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Ecological Risk Evaluation of Heavy Metal Accumulation in Aba River Bottom Sediments: Implications for Soap and Detergent Industry Wastewater Management

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Abstract: Industrial activities have contributed so much to the pollution of water bodies and these pollutions have adversely affected the aquatic ecosystem. This study aimed to investigate the ecological risk evaluation of heavy metal accumulation in Aba River bottom sediments: implications for soap and detergent industry wastewater management. Varian AA240 Atomic absorption spectrometer was used to analyse heavy metals. Individual and complex ecological indices were used to evaluate heavy metal contamination in bottom sediments. According to the results, the heavy metal properties of the wastewater indicated that Fe, Pb, Cd, Cr and Cu mean concentration values were higher than the World Health Organization (WHO) and the National Environmental Standards and Regulations Enforcement Agency (NESREA) permissible limits. Heavy metal properties of the surface water in Aba River (dry seasons) showed that Pb, Cd, Cu, Mn, Fe, and Cr, mean concentrations were above the NESREA, WHO and U.S. Environmental Protection Agency (USEPA) permissible limits. Heavy metal properties of the bottom sediments of Aba River (wet and dry season) showed that Pb, Cd, and Fe mean concentrations were significantly higher than the NESREA, WHO and USEPA permissible limits. The heavy metal contamination factor (CF) of sediments obtained from Aba River during the wet and dry season was low and the CFs of each of the assayed heavy metals were less than 1 (CD < 1). This also signifies the existence of a low contamination in the sediments of the course streams of Aba River during wet and dry season. The pollution load index (PLI) values of Aba River (sediment) indicated that there is no metal pollution at PLI < 1 in the sampled sediments. The potential ecological risk index (RI) of Aba River was less than 150 (RI < 150) indicating a low ecological RI. Abatement of pollutants in the wastewater to permissible concentrations required for natural environment protection is needed.

Key words: Ecological risk, contamination, sediment, wastewater, heavy metal, pollution, aquatic-ecosystem.

1. Introduction

Effluent discharges into the environment with enhanced concentration of nutrients and sediments will have serious negative impact on the quality and life forms of the receiving water body when discharged untreated or partially treated (Schulz and Howe, 2003; Forenshell, 2001). Water pollution by industrial effluents has become a question of considerable public and scientific concern in the light of evidence of their extreme toxicity to human health and to biological ecosystems (Katsuro *et al.,* 2004). The occurrence of heavy metals in industrial effluents and municipal sewage constitute a major source of the pollution entering aquatic ecosystem.

Industrial activities have contributed so much to the pollution of water bodies and these pollutions has adversely affected the aquatic ecosystem which calls for serious concern and needs urgent attention since rivers are water sources for irrigation and many other domestic purposes.

In Nigeria, cities like Kaduna, Lagos, Kano and Aba depend very much on its river for water supplies. However, the rush by African countries to industrialize has resulted in discharge of partially treated or raw

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wastes into the surrounding bodies of water since the development of treatment facilities cannot keep pace with the rate at which the wastes are generated by the industries. The industrial discharge, therefore contributes a larger portion of the flow of the river during the dry season, with the result that the water quality of the river is further deteriorated. Uses, for which the river is employed involving body contact, expose serious hazards to users due to the bacterial situation. Many bodies of water in Nigeria experience seasonal fluctuation, leading to a higher concentration of pollutants during the dry season when effluents are least diluted [8].

This study aimed to investigate the ecological risk evaluation of heavy metal accumulation in Aba River bottom sediments: implications for soap and detergent industry wastewater management.

2. Methodology

2.1 Study Area

The research was carried out in a soap detergent company in Aba, Abia State in south eastern Nigeria. Aba is located with longitude 07°33′ N and latitude 05°29′ E on an altitude of a hundred and twenty-two meters (122 m), and within the tropical humid rainforest. It has the following mean annual climatic data: rainfall 2,300 mm, with the rainy season between March and November and the dry season starting from December and ending in February/March; minimum and maximum temperatures of 22 ℃ and 31 ℃ respectively; relative humidity of 60%-80%. Aba has two local government areas: Aba North and Aba South LGAs with an estimated population of 534,265 based on the 2006 population census (Fig. 1).

2.2 Water Sample Collection

The effluent samples were collected at the point of discharge from the plant. Sample collection was done with 2 L plastic bottles, pre-treated by washing with dilute hydrochloric acid and rinsed with distilled water. The bottles were later dried in an oven for 1 h at 110 ± 5 ℃, and allowed to cool to ambient temperature. Before use, they were rinsed with the sample twice.

2.3 Water Sample Preparation

Three samples were collected at 1 h intervals and pooled together to form the composite sample for the week, preserved in ice-chests and transported to the laboratory for analysis. The samples were properly labelled and analysed using standard methods for the examination of water and wastewater.

2.4 Sediment Sample Collection

Sediment samples were collected from the river banks using Ponar grab sampler. In each of the study rivers, the grab was lowered down at various distances from the water’s edge and global positioning system (GPS) coordinates were recorded. Sediment samples were collected and stored in aluminum foil and stored in glass sample jars in the dark at 4 ℃ until analysis. Samples for heavy metal analysis were collected in polythene bags. Sediment samples were obtained from four various sites of the river. Each sampling was carried out in three replicates.

2.5 Digestion of Water Sample (Trace Metal Analysis)

Whatman No. 1 filter paper was used to filter 100 cm^3 of the water sample into a 250 mL conical flask; 10 cm^3 concentrated nitric acid was added followed by 10 cm^3 of 50% HCl. The sample was digested on a hot plate at 115 ℃ with anti-pumps for 2 h in a fume cup board. After cooling the water samples were quantitatively transferred to a 100 cm^3 volumetric flask, labeled and dated. Distilled de-ionized water was used to make up to the mark before determination of concentrations of trace metals was made, by the use of Buck 206, Atomic Absorption Spectrophotometer (AAS) (Ademorati,1996, AOAC, 1980).

2.6 Sample Blanks (Trace metals)

Sample blanks were prepared as per respective sample preparations with non-inclusion of the sample (salt or metal). The prepared blank was stored in plastic containers and labeled accordingly for the determinations of metal concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn respectively.

