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Assessment of Heavy Metal Pollution Level of Abonnema River in Nigeria

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Abstract
This study assessed the pollution level of Abonnema River by some priority heavy metals with a view to evaluating the heavy metal pollution index (HPI) and individual metal pollution index (MPI). Five sampling stations (A, B, C, D and D) were selected based on the increased level of anthropogenic activities taking place in the river. Water samples were analysed for cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn) and mercury (Hg) using the Atomic Absorption Spectrophotometer. Their mean concentrations were compared with standards set by the World Health Organization (WHO), Nigerian Federal Ministry of Environment (FMEnv.), and Canadian Council for the Ministers of the Environment (CCME). The results from the study showed that the mean concentrations of the metals exceeded these standards with Cu having the highest mean concentration of 0.105mg/l. The heavy metal pollution index (HPI) and individual metal pollution index (MPI) values calculated were well above the critical pollution index (100) at each of the stations. Station D has the highest HPI of 2615.23, 2877.11 and 3294.32 using CCME, FMEnv, and WHO standards respectively while Hg had the highest MPI value of 466.67 with respect to CCME standards. The profile in terms of increasing MPI concentration is Hg> Cd> Cu> Pb>Fe>Mn. Based on these results, Abonnema River could be said to be polluted with heavy metal.

Keywords: *Abonnema, Heavy metals, Assessment, River, Pollution*

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I. Introduction

Rural communities around the world traditionally take their water supplies from rivers or from shallow dug wells. Population growth combined with increasing industrialization has resulted in many rivers being highly polluted. Sometimes the pollution levels can cause the rivers to become biologically dead and very unfit for drinking. Treatment of contaminated water for drinking is usually difficult and requires huge financial and human resources. Even after treatment, the quality of the water is hardly returned to its original state and the remaining subtle pollutants in trace quantities can still pose health risks.

The key pollutants in the water system are typically pathogens arising from human waste, heavy metals and organic chemicals from industrial waste. The common pathway through which pollutants get into our bodies are through drinking contaminated water or eating food prepared with contaminated water. Furthermore, eating fish from contaminated water can be risky, since the fish can absorb and accumulate pollutants such as heavy metals and persistent organics. In addition, human health may be affected by crops that take up pollutants from contaminated water used for irrigation or from land flooded by polluted rivers.

The major sources of heavy metal pollution in urban areas of Africa are anthropogenic, while contamination from natural sources predominates in rural areas. In Nigeria, sources of heavy metal pollution include atmospheric release from fossil fuels burning, industrial wastes of various kinds, domestic sewage discharge, land run-off or stormwater, acid rain which occurs because of releases from industrial operations such as mining, canning, electroplating, refining and gas processing, and extensive drilling and utilization of crude oil (Marr and Creasser, 1983; El-Nabawi et al., 1987; Egborge, 1994; Ayenimo et al., 2005; Lenntech, 2011). Though some heavy metals (e.g., copper, selenium, zinc) are essential to maintain the metabolism of the human body, their concentration above desirable levels can be poisonous (Duruibe et al., 2007; Raikwar, 2008; Lenntech, 2011; Jeje and Oladepo, 2014).

Although the sediment and surface water of Sombriero River in Abonnema in Akuku Toru Local Government Area of Rivers State has been studied to assess the level of pollution by some heavy metals about sixteen years ago, little or nothing is known about the current state of heavy metal concentration in the river. Thus, the aim of this study is to determine the baseline concentration status of some heavy metals (Cadmium (Cd), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn) and Mercury (Hg)) along Abonnema River in Rivers

State with a view to finding the heavy metal pollution index and comparing results obtained with acceptable standards.

II. Materials and Methods

2.1 Study Area

Abonnema, a typical riverine area, is bounded to the north by Degema local government area, to the south by the Atlantic Ocean, to the east by Asari-Toru and to the west by Nembe. Abonnema is blessed with abundant oil and gas reserves and its communities have network of oil and gas pipelines leading to the multi-million-naira gas plant at Soku and Belema flow stations. The coastal waters of Abonnema shoreline (River Sombriero) leads to these oil and gas bearing communities where oil and gas exploration often occur alongside with major transportation, fishing, and agricultural practices. The shoreline of Abonnema has served as harbour for many decades before it was abandoned. However, it is occasionally inundated by oil spills which causes hydrocarbon as well as heavy metal contamination. Also, the building of the Abonnema-Degema Bridge has contributed its share of toxic heavy metal pollution. The map of the study area is shown in Figure 1.

