPSS 23 software.

### **Evaluation of ecological risk indices**

#### **Ecological risk index**

The prospective ecological risk coefficient ( $E_r^i$ ) of an element and the probable ecological risk index (RI) of the elements were computed using the following equations:

$$C_f^j = C_s^i / C_n^i \dots\dots\dots (1)$$

$$E_r^i = T_r^i \times C_f^j \dots\dots\dots (2)$$

$$RI = \sum E_r^i \dots\dots\dots (3)$$

Where:  $C_r^i$ = pollution coefficient of 1 element “i”;  $C_s^i$ = measured level of toxic metal in (Soil Sediment/Surface water);  $C_n^i$ = background intensity of toxic metal.

The average shale background conc. of global deposit was chosen as the indication baselines in this study:

$C_n^i$  for As = 13, Cd = 0.3, Hg = 0.4, Mn = 850, and Pb = 20 Ave. global shale values and average crustal loads have been adopted to afford elemental background concentrations.

$T_r^i$  is the toxic reaction factor for the given element of “i”, depicting the lethal and sensitivity requisites. The toxic response factors for As, Cd, Hg, Mn. and Pb, are 10, 30, 40, -, and 5 respectively.

**Grading of  $E_r^i$  and RI values.**

Table 1 shows the grading of the ecological risk index and Risk Indices of the various toxic metals.

**Table 1: Risk grade indices and grades of potential ecological risk of heavy or toxic metal pollution (Hakanson, 1980).**

$E_r^i$	Risk Grade	RI Value	Risk Level	Risk Degree
$E_r^i < 30$	Slight	$RI < 40$	A	Slight
$30 \leq E_r^i < 60$	Medium	$40 \leq RI < 80$	S	Medium
$60 \leq E_r^i < 120$	Strong	$80 \leq RI < 160$	C	Strong
$120 \leq E_r^i < 240$	Very Strong	$160 \leq RI < 320$	D	Very Strong
$E_r^i \geq 240$	Extremely Strong	$RI \geq 320$	E	Extremely Strong

**Results and Discussion**

**Results of Analysis**

**Table 2: Concentration of toxic metals in the environment, Isaka Creek**

Parameters and Units	Surface Water (mg/l)	Soil Sediment (mg/kg)	Air Quality
Arsenic (As)	0.002±0.00	0.001±0.00	0.001±0.00
Cadmium (Cd)	0.032±0.001	0.064±0.003	0.002±0.00
Mercury (Hg)	0.002±0.00	0.001±0.00	0.001±0.00
Manganese (Mn)	0.055±0.004	2.44±0.34	0.005±0.00
Lead (Pb)	0.232±0.10	0.704±0.043	0.002±0.00

The results of Table 2 are the average values of the noxious elements in the ecosystem of Isaka creek. The result of the experiment shows that As is of a conc. of 0.002±0.00 mg/l in surface water, 0.001±0.00mg/kg in soil sediment and 0.001±0.00ppm in the air. Cd was found to be 0.032±0.001mg/l concentration in surface water, 0.064±0.003mg/kg in soil sediment and 0.002±0.00ppm in air. For Hg, a concentration of 0.002±0.00mg/l was found in surface water, and 0.001±0.00mg/kg and 0.001±0.00ppm in soil sediment and air respectively. The concentration of Mn was found to be 0.055±0.004mg/l in surface water, 2.406±0.34mg/kg in soil sediment and 0.005±0.00ppm in the air analysis. On the other hand, a concentration of 0.232 ±0.10mg/l of Pb was found in surface water, 0.704±0.043mg/kg in the soil sediment and 0.002±0.00ppm in the air.

**Table 3: Concentration of Toxic Metals in the Environment, Marine Base Creek**

Parameters and Units	Surface Water (mg/l)	Soil Sediment (mg/kg)	Air Quality (ppm)
Arsenic (As)	0.007±0.00	0.002±0.00	0.001±0.00
Cadmium (Cd)	0.023±0.001	0.041±0.001	0.001±0.00
Mercury (Hg)	0.0005±0.00	0.002±0.00	0.0005±0.00
Manganese (Mn)	0.067±0.001	37.632±0.064	0.011±0.002
Lead (Pb)	0.166±0.001	1.407±0.188	0.002±0.003

**Table 3: Concentration of Toxic Metals in the Environment, Marine Base Creek**

The result of Table 3 is the mean concentrations of Toxic Metals within the surrounding of marine base creek. The result of the experimentation showed As to be of a conc. of 0.007±0.00mg/l in surface water, 0.002±0.00mg/kg in soil sediment and 0.001±0.00ppm in the air. The concentration of Cd was found to be 0.023±0.001mg/l in surface water, 0.041±0.001mg/kg in soil sediment and 0.001±0.00ppm in the air. For Hg, the concentration was found to be 0.0005±0.00mg/l in surface water, 0.002±0.00mg/kg in soil sediment and 0.0005±0.00ppm in air, while that of Mn was observed to be 0.067±0.001mg/l in surface water, 37.632±0.064mg/kg in soil sediment and 0.011±0.002ppm in the air. Concentration for Pb metal was found to be 0.166±0.001mg/l in surface water, 1.407±0.188mg/kg in soil sediment and 0.002±0.00ppm in the air.