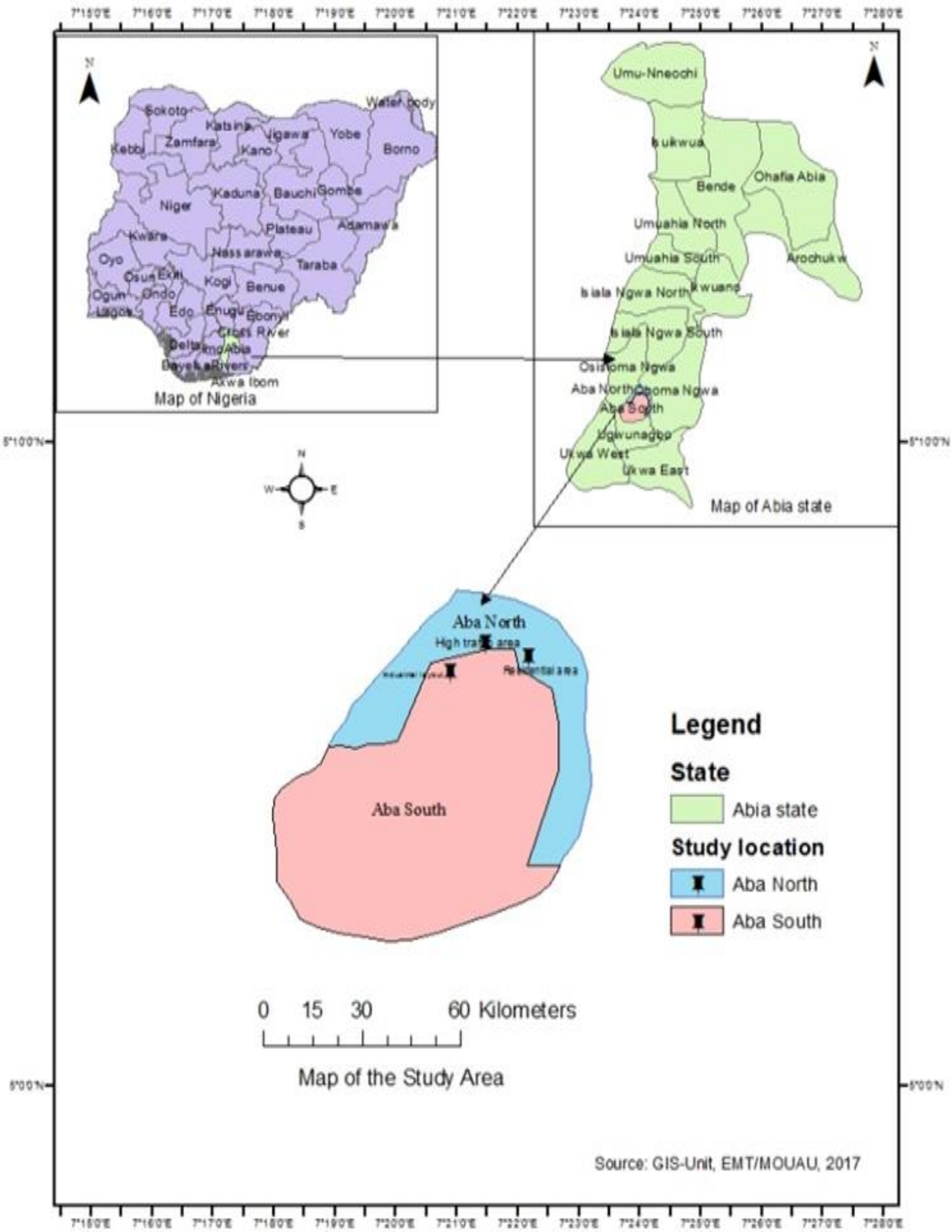

Fig. 1 Map of Abia State, showing Aba the study area.

2.6.1 Determination of Trace Elements Using AAS

Determination of manganese, iron, lead, cadmium, zinc, chromium and copper was done by AAS (BUCK Scientific 206).

Standard metal solution: A series of standard metal solutions will be prepared by dilution of the following stock metal solution with water containing 1.5 cm^3 conc. HNO_3.

Manganese: 3.076 g manganese sulphate ($MnSO_4 \cdot H_2O$) was dissolved in 200 cm^3 distilled water, 1.00 cm^3 = 1.00 mg Mn.

Lead: 1.598 g lead nitrate was dissolved in about 200 cm^3 of distilled water and 1.5 cm^3 conc. HNO_3 added, mixed and made up to 1,000 cm^3 with distilled water, 1.0 cm^3 = 1.0 mg Pb.

Cadmium: 1.00 g cadmium metal was dissolved in a minimum volume of 1 M HNO_3, 1.00 cm^3 = 1.00 mg Cd.

Nickel: 1.273 nickel oxide (NiO) was dissolved in a minimum volume of 10% (*v*/*v*) HCl and then diluted with 1,000 cm^3 of distilled water, 1.00 cm^3 = 1.00 mg Ni.

Zinc: 1.00 g zinc metal was dissolved in 20 cm^3 1 M HCl and diluted with 1,000 cm^3 of distilled water, 1.00 cm^3 =1.0 mg Zn.

Iron: 5.0503 g of iron (ii) ammonium sulphate, $Fe(NH_4)_2 (SO_4)_2$, was dissolved in distilled water and then made up to 1 L with distilled water, 1 mL = 1 mg Fe.

Chromium: 2.8285 g of anhydrous $K_2Cr_2O_7$ was dissolved in distilled water and made up to 1 L, 1 cm^3 = 1 mg Cr.

Copper: 1.0 g copper metal will be dissolved in 50 cm^3 of 5 M HNO_3. The solution was diluted to 1 L with de-ionized water in a 1 dm^3 volumetric flask, 1 cm^3 = 1 mg Cu.

2.6.2 Standardization

At least five concentrations of each stock standard metal solution was prepared by diluting aliquots of the stock solution to 100 cm^3. Each standard was aspirated in turn into the flame and the absorbance recorded. A calibration curve for each element to be determined was plotted on a linear graph paper, the absorbance of standards versus their concentrations in mg/L.

2.6.3 Analysis of Samples

The nebulizer was rinsed by aspirating water containing 1.5 cm^3 conc. HNO_3. The instrument was zeroed by aspirating the blank. The samples were atomized and the absorbance recorded.

2.6.4 Calculation

The concentration of each metal ion in mg/L was calculated by referring to the appropriate calibration curve (this was obtained automatically from an attached software computer system).

2.7 Digestion of Sediment Sample for Heavy Metal Analysis

Two grams (2 g) of sediment sample was weighed with the aid of digital weighing balance into crucible, covered and inserted into the muffle furnace at the temperature of 550 ℃ for 3 h, allowed to cool and then 20 mL of 20% sulphuric acid was measured into 250 mL beaker containing the sample, stirred and digested on hot plate at the temperature of 80 ℃ for 10 min, allowed to cool and filter with Whatman No. 4 filter paper and the volume was made up to 50 mL with distilled water and stored in a reagent bottle for heavy metal analysis.

2.8 Working Principle of AAS

AAS's working principle is built basically on the sample being aspirated into the flame and atomized when the AAS's light beam from the monochromator is directed through the flame onto the detector that measures the amount of light absorbed by the atomized element in the flame when ignited. Metal elements on their own have distinct characteristic wavelength on the source hollow cathode lamp composed of the element/ metals to be analyzed. The amount of energy of the characteristic wavelength absorbed in the flame is directly proportional to the concentration of the element in the tested sample. The sample is aspirated into the oxidizing air-acetylene flame. When the aqueous sample is aspirated, the sensitivity for 1% absorption is observed.