Figure 1: Map showing study area.

2.2 Collection of Samples and Sampling Points

Water samples were taken from the surface water at different sampling stations selected according to the different anthropogenic activities taking place at the river. The locational co-ordinates (longitudes and latitudes) of each of the stations were noted and the sampling locations were referred to as A, B, C, D and E. Sampling station A was located at the uppermost part of Sombriero river and the major anthropogenic activities in this station were marine transportation and agricultural activities (fermentation of cassava). Sampling station B was located at pipeline manifold which transports crude oil and condensate to Soku gas plant. This station also receives bulk of wastewater discharges/runoff from domestic and municipal activities from nearby communities and industrial waste from Soku gas plant, in addition to the heavy marine transportation activities around there. Sampling station C and E were located near fishing settlement where bunkering activities takes place with barges and tugboats plying adjourning creeks while sampling station D was located in an oil field flow station with well heads, manifold and waste pits with flare point.

The water samples were collected weekly from August to October 2015. Five numbers of 1 litre high density polyethylene (HDPE) bottles were used to collect the water samples. The polyethylene bottles were washed twice with 10% and 3% analytical grade nitric acid (HNO_3) respectively, and then rinsed with distilled water. The sample bottles were well labelled with date of collection and the sampling station. The temperature and pH of water samples were recorded in-situ using a digital thermometer and portable pH meter, respectively. The water samples were properly corked and preserved with ultra-pure HNO_3 (pH<2) to prevent precipitation of metal hydroxides or adsorption of metals on the walls of the plastic container and thereafter stored in a refrigerator at 4^oC to minimize microbial activity. The preserved samples were sent to the laboratory for analysis in an ice chest cooler to maintain sample quality.

2.2 Laboratory Analysis

The concentration of heavy metals in the preserved water samples was determined by spectrometric analysis using Atomic Absorption Spectrophotometer, Model 210 VGP. The heavy metals analysed include cadmium (Cd), copper (Cu), iron (Fe), Mercury (Hg), lead (Pb) and manganese (Mn).

2.3 Analysis of Data

Basic statistics such as mean, median, range and standard deviation were used to determine the heavy metal concentrations at the different sampling stations for the different months. Bar chats and other forms of charts were used to show differences in concentration levels of heavy metals at the different sampling stations and for the different months. Comparisons were made of the results obtained with Nigerian Federal Ministry of Environment (FMEnv, 2007), World Health Organization (WHO, 2006), and the Canadian Water Quality Guidelines set for the protection of Aquatic lives (Courtesy of the Canadian Council for the Ministers of the Environment, CCME 2005).

Analysis of variance (ANOVA) was used to determine the difference in concentration of heavy metals within the different stations and the various metals at different months. A two-way analysis of variance was used for the analysis. Heavy Metal Pollution Index (HPI) was used to evaluate the extent of pollution in the river. HPI is a method of rating that shows the composite influence of each individual heavy metal on the overall quality of water. The rating is between 0 and 100, reflecting the relative importance of individual quality considerations and defined as inversely proportional to the recommended standard (**S_i**) for each parameter. The HPI was calculated for the entire river and for each sampling station and the value obtained was compared with the Critical Pollution Index (1000) for heavy metals. The HPI was calculated using Equations (1) to (3) (Reza and Singh, 2010).

First, the weightage of the i^{th} parameter (the heavy metals) was calculated using Equation (1).

$$W_i = \frac{k}{S_i} \qquad (1)$$

where W_i = Weightage of the i^{th} parameter, k = constant of proportionality which is usually 1 and S_i = Maximum Allowable/Permissible Concentration for the heavy metal as set by standards.

Secondly, the quality rating of each heavy metal (Q_i) was calculated using Equation (2).

$$Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i} X\ 100 \qquad (2)$$

where M_i = monitored value of the i^{th} parameter (the average concentrations of each heavy metals for the three sampling months) and I_i = Ideal/Desirable Max value of the i^{th} parameter.