**Table 4: Maximum Permissible Limit for Toxic Metals in the Air as per US EPA and OSHA compared with present study.**

Metals	US EPA	OSHA	Present Study Isaka Creek (ppm)	Present Study Marine Base Creek (ppm)
	PCL (µg/m <sup>3</sup> )	MPL (µg/m <sup>3</sup> )		
Arsenic	0.006	NR	0.001 = 1 µg/m <sup>3</sup>	0.001 = 1 µg/m <sup>3</sup>
Cadmium	0.1000	NR	0.002 = 2 µg/m <sup>3</sup>	0.001 = 1 µg/m <sup>3</sup>
Mercury	NR	NR	0.001 = 1 µg/m <sup>3</sup>	0.0005 = 0.5 µg/m <sup>3</sup>
Manganese	NR	5000	0.005 = 5 µg/m <sup>3</sup>	0.011 = 11 µg/m <sup>3</sup>
Lead	0.5000	1.000	0.002 = 2 µg/m <sup>3</sup>	0.002 = 2 µg/m <sup>3</sup>

PCL: Prescribed Concentration Limit; MCL: Maximum Concentration Limit.

**5. Maximum Permissible Limit for Toxic Metals in the Air as per US EPA and OSHA**

Table 5 depicts standard permissible concentration of the toxic metals compared to the concentrations obtained in the air of the creeks under study. From the acquired data, the concentration of As, Cd, and Pb, from the air samples of both creeks were found to be greater than the prescribed concentration for both US EPA and OSHA. Hence, the outcome indicate that the particulate matter contained in the atmosphere do have the tendency to alter the natural atmospheric condition negatively. The concentration of Mn from both creeks on the order hand is much more insignificant compared to the maximum permissible limit of OSHA, as such does not have the potential to change the natural atmospheric condition negatively. As for Hg, no records presently from USEPA and OSHA for assessment.

**Ecological Risk Index (ERI) for Toxic Metals**

Values for contamination factor ( $C_f^i$ ) and Ecological risk index ( $E_r^i$ ) determined are shown in tables below.

**Table 5. Ecological risk index (ERI) for toxic metals in Surface Water, Isaka Creek**

Toxic Metal	Mean $C_s^i$	$C_n^i$	$C_f^i$	$T_r^i$	$E_r^i$	Risk Grade
As	0.002	13	$1.5385 \times 10^{-4}$	10	$1.5385 \times 10^{-3}$	Slight
Cd	0.032	0.3	$1.0667 \times 10^{-4}$	30	3.2	Slight
Hg	0.002	0.4	$5 \times 10^{-3}$	40	0.2	Slight
Mn	0.055	850	$6.470 \times 10^{-5}$	-	-	
Pb	0.232	20	$1.16 \times 10^{-2}$	5	0.058	Slight

Ecological Risk Index,  $RI = \sum E_r^i = 3.459$ ; *Slight Ecological Risk.*

**Table 6: ERI for toxic metals in Sediment, Isaka Creek.**

Toxic Metal	Mean $C_s^i$	$C_n^i$	$C_f^i$	$T_r^i$	$E_r^i$	Risk Grade
As	0.001	13	$7.692 \times 10^{-5}$	10	$7.692 \times 10^{-4}$	Slight
Cd	0.064	0.3	$2.133 \times 10^{-1}$	30	6.4	Slight
Hg	0.001	0.4	$2.5 \times 10^{-3}$	40	0,1	Slight
Mn	2.406	850	$2.83 \times 10^{-3}$	-	-	
Pb	0.704	20	$3.521 \times 10^{-2}$	5	0.176	Slight

Ecological Risk Index  $RI = \sum E_r^i = 6.677$ , *Slight Ecological Risk*

**Table 6: risk index (ERI) for toxic metals in Surface Water, Marine Base Creek**

Toxic Metal	Mean $C_s^i$	$C_n^i$	$C_f^i$	$T_r^i$	$E_r^i$	Risk Grade
As	0.007	13	0.00053846	10	0.00538462	Slight
Cd	0.023	0.3	0.07666667	30	2.3	Slight
Hg	0.0005	0.4	0.00125	40	0.05	Slight
Mn	0.067	850	$7.8824 \times 10^{-5}$	-	-	
Pb	0.166	20	0.0083	5	0.0415	Slight

Ecological Risk Index,  $RI = \sum E_r^i = 2.30688$ ; *Slight Ecological Risk.*

**Table 7: ERI for toxic metals in Sediment, Marine Base Creek**

Toxic Metal	Mean $C_s^i$	$C_n^i$	$C_f^i$	$T_r^i$	$E_r^i$	Risk Grade
As	0.002	13	0.00015385	10	0.00153846	Slight
Cd	0.041	0.3	0.13666667	30	4.1	Slight
Hg	0.002	0.4	0.005	40	0.2	Slight
Mn	37.632	850	0.04427294			
Pb	1.407	20	0.07035	5	0.35175	Slight

Ecological Risk Index,  $RI = \sum E_r^i = 4.6533$ ; *Slight Ecological Risk.*

As shown Table 7 from tables 1,2,3 and 4, the contamination factor ( $C_f^i$ ) is less than one (1) for all the assayed noxious metals in the surface H<sub>2</sub>O and soil deposit for both creeks, an

indication of minimal prospect of contamination from these elements via any of the assayed medium.

**Ecological Risk Index ( $E_r^i$ )** value for all the deleterious elements in the surface water and sediments were  $< 30$ , indicating trivial potential of lethal metal intoxication from ingestion of water or dermal source for intake of sediment, indicating the safety of water/sediment from the two creeks as it poses no ecological threat to human lives.

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The sum **Risk index (RI)** for all the noxious elements in surface H<sub>2</sub>O and soil deposit from both creeks is to be categorized slight since the values are very low below 40.

## **Conclusion**

The concentration of the toxic metals in the surface water and soil sediment of both creeks did not pose any ecological risk to man. There should however be control over the sources of these pollutants to forestall gradual accumulation that may lead to public health issues.

On the other hand, the particulate matter consisting of the toxic metals Arsenic, Cadmium, and Lead contained in the atmosphere do have the tendency to alter the natural atmospheric condition negatively. There should therefore be control over the sources of these pollutants to prevent ecological problems.

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