2.9 Pollution Load Index (PLI)

The PLI allows for knowing the degree of contamination of sediments by heavy metals and is used to determine the degree of deterioration..

PLI is calculated using Eq. (1).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times ... CF_n)1/n \quad (1)$$

where CF_n is the contamination factor (CF) of each metal and n is the number of metals evaluated.

2.10 Modified Degree of Contamination (mCd)

mCd allows for assessing the overall degree of sediment contamination by heavy metals and for incorporating as many metals as the study includes. mCd is calculated by Eq. (2).

$$\text{mCd} = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (2)$$

where C_f is the CF, i represents the "i-th" metal, and n is the number of metals evaluated.

2.11 Potential Ecological Risk (RI)

The potential RI is an index applicable for the evaluation of the degree of ecological risk caused by heavy metal concentrations in water, air, and soil. RI is calculated by Eq. (3).

$$E^i_r = T^i_r \times CF^i_r; \; RI = \sum^n E^i_r \quad (3)$$

where E_r is the ecological risk index (RI) of each metal, T_r is the biological toxic factor of each metal, and i represents the "i-th" metal.

2.12 Statistical Analysis

All statistical analyses were conducted using the statistical analysis package: Statistical Package for the Social Sciences (SPSS) (version 25), and the significance level was at $p \leq 0.05$. Comparative statistics was computed, and data analyzed using one-way analysis of variance (ANOVA) and independent *t*-test.

3. Results and Discussion

3.1 Heavy Metal Properties of Wastewater Obtained from a Soap Detergent Industry (Pz Cussons Nigeria. Plc.) in Aba (Wet and Dry Season)

3.1.1 Iron (mg/L)

According to Table 1 below, the iron mean concentrations in wet and dry season are 13.22 and 15.28 mg/L respectively. Dry season recorded a higher iron mean value when compared to wet season. The recorded iron mean values for both seasons were above the permissible limits of 0.3 mg/L.

3.1.2 Zinc (mg/L)

With respect to Table 1 below, zinc mean values for both wet and dry seasons are 5.39 and 6.30 mg/L respectively. Dry season recorded a higher zinc mean value when compared to wet season. The zinc mean values for both seasons are above the permissible limits of 3.000 mg/L.

3.1.3 Lead (mg/L)

In line with Table 1 below, wet and dry seasons recorded lead mean concentration values of 1.16 and 2.14 mg/L respectively. Dry season recorded a higher lead mean value when compared to wet season. The recorded lead mean values were above the permissible limits of 0.01 mg/L.

3.1.4 Arsenic (mg/L)

The mean concentrations of arsenic in both wet and dry seasons of Aba River are 0.02 mg/L and 0.06 mg/L respectively. Dry season recorded an arsenic mean concentration value slightly higher than wet season.

3.1.5 Cadmium (mg/L)

The mean concentration value of cadmium in both wet and dry season are 0.02 mg/L and 0.05 mg/L respectively. The recorded cadmium mean concentration values recorded in both seasons were above the permissible limits.

3.1.6 Mercury (mg/L)

There was no record of mercury in the wet and dry seasons of the study river.

3.1.7 Chromium (mg/L)

The mean concentration of chromium in both wet and dry seasons of the study river is 0.07 mg/L and 0.06 mg/L respectively. Chromium mean concentrations recorded in both seasons were above permissible limit.

3.1.8 Copper (mg/L)

Copper mean concentration values in wet and dry seasons are 3.40 mg/L and 4.49 mg/L respectively. The copper mean concentration in dry season was slightly higher than wet season. The recorded copper mean concentration values were higher than the permissible limit of 1.00 mg/L.

3.2 Correlation Matrix for Heavy Metal Properties of Wastewater Obtained from a Soap Detergent Industry in Aba River (Wet Season)

The correlation matrix in Table 2 above showed different types of correlation matrix for the heavy metal parameters; stronger positive, weak positive and negative type of correlation coefficient. During wet season, a very strong positive significant correlation matrix exits between the following heavy metal parameter pairs: Fe/Zn (r = 0.972), Fe/Pb (r = 0.894), Cd/Cr (r = 0.883) and Pb/Cr (r = 0.967), while a strong negative correlation exits between the following heavy metal pairs: Pb/As (r = -0.939), As/Cd (r = -0.923), and As/Cr (r = -0.996).

3.3 Correlation Matrix for Heavy Metal Properties of Wastewater Obtained from a Soap Detergent Industry in Aba River (Dry Season)

The correlation matrix in Table 3 below showed different types of correlation matrix for the heavy metal parameters; stronger positive, weak positive and negative type of correlation coefficient. During dry season, a very strong positive significant correlation matrix exits between the following heavy metal parameter pairs: Fe/Zn (r = 0.916), Zn/Cr (r = 0.996), and As/Cu (r = 0.912), while a strong negative correlation exits between the following heavy metal parameter pairs: Pb/Cd (r = -0.832), As/Cd (r = -0.961), Cd/Cu (r = -0.763) and Cr/Cu (r = -0.811).

Table 1 Heavy metal properties of wastewater obtained from a soap detergent industry (Pz Cussons Nigeria. Plc.) in Aba (wet and dry season).

Parameters (mg/L)	Wet season	Dry season	WHO (2008)	NESREA (2015)
Fe	13.22 ±0.23	15.28 ±0.24	0.3	0.3
Zn	5.39 ±0.49	6.30 ±0.28	3.000	-
Pb	1.16 ±0.14	2.14 ±0.16	0.01	0.01
As	0.02 ±0.01	0.06 ±0.01	-	-
Cd	0.02 ±0.01	0.05 ±0.02	0.003-0.005	0.003
Hg	ND	ND	ND	ND
Cr	0.07 ±0.02	0.06 ±0.03	0.05-0.10	0.05
Cu	3.40 ±0.16	4.49 ±0.14	1.00	-

Different alphabetical superscripts in the same column refer to a significant increase at $p < 0.05$ between mean ±standard deviation values of different course streams according to Duncan multiple range test, while same alphabetical superscripts in the same column signify an not significant increase at $p > 0.05$ between mean ±standard deviation values of different course stream according to Duncan multiple range test, CV% = coefficients of variation. WHO: World Health Organisation Guidelines for Drinking Water Quality (2014). NESREA: National Environment Standard, Regulation and Enforcement Agency Guidelines and Standards for Water Quality in Nigeria (2015).

Table 2 Correlation matrix for heavy metal properties of wastewater obtained from a soap detergent industry in Aba River (wet season).