Then, the overall HPI was calculated using Equation (3).

$$\text{HPI} = \frac{\sum QiWi}{\sum Wi} \qquad (3)$$

The Individual Metal Pollution Index (MPI) which represents the sum of the ratio between the analysed parameters and their corresponding national standard values (Tamasi and Cini, 2004) was calculated using Equation (4).

$$MPI = \sum_{i=1}^{n} \frac{M_i}{(MAC)_i} \qquad (4)$$

where M_i = Mean Concentration of the i^{th} parameter, and MAC = Maximum Allowable Concentration of the i^{th} parameter.

Finally, a correlation analysis was done using excel software to show the relationship between metals.

2.4 Water Quality Rating

To describe how each individual heavy metal affects water quality, Lyulko et al. (2001) and Caerio et al. (2005) classified water quality using Metal Pollution Index by setting the standard as shown in Table 1.

Table 1: Water quality classification using metal pollution index

Class	Characteristics	MPI Values
I	Very pure	< 0.3
II	Pure	0.3-1.0
III	Slightly affected	1.0-2.0
IV	Moderately affected	2.0-4.0
V	Strongly affected	4.0-6.0
VI	Seriously affected	> 6.0

III. Results and Discussion

3.1 pH and Temperature Values

The mean pH and temperature recorded for each of the sampling stations for the three months period are shown in Table 2. From the table it was observed that the pH values of the five sampling stations indicate typical values for a moderate to high salinity river with pH value ranging from 6.74 to 7.2. Station D had the lowest pH of 6.74 while Station C had the highest pH of 7.2. Also, the temperature at the sampling Stations ranged from 18.9°C to 21.3°C indicating typical temperatures observed for a sea water during a rainy season (Moustafa, 2013).

Table 2: Results of pH and temperature for each sampling station

Stations	pH	Temperature
A	7.1	20.7°C
B	6.81	19.5°C
C	7.2	21.3°C
D	6.74	18.9°C
E	7.08	20°C

3.2 Heavy Metal Concentration

The results for the monthly heavy metal concentration from each sampling stations for the three months period are shown in Figures 2 to 6. From Figure 2, cadmium has the highest concentration in October (0.116mg/l) and (0.112mg/l) at Stations B and D respectively while copper has the highest concentrations at Station D in August (0.117mg/l), September (0.168mg/l) and October (0.17mg/l) as shown in Figure 3. Concentration of iron was highest at Station D (0.124mg/l) in September (Figure 4) while lead concentration was highest at Station D (0.111mg/l) in August (Figure 5). Also, from Figure 6, manganese concentration was highest at Station B (0.104mg/l) in September while mercury concentration was highest at station D (0.09mg/l) in September as shown in Figure 7.