		Correlation matrix							
		Fe	Zn	Pb	As	Cd	Hg	Cr	Cu
Correlation	Fe	1.000							
	Zn	0.972	1.000						
	Pb	0.894	0.762	1.000					
	As	-0.685	-0.493	-0.939	1.000				
	Cd	0.351	0.119	0.733	-0.923	1.000	0		
	Hg	0	0	0	0	0	1.000	0	0
	Cr	0.750	0.571	0.967	-0.996	0.883	0	1.000	
	Cu	0.417	0.621	-0.034	0.376	-0.705	0	-0.289	1.000

Table 3 Correlation matrix for heavy metal properties of wastewater obtained from a soap detergent industry in Aba River (dry season).

		Correlation matrix							
		Fe	Zn	Pb	As	Cd	Hg	Cr	Cu
Correlation	Fe	1.000							
	Zn	0.916	1.000						
	Pb	0.750	0.422	1.000					
	As	-0.020	-0.419	0.646	1.000				
	Cd	-0.258	0.151	-0.832	-0.961	1.000	.		
	Hg	0	0	0	0	0	1.000	0	0
	Cr	0.876	0.996	0.338	-0.500	0.240	0	1.000	0
	Cu	-0.428	-0.754	0.276	0.912	-0.763	0	-0.811	1.000

3.4 Heavy Metals in Surface Water of Aba River during Wet and Dry Seasons

3.4.1 Lead (Pb) (mg/L)

Aba River (wet season) recorded lead mean concentrations of 0.04 mg/L. There is no significant difference at $p > 0.05$ in the lead (Pb) mean values in the sampled rivers. The recorded lead (Pb) concentrations were above the NESREA WHO and USEPA limit concentrations in surface water values of 0.01 mg/L, 0.01 mg/L and 0.015 mg/L respectively.

In dry season, the lead mean concentration is 0.09 mg/L. There is no significant increase at $p < 0.05$ in the mean concentrations of lead in the study rivers. The lead concentrations were above the NESREA, WHO and USEPA permissible standards of 0.01 mg/L, 0.01 mg/L and 0.015 mg/L respectively.

3.4.2 Cadmium (Cd) (mg/L)

Aba River recorded a mean cadmium concentration values that were above the NESREA, WHO and USEPA limits of 0.003 mg/L, 0.003-0.005 mg/L and 0.005 mg/L respectively.

In dry season, the cadmium mean concentration value was 0.09 mg/L. There is no significant increase in the cadmium mean concentration values across the rivers. The recorded cadmium mean concentrations were above the NESREA WHO and USEPA permissible standards of 0.003 mg/L, 0.003-0.005 mg/L and 0.005 mg/L respectively.

3.4.3 Cupper (Cu) (mg/L)

Heavy metal copper was not detected in Aba River respectively. In dry season, the copper mean concentration value was 0.17 mg/L. The copper concentrations were within the permissible standards of 1.00 mg/L and 1.3 mg/L respectively.

3.4.4 Manganese (Mn) (mg/L)

There was no record of heavy metal manganese in Aba River in wet season. In dry season, manganese mean concentration in Aba River was 0.17 mg/L.

3.4.5 Zinc (Zn) (mg/L)

The heavy metal zinc was not found in Aba River in wet season. In dry season, the zinc mean concentrations were within the WHO and USEPA permissible standards of 3.0 mg/L and 5.0 mg/L respectively.

3.4.6 Iron (Fe) (mg/L)

The metal iron (Fe) was not recorded in Aba River in wet season. In dry season, the iron mean concentration in Aba River is 3.17 mg/L. There is no significant difference at $p < 0.05$ in the mean values. The iron mean concentration is above the NESREA WHO and USEPA permissible limits of 0.03 mg/L.

3.4.7 Mercury (Hg) (mg/L)

Heavy metal mercury (Hg) was not detected in Aba River in wet season. In dry season, the mean values were above the NESREA WHO and USEPA permissible standards of 0.001 mg/L, 0.002 mg/L and 0.002 mg/L respectively.

3.4.8 Chromium (Cr) (mg/L)

Aba River recorded mean chromium concentration value of 0.02 mg/L in wet season. The recorded chromium concentration in the sampled river is within the NESREA WHO and USEPA limits of 0.05, 0.05-

0.10 and 0.05-1.00 respectively. In dry season, chromium mean concentration in Aba River was above the permissible standard.

3.4.9 Nickel (Ni) (mg/L)

Aba River recorded a nickel mean concentration of 0.01 mg/L in wet season. There is no significant increase at $p > 0.05$ in the nickel concentration values across the rivers. The nickel mean concentration was within the NESREA WHO and USEPA limit of 0.02 mg/L. In dry season, the mean concentration in the river was 0.02 mg/L. This was within the NESREA WHO and USEPA standards of 0.02 mg/L.

3.5 Correlation Matrix for Heavy Metal Parameters in Surface Water of Aba River during Wet Season

The correlation matrix in Aba River surface water (wet season) shows different types of correlation matrix for surface water heavy metal parameter: stronger positive, weak positive and negative type of correlation coefficient. During wet season, a strong positive significant correlation matrix exits between the following heavy metal parameter pairs: Cd/Ni (r = 1.000), while a very strong significant negative correlation matrix exits in Pb/Cd (r = -0.866), Pb/Ni (r = -0.866), Cr/Ni (r = -0.866). The positive correlation implies that the heavy metal parameters are from same source while the negative heavy metal parameters imply that they are not of the same source.

3.6 Correlation Matrix for Heavy Metal Parameters in Surface Water of Aba River during Dry Season

In dry season, a strong positive significant correlation matrix exits between the following heavy metal parameter pairs: Pb/Cr (r = 0.993), Pb/Cu (r = 0.710), Cd/Hg (r = 0.866), Cu/Cr (r = 0.786), Cu/Ni (r = 0.929), Mn/Fe (r = 0.931). A strong negative correlation exits between the following parameters: Pb/Mn (r = -0.972), Cu/Fe (r = -0.985), Mn/Cr (r = -0.993), and Zn/Hg (r = -1.000). The positive correlation implies that the heavy metal parameters are from same source.

Table 4 Heavy metals in surface water of Aba River (wet and dry season).