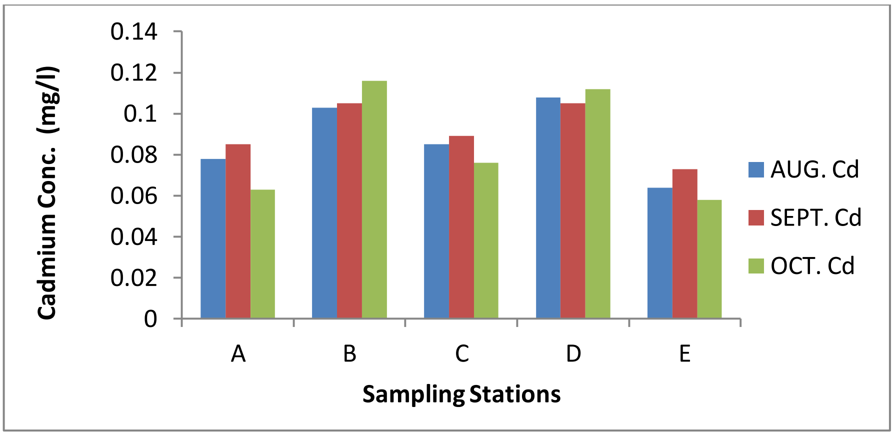

Figure 2: Monthly concentration of cadmium

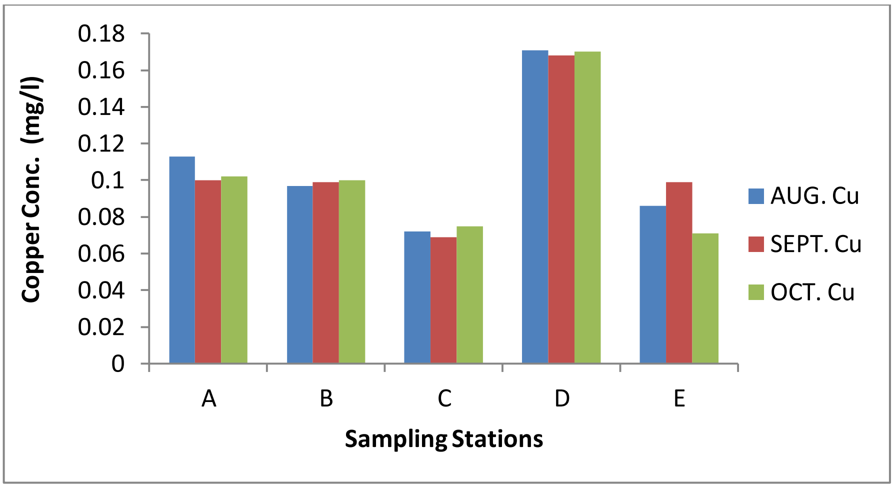

Figure 3: Monthly concentration of copper

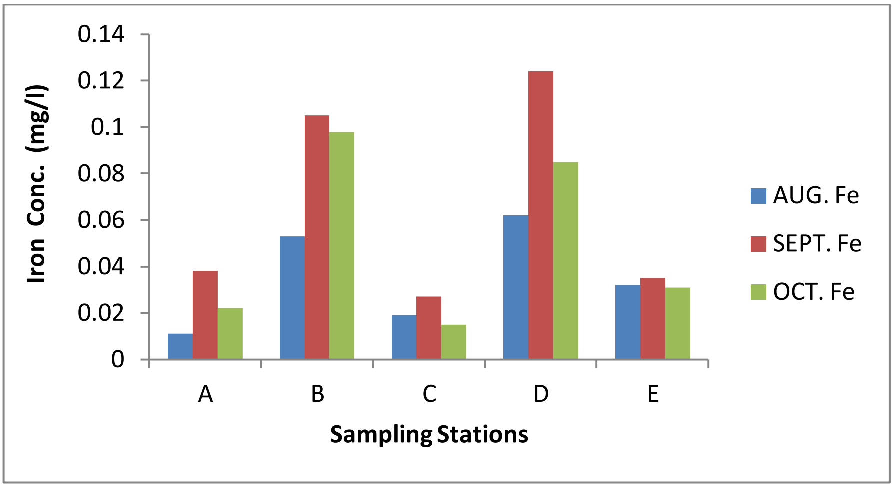

Figure 4: Monthly concentration of iron

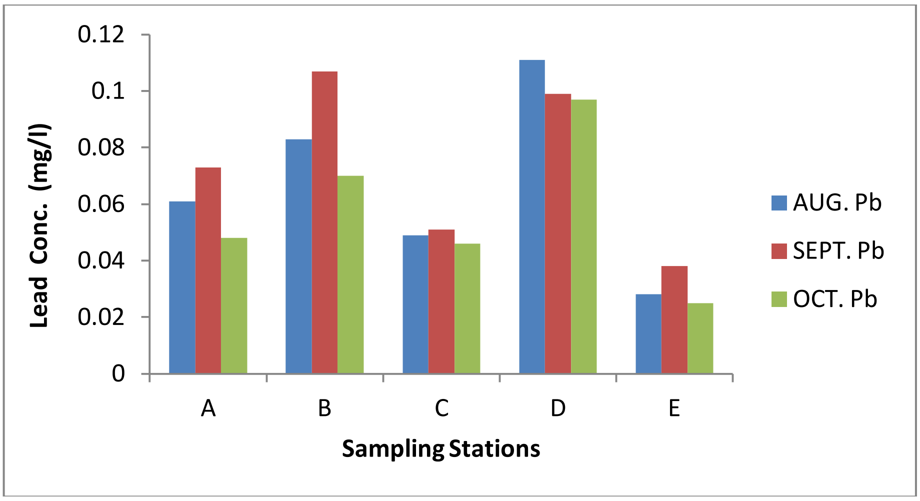

Figure 5: Monthly concentration of lead

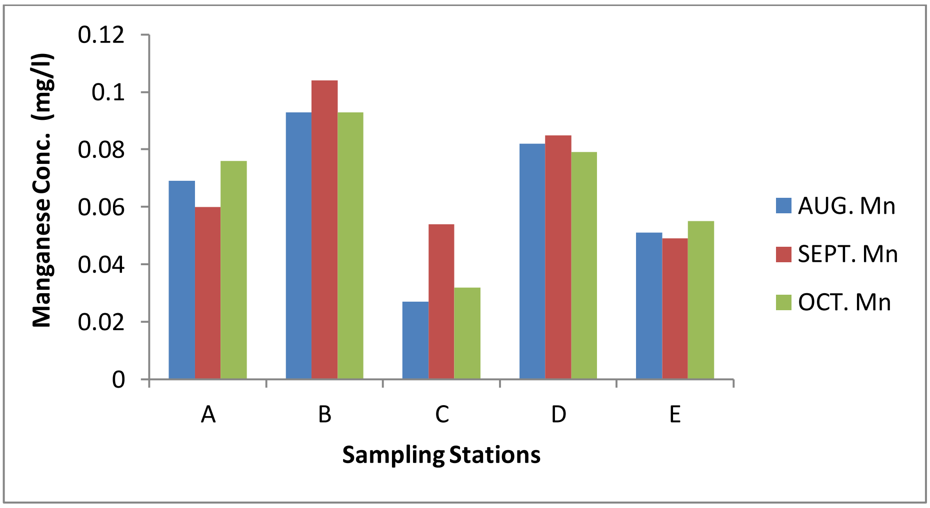

Figure 6: Monthly concentration of manganese

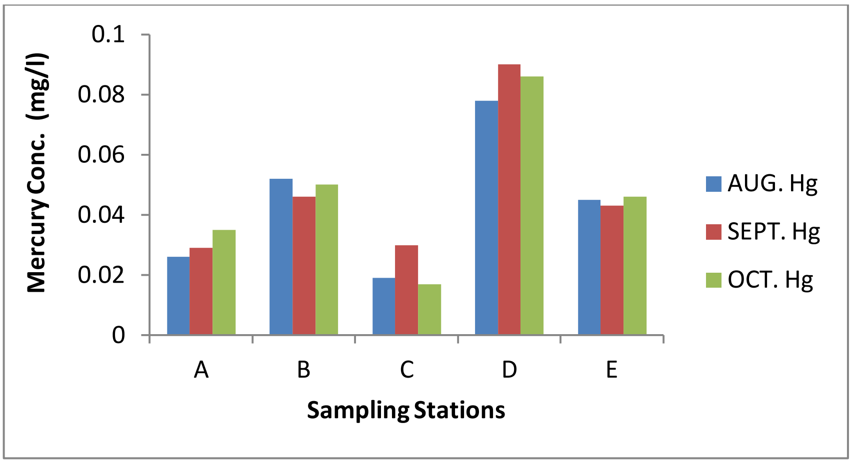

Figure 7: Monthly concentration of mercury

3.3 Concentration Difference among Sampling Stations and Tested Metals

A two-way analysis of variance was done at 5% level of significance to determine the difference in concentration within stations and within the various metals. As seen in Table 3, the variance among the stations and metals has P-values of 3.41E-06 and 2.57E-05, respectively. The calculated P-values are less than the alpha value (0.05) hence an alternate hypothesis is accepted. This implies that concentration of the heavy metals varies significantly from station to station and within the group of metals tested.

Table 3: Difference in concentration among stations and various metals

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Stations	0.015	4	0.0038	16.86	3.41E-06	2.87
Metals	0.013	5	0.0026	11.45	2.57E-05	2.71
Error	0.005	20	0.0002			
Total	0.033	29				

A two-way analysis of variance was done at 5% level of significance to determine the difference in concentration among various metals and between different months. As seen in Table 4, the variances among the various metals and months have P-values of 3E-06 and 8E-02, respectively. The P-value of the variance within metals is less than the alpha value (0.05), which agrees with Table 3. However, the P-value of variance within months is greater than the alpha value indicating that there is no significant difference in the concentration of metals across the different months of measurement. This may mean that the pollution source was consistent in the quality of effluent discharged into the river.