Heavy metals (mg/L)	Aba River (wet season)	Aba River (dry season)	NESREA (2015)	WHO (2008)	USEPA (2010)
Pb	0.03 ± 0.01^a	0.09 ± 0.04^a	0.01	0.01	0.015
Cd	0.02 ± 0.00^a	0.09 ± 0.01^a	0.003	0.003-0.005	0.005
Cu	ND	0.06 ± 0.04^a	-	1.00	1.3
Mn	ND	0.17 ± 0.12^a	0.2	-0.05	0.05
Zn	ND	0.07 ± 0.00^b	-	3.000	5
Fe	ND	3.17 ± 2.11^a	0.3	0.3	0.3
Hg	ND	0.02 ± 0.00^a	0.001	0.002	0.002
Cr	0.02 ± 0.01^b	0.17 ± 0.02^b	0.05	0.05-0.10	0.05-1.00
Ni	0.01 ± 0.00^a	0.02 ± 0.00^a	0.02	0.02	0.02

Different alphabetical superscripts in the same row refer to a significant increase at $p < 0.05$ between mean ± standard deviation values of different course streams according to Duncan multiple range test, while same alphabetical superscripts in the same row signify a not significant increase at $p > 0.05$ between mean ± standard deviation values of different course stream according to Duncan multiple range test. WHO: World Health Organisation Guidelines for Drinking Water Quality (2014). NESREA: National Environment Standard, Regulation and Enforcement Agency Guidelines and Standards for Water Quality in Nigeria (2015). USEPA: United States Environmental Protection Agency.

Table 5 Correlation matrix for heavy metal parameters in surface water of Aba River during wet season.

	Pb	Cd	Zn	Cr	Ni
Pb	1				
Cd	-0.866	1			
Zn	0.000	0.000	1		
Cr	0.500	-0.866	0.000	1	
Ni	-0.866	1.000	0.000	-0.866	1

0.05 level (2-tailed).

3.7 Heavy Metals in Bottom Sediments of Aba River during Wet and Dry Season

3.7.1 Lead (Pb)

In wet season, Aba River recorded lead mean value of 0.04 mg/L (Table 6). There is no significant increase at $p < 0.05$ in the mean concentration of lead in the study river. The lead mean concentration was below the NESREA WHO and USEPA permissible limits of 10, 32 mg/L, 35 mg/L respectively.

While in dry season, Aba River recorded lead mean value of 0.12 mg/L. The lead mean concentration was within the NESREA WHO and USEPA permissible limits of 10 mg/L, 32 mg/L, 35 mg/L respectively.

3.7.2 Cadmium (Cd)

In wet season, sediment samples obtained from Azumini Blue River recorded cadmium mean concentrations of 0.02 mg/L. The obtained cadmium mean concentration in the study river was within the NESREA WHO and USEPA permissible limits of 3 mg/L, 0.68 mg/L and 5 mg/L respectively.

While in dry season, sediment samples obtained from Aba River recorded cadmium mean concentration of 0.62 mg/L. The obtained cadmium mean concentration in the study river was within the NESREA WHO and USEPA permissible limits of 3 mg/L, 0.68 mg/L and 5 mg/L respectively.

3.7.3 Copper (Cu)

In wet season, there was no record of copper in Aba River.

In dry season, sediment samples obtained from Aba River recorded copper mean concentration of 0.06 mg/L. The obtained cadmium mean concentration in the study rivers was within the NESREA WHO and USEPA permissible limits of 3 mg/L, 0.68 mg/L and 5 mg/L respectively.

3.7.4 Manganese (Mn)

In wet season, there was no record of manganese in Aba River. While in dry season, sediment samples obtained from Aba River recorded manganese mean concentration 0.07 mg/L. The obtained manganese mean concentration in the study river was within the NESREA permissible limits of 200 mg/L.

3.7.5 Zinc (Zn)

In wet season, sediment samples obtained from Aba River recorded zinc mean concentration of 0.04 mg/L. The obtained zinc mean concentration in the study river was within the permissible limits of 123 mg/L and 300 mg/L respectively.

While in dry season, sediment samples obtained from Aba River recorded zinc mean concentrations of 0.08 mg/L. The obtained zinc mean concentration in the study rivers was within the NESREA WHO and USEPA permissible limits of 123 mg/L and 300 mg/L respectively.

3.7.6 Iron (Fe)

In wet season, sediment samples obtained from Aba River recorded iron mean concentration of 0.21 mg/L. The obtained iron mean concentration in the study river was within the permissible limits of 3.0 mg/L and 5,000 mg/L respectively.

While in dry season, sediment samples obtained from Aba River recorded iron mean concentration of 0.78 mg/L. The obtained iron mean concentration in the study river was within NESREA WHO and USEPA. permissible limits of 3.0 mg/L and 5,000 mg/L respectively.

3.7.7 Mercury (Hg)

In wet season, there was no record of mercury in Aba River in wet season. While in dry season, sediment samples obtained from Aba River recorded mercury mean concentration of 0.05 mg/L respectively.

3.7.8 Chromium (Cr)

In wet season, the chromium mean concentrations in Aba River was 0.01 mg/L. The chromium mean concentration recorded in the Study Rivers was lower and within the NESREA 20 mg/L permissible limits.

In dry season, the chromium mean concentrations in Aba River was 0.08 mg/L. Congruently, the obtained chromium mean concentration in sediments of the study areas was way below and within the NESREA 20 mg/L permissible limits.

3.7.9 Nickel (Ni)

In wet season, the nickel mean concentrations in Aba River was 0.01 mg/L (Table 6). The nickel mean concentration recorded in the study river was lower and within the NESREA WHO and USEPA of 20 mg/L, 15.9 mg/L and 140 mg/L permissible limits.

In dry season, the nickel mean concentration in Aba River was 0.20 mg/L. Congruently, the obtained nickel mean concentration in sediments of the study areas was below and within the NESREA WHO and USEPA of 20 mg/L, 15.9 mg/L and 140 mg/L permissible limits.

Table 6 Heavy metals in bottom sediments of Aba River wet and dry season.

Heavy metals (mg/L)	Aba River (wet season)	Aba River (dry season)	NESREA (2015)	WHO (2008)	USEPA (2010)
Pb	0.04 ± 0.00^a	0.12 ± 0.03^b	0.01	0.01	0.015
Cd	0.02 ± 0.01^b	0.62 ± 0.10^b	0.003	0.003-0.005	0.005
Cu	ND	0.06 ± 0.01^b	-	1.00	1.3
Mn	ND	0.07 ± 0.01^a	0.2	-0.05	0.05
Zn	0.04 ± 0.00^b	0.08 ± 0.01^a	-	3.000	5
Fe	0.21 ± 0.07^a	0.78 ± 0.13^b	-0.3	0.3	0.3
Hg	ND	0.05 ± 0.01^a	0.001	0.002	0.002
Cr	0.01 ± 0.00^a	0.08 ± 0.03^a	0.05	0.05-0.10	0.05-1.00
Ni	0.01 ± 0.02^a	0.20 ± 0.11^a	0.02	0.02	0.02

Different alphabetical superscripts in the same row refer to a significant increase at $p < 0.05$ between mean ± standard deviation values of different course streams according to Duncan multiple range test, while same alphabetical superscripts in the same row signify a not significant increase at $p > 0.05$ between mean ± standard deviation values of different course stream according to Duncan multiple range test. WHO: World Health Organisation Guidelines for Drinking Water Quality (2013). NESREA: National Environment Standard, Regulation and Enforcement Agency Guidelines and Standards for water quality in Nigeria (2022). USEPA: United States Environmental Protection Agency.

Table 7 Contamination factor (CF), modified degree of contamination (mCd) and pollution load index (PLI) of heavy metals in sediments of Aba River during wet season.

Location	Course Streams	Pb	Cd	Cu	Mn	Zn	Fe	Hg	Cr	Ni	mCD	PLI
Aba River	Upper Stream	0.002	0.0067	ND	ND	0.0005	2.86E-05	ND	0.0001	0.0000	0.001	0.1027
	Middle Stream	0.002	0.0067	ND	ND	0.0005	1.43E-05	ND	0.0001	0.0003	0.001	0.1029
	Down Stream	0.0025	0.0083	ND	ND	0.0004	2.35E-05	ND	0.0001	0.0001	0.0012	0.0699

ND = not detected. If CF<1, it means that low contamination exists; if 1<CF<3, it means that moderate contamination exists; if 3<CF<6, it means that considerable contamination exists; if CF>6, it means that very high contamination exists. CD<6 = low degree of contamination; 6≤CD<12 = moderate degree of contamination; 12≤CD<24 = considerable degree of contamination; CD≥24 = very high degree of contamination. When PLI>1, it means that pollution exists; at PLI<1, there is no metal pollution.

Table 8 CF, mCD and PLI of heavy metals in sediments of Aba River during dry season.

Location	Course Streams	Pb	Cd	Cu	Mn	Zn	Fe	Hg	Cr	Ni	mCD	PLI
Aba River	Upper Stream	0.0020	0.3333	0.0007	0.0004	0.0008	0.0005	0.0005	0.0016	0.0003	0.0378	0.3396
	Middle Stream	0.0060	0.3667	0.0013	0.0001	0.0007	0.0003	0.0008	0.0021	0.0003	0.0420	0.3776
	Down Stream	0.0055	0.3000	0.0024	0.0001	0.0008	0.0001	0.0005	0.0021	0.0004	0.0347	0.3116

ND = not detected. If CF<1, it means that low contamination exists; if 1<CF<3, it means that moderate contamination exists; if 3<CF<6, it means that considerable contamination exists; if CF>6, it means that very high contamination exists. CD<6 = low degree of contamination; 6≤CD<12 = moderate degree of contamination; 12≤CD<24 = considerable degree of contamination; CD≥24 = very high degree of contamination. When PLI>1, it means that pollution exists; at PLI<1, there is no metal pollution.

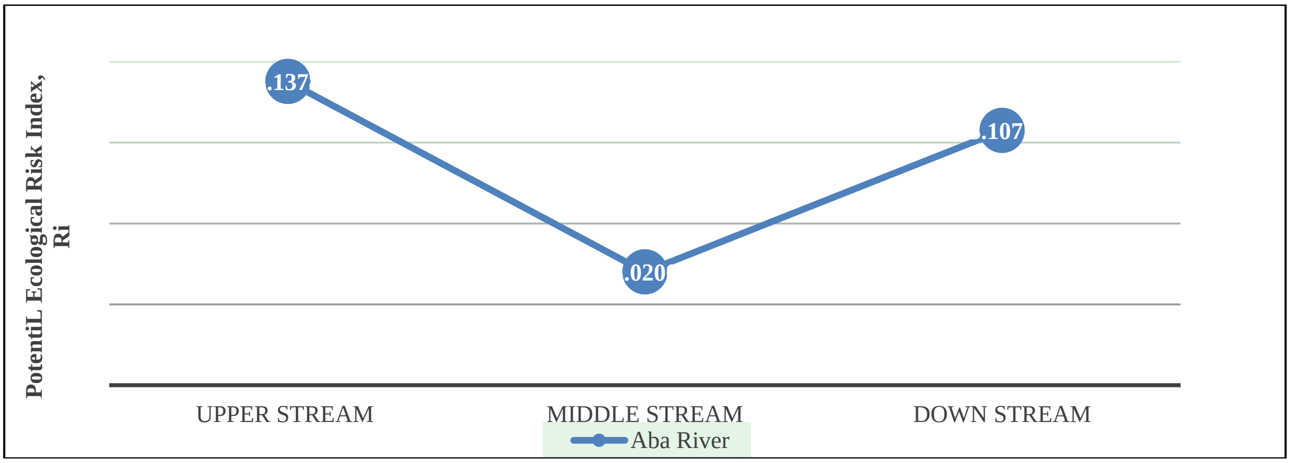

Fig. 2 Potential ecological risk index (RI) of the upper, middle and down streams of Aba River during wet season.

ERI < 40, low potential ecological risk; 40 ≤ ERI < 80, moderate potential ecological risk; 80 ≤ ERI < 160, considerable potential ecological risk; 160 ≤ ERI < 320, high potential ecological risk; and ERI ≥ 320, very high ecological risk. RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, high ecological risk and RI > 600, very high ecological risk..

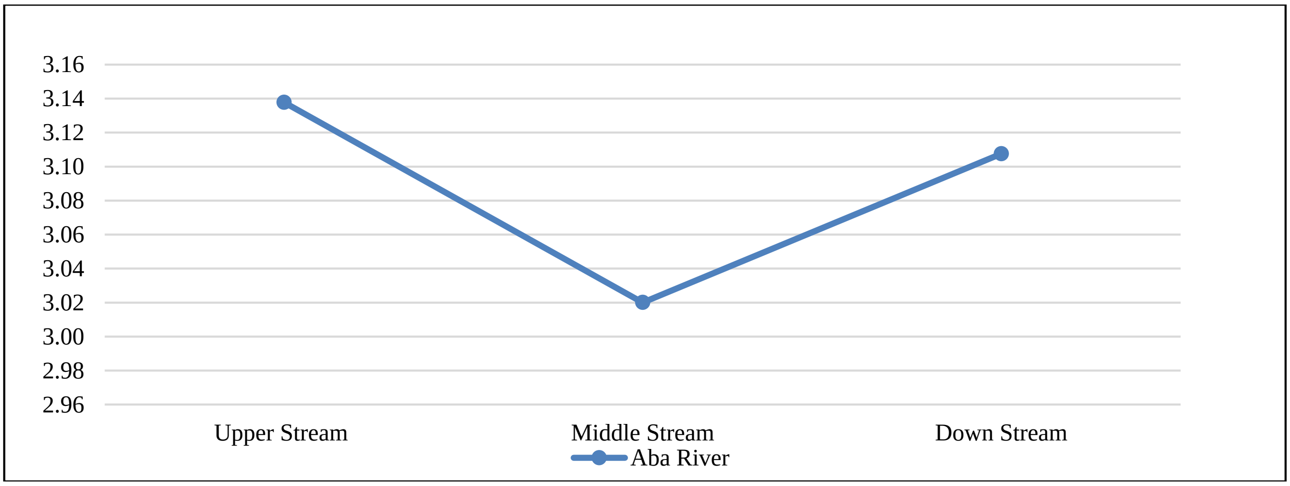

Fig. 3 Potential ecological RI of the upper, middle and down streams of Aba River during dry season.

ERI < 40, low potential ecological risk; 40 ≤ ERI < 80, moderate potential ecological risk; 80 ≤ ERI < 160, considerable potential ecological risk; 160 ≤ ERI < 320, high potential ecological risk; and ERI ≥ 320, very high ecological risk. RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, high ecological risk and RI >600, very high ecological risk.

4. Discussion

4.1 Heavy Metal Properties of Wastewater Obtained from a Soap Detergent Industry (Pz Cussons Nigeria. Plc.) in Aba (Wet And Dry Season)

4.1.1 Iron (mg/L)

Iron at high concentration, causes tissues damage and some other diseases in humans. It is also responsible for anemia and neurodegenerative conditions in human being [5]. The iron mean concentrations in wet and dry season are 13.22 and 15.28 mg/L respectively. Dry season recorded a higher iron mean value when compared to wet season. The recorded iron mean values for both seasons were above the WHO and NESREA permissible limits of 0.3 mg/L. This value shows that the raw water is safe for malting of barley, drinking, and other domestic purposes. This indicated that, in terms of Fe content, the wastewater is not safe for irrigation and domestic purposes. Wastewater containing high concentration of Fe can increase soil acidity and diminish phosphorous in soil.

4.1.2 Zinc (mg/L)

Zinc mean values for both wet and dry seasons are 5.39 and 6.30 mg/L respectively. Dry season recorded a higher zinc mean value when compared to wet season. The zinc mean values for both seasons are above the permissible limits of 3.000 mg/L. Zn is the least toxic and is an essential element in the human diet as it is required to maintain the proper functioning of the immune system, normal brain activity and is fundamental in the growth and development of the foetus, but a very high concentration of zinc is very toxic, hence harmful to the human body [6]

4.1.3 Lead (mg/L)

Lead has been used widely for application in metal products, cables and pipelines, as well as paints and pesticides. Lead is one of the metals that have the most damaging effects on human health [1]. It is a non-essential heavy metal. Pb causes oxidative stress and contributes to the pathogenesis of lead poisoning by disrupting the delicate antioxidant balance of the mammalian cells. High level accumulation of Pb in body causes anemia, colic, headache, brain damage, and central nervous system disorder [20]. Wet and dry seasons recorded lead mean concentration values of 1.16 mg/L and 2.14 mg/L respectively. Dry season recorded a higher lead mean value when compared to wet season. The recorded lead mean values were above the permissible limits of 0.01 mg/L. This marks the water unsuitable for human consumption as Pb is known to be toxic even at low levels with resultant ill-health effects as chronic exposure has been linked to growth retardation in children [11].

4.1.4 Cadmium (mg/L)

Cadmium is also a non-essential heavy metal. It is extremely toxic even at low concentration. It causes learning disabilities and hyperactivity in children [7]. The mean concentration values of cadmium in both wet and dry seasons are 0.02 mg/L and 0.05 mg/L respectively. The recorded cadmium mean concentration values recorded in both seasons were above the permissible limits. The toxicity of Cd in wastewater is influenced by wastewater hardness. This value is much higher than the maximum allowed limit. This indicated that, the wastewater is not safe for irrigation and domestic purposes after discharge of Cd content. Cadmium used in industry finds its way into many water supplies. Old galvanized pipes and new plastic (PVC) pipes are sources of cadmium in water pump [23].

4.1.5 Chromium (mg/L)

Chromium plays a vital role in the metabolism of cholesterol, fat, and glucose. Its deficiency causes hyperglycemia, elevated body fat, and decreased sperm count, while at high concentration it is toxic and carcinogenic [2]. The mean concentration of chromium in both wet and dry seasons of the study river is 0.07 mg/L and 0.06 mg/L respectively. Chromium mean concentrations recorded in both seasons were above the permissible limit. The possible sources of Cr may be barley or the dust particles of the barley used for malting. So in terms of Cr, the wastewater samples were not safe for irrigation. Continuous exposure to high Cr levels causes lung cancer in men, liver and kidney damage in animals, and skin irritation. However, Cr supplementation lowers glucose, and lipid levels in elderly diabetics [22]

4.1.6 Copper (mg/L)

Copper mean concentration values in wet and dry seasons are 3.40 mg/L and 4.49 mg/L respectively. The copper mean concentration in dry season was slightly higher than wet season. The recorded copper mean concentration values were higher than the permissible limit of 1.00 mg/L. This could be attributed to the reason of anthropogenic activities and industrial effluent released without treatment.

4.2 Heavy Metal Properties in Surface Water of Aba River during Wet and Dry Season

4.2.1 Lead (Pb) (mg/L)

Aba River (wet season) recorded lead mean concentrations of 0.03 mg/L. There is no significant difference at $p > 0.05$ in the Pb mean concentration values in the sampled rivers. The recorded lead (Pb) concentrations were above the limit concentrations in surface water values of 0.01 mg/L, 0.01 mg/L and 0.015 mg/L respectively.

In dry season, the lead mean concentration is 0.09 mg/L. There is no significant increase at $p < 0.05$ in the mean concentrations of lead in the study rivers. The lead concentrations were above the permissible standards of 0.01 mg/L, 0.01 mg/L and 0.015 mg/L respectively.

4.2.2 Cadmium (Cd) (mg/L)

In wet season, Aba River recorded a mean cadmium concentration value that was above the limits of 0.003, 0.003-0.005 and 0.005 respectively. In dry season, the cadmium mean concentration value was 0.09 mg/L. There is no significant increase in the cadmium mean concentration values across the rivers. The recorded cadmium mean concentrations were above the permissible standards of 0.003 mg/L, 0.003-0.005 mg/L and 0.005 mg/L respectively.

4.2.3 Copper (Cu) (mg/L)

Copper is a natural element which is widely distributed in soils, rocks and in rivers. It is released into water as a result of natural weathering of soil and discharges from industries and sewage treatment plants. Heavy metal copper was not detected in Aba River respectively in wet season. In dry season, the copper mean concentration value was 0.06 mg/L. The copper concentrations were within the permissible standards of 1.00 mg/L and 1.3 mg/L respectively. In the dissolved form, Cu is potentially very toxic to aquatic animals and plants, especially to young life-stages such as fish larvae. However, the toxicity is greatly reduced when Cu is bound to particulate matter in the river water and when the water is hard) [3]

4.2.4 Manganese (Mn) (mg/L)

There was no record of heavy metal manganese in Aba River in wet season. In dry season, manganese mean concentration in Aba River was 0.17 mg/L respectively. Mn is an abundant metal in earth's crust and usually occurs with iron. It is used in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient in various products. It gets into the aquatic ecosystems from industries manufacturing dry-cell batteries, glass, and fertilizer and in leather and textile [25]. The high levels observed at Kathini could be due to industrial activities in the Thika sub-catchment while at Tumutumu the Mn levels recorded may be due to high use of agricultural fertilizers, soil erosion and quarry activities within the catchment. Comparable studies carried out in Kenya have recorded higher mean Mn values than observed in Masinga reservoir. These studies include those done by [10] in Winam Gulf, Lake Victoria (0.05-3.276 mg/L) and [13] in Lake Kanyaboli, Kenya (0.185-0.376 mg/L). Also. [13] obtained higher mean levels of Mn in five rift valley lakes (0.050-0.282 mg/L). recorded similar mean Mn values ranging from 0.099-0.140 mg/L in Owabi reservoir, India observed (0.0001-0.107 mg/L) and in River Nile, Egypt (0.033-0.099 mg/L[17] recorded higher Mn values (0.346 ± 0.391 mg/L) in Owen Multi-purpose Dam Water, Nigeria.

4.2.5 Zinc (Zn) (mg/L)

The heavy metal zinc was not found in Aba River in wet season. In dry season, the zinc mean concentration was within the permissible standards of 3.0 mg/L and 5.0 mg/L respectively. Zn is introduced into water bodies through artificial pathways such as by-products of steel production or coal-fired power stations and burning of waste materials [3]. It is also through leaching from fertilizers, effluents of commercial industries during mining and smelting (metal processing) activities. Other sources of Zn into aquatic ecosystems include urban runoff and municipal sewages [3]

4.2.6 Iron (Fe) (mg/L)

The metal iron (Fe) was not recorded in Aba River in wet season. In dry season the iron mean concentration in Aba River is 3.17 mg/L. There is no significant difference at $p < 0.05$ in the mean values. The iron mean concentration is above the permissible limits of 0.03 mg/L.

4.2.7 Mercury (Hg) (mg/L)

Heavy metal mercury (Hg) was not detected in Aba River in wet season. In dry season, the mean value concentration was above the permissible standards of

0.001 mg/L, 0.002 mg/L and 0.002 mg/L respectively.

4.2.8 Chromium (Cr) (mg/L)

The main sources of Cr are industrial wastes such as Cr pigment, tannery wastes, leather manufacturing wastes and municipal sewage [19]In wet season, Aba River recorded mean chromium concentration value of 0.02 mg/L. The recorded chromium concentration in the sampled river is within the limits of 0.05 mg/L, 0.05-0.10 mg/L and 0.05-1.00 mg/L respectively. In dry season, chromium mean concentration in Aba River was above the permissible standard. Compared to other studies, the mean Cr levels in surface water of Masinga reservoir were lower than 0.23-0.79 mg/L recorded in Lake Victoria [18], 0.025-0.188 mg/L in five rift valley lakes [14] and 0.068 mg/L in Athi River tributaries [11]. [14] found mean Cr levels of 0.005-0.061 mg/L at different sites in Lake Kanyaboli while [15] recorded a much higher mean Cr levels of 1.19-3.16 mg/L in River Niger, Nigeria compared to Cr levels in Masinga reservoir. A higher mean Cr level of 0.049 $\pm$ 0.02 mg/L has been recorded in Owen Multi-purpose Dam Water, Nigeria [17]. However, mean Cr levels observed at Masinga reservoir were within the range of 0.003-0.088 mg/L recorded in River Nile, [16]

4.2.9 Nickel (Ni) (mg/L)

Aba River recorded a nickel mean concentration of 0.01 mg/L in wet season. There is no significant increase at $p > 0.05$ in the nickel concentration values across the rivers. The nickel mean concentration was within the limit of 0.02 mg/L.

In dry season, the mean concentrations in the river was 0.02 mg/L. This was within the standards of 0.02 mg/L. Even though some of these metals were recorded at below allowable limits, the fact that they are present in the water is a cause for concern since they can bio-accumulate in organisms' overtime causing health hazards.

4.3 CF, mCd and PLI of Heavy Metals in Sediments of Aba River in Wet and Dry Seasons

Contamination and pollution by anthropogenic or natural processes were assessed using CFs, mCd and PLI. The CFs of each of the assayed heavy metals were less than 1 (CD < 1). Adopting the method of the degree of metal (Pb, Cd, Cu, Mn, Zn, Fe, Hg, Cr and Ni) contamination in the sediment samples obtained from the upper, middle and down streams recorded a low degree of contamination CD<6 = low degree of contamination. Using the methods of, the PLI values in Aba River across the streams indicated that there is no metal pollution at PLI < 1 in the sampled sediments, while the middle stream of Aba River (sediment) in dry season recorded the highest PLI value of 0.3776. The PLI values in the course streams of Aba River (sediment) indicated that there is no metal pollution at PLI < 1 in the sampled sediments. On a broad scale, Aba River during wet and dry season is not polluted with heavy metals beyond the limits of tolerance at present as revealed in the study.

4.4 Potential Ecological RI of the Upper, Middle and Down Streams of Aba River during Wet and Dry Seasons

Due to “toxic-response” factor, compared with other approaches, the potential ecological RI can distinguish the differences among substances and aquatic systems. Therefore, this approach has outstanding advantages to assess the risk of water system as a widely used approach which can provide a better overall ecological risk to the aquatic system. The overall order of magnitude of the potential ecological risk index (PERI) across the course streams (upper, middle and down streams) in Aba River during wet and dry season followed a potential ecological RI sequence order of middle stream > upper stream > downstream. The potential ecological RI across the course streams (upper, middle and down streams) in Aba River was less than 150 (RI < 150) indicating a low ecological RI.

5. Conclusion

The heavy metal properties of the wastewater indicated that Fe, Pb, Cd, Cr and Cu mean concentration values were higher than the permissible limits. Heavy metal properties of the surface water in Aba River (dry seasons) showed that mean concentrations of Pb, Cd, Cu, Mn, Fe, and Cr, were above the permissible limits. Heavy metal properties of the bottom sediments of Aba River (wet and dry season) showed that mean concentrations of Pb, Cd, and Fe were significantly higher than the permissible limits. The heavy metal CF of sediments obtained from Aba River during the wet and dry seasons was low and the CFs of each of the assayed heavy metals were less than 1 (CD < 1). This also signifies the existence of a low contamination in the sediments of the course streams of Aba River during wet and dry seasons. The PLI values of Aba River (sediment) indicated that there is no metal pollution at PLI < 1 in the sampled sediments. The potential ecological RI of Aba River was less than 150 (RI < 150) indicating a low ecological RI. Abatement of pollutants in the wastewater to permissible concentrations required for natural environment protection is needed. The industrial effluents from a soap detergent industry (PZ Cussons Nigeria. Plc.) in Aba are to be effectively treated before disposal to the outside as they are posing serious risk for the health of the people.

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