Table 4: Difference in concentration among various metals and different months

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Metals	0.0078	5	0.00156	38.21	3E-06	3.33
Months	0.0003	2	0.00014	3.36	8E-02	4.10
Error	0.0004	10	0.00004			
Total	0.0085	17				

3.4 Correlation of Metal Pairs

A correlation analysis was done to show the relationships between two metal pairs. Table 5 summarises the correlation matrix with the correlation coefficients. A moderate to strong correlation exits between the metals measured at the different stations with lead-cadmium and mercury-copper pairs showing very high correlations of 0.938099 and 0.903404, respectively. This is an indication of inter-dependence of the various metals measured. These metals may be by-products of the same manufacturing process, such that they are always released at the same time.

Table 5: Correlation of various metals across the different stations

	Cadmium	*Copper*	*Iron*	*Lead*	*Manganese*	*Mercury*
Cadmium	1					
Copper	0.610777	1				
Iron	0.890424	0.716393	1			
Lead	0.938099	0.79748	0.865168	1		
Manganese	0.754046	0.577785	0.85735	0.811803	1	
Mercury	0.627986	0.903404	0.84648	0.708087	0.601921	1

3.5 Basic Statistical Concentration Values of Heavy Metals and Standards

The results of the basic statistics of the heavy metal concentration obtained from all the sampling stations of the river for the three months research period are shown in the Table 6. These results were compared with (FMEnv 2007), (WHO 2006) and (CCME 2005) standards. From the result, Cd, Cu and Hg were above the limits having mean concentration values of 0.075, 0.105 and 0.03mg/l respectively while Fe, Pb and Mn were within limits.

Table 6: Comparison of basic statistical concentration values of heavy metals with some water quality standards.

Parameters	**Mean (mg/l)**	**Median (mg/l)**	**Standard Deviation**	**CCME Standard (2005) (mg/l)**	**FMEnv. Standard (2007) (mg/l)**	**WHO Standard (2006) (mg/l)**	**Ideal/Desirable Maximum Value (I_i)**
Cd	0.075	0.080	0.05	0.0018	0.003	0.005	0.02
Cu	0.105	0.107	0.023	0.004	1	0.02	0.04
Fe	0.024	0.03	0.03	0.3	0.3	1	0.64
Pb	0.061	0.066	0.028	0.007	0.01	0.05	0.17
Mn	0.068	0.067	0.024	-	0.02	0.05	0.48
Hg	0.03	0.040	0.029	0.0001	0.001	0.001	0.003

3.6 Heavy Metal Pollution Index

The Heavy Metal Pollution Index (HPI) for each sampling station and the overall HPI for the river was calculated using Equations (1) to (3) applying the different water quality standards. The overall mean concentration value of the metals for each sampling station was used for the calculation. A table for HPI calculation was constructed for Station A as shown in Table 7 using CCME (2005) standard for aquatic life protection, and from which HPI was calculated by diving the $\sum W_iQ_i$ by $\sum W_i$ to give 871.13.

Table 7: HPI calculation for Station A using CCME (2005) Standards

Metal (i)	**Mean Value (M_i)**	**Standard Permissible Value (S_i)**	**Ideal/ Desirable Maximum Value (I_i)**	**Unit Weightage (W_i)**	**Quality rating of each Metal (Q_i)**	**$W_i Q_i$**
Cd	0.075	0.0018	0.02	555.56	302.20	167890.23
Cu	0.105	0.004	0.04	250	180.55	45137.5
Fe	0.024	0.3	0.64	3.33	117.65	391.77
Pb	0.061	0.007	0.17	142.86	116.56	16651.76
Mn	0.068	-	0.48	-	-	-
Hg	0.03	0.0001	0.003	10000	931.03	9310300
				∑10951.75		∑9540371.26

The HPI values for the different stations were calculated using the different water quality standards and shown in Tables 8 to 10. The ratio of the HPI to the critical Index and the critical difference were also calculated. The results of HPI as seen in Tables 8 to 10 shows that the five sampling stations were heavily polluted above the critical pollution index which is usually set at 100. Station D has the highest HPI of 2615.23, 2877.11 and 3294.32 using CCME (2005), FMEnv (2007) and WHO (2006) standards, respectively. This Station D was located close to an oil field station with well heads, manifold, and waste pits. The HPI values of each of the sampling points is also represented in Figure 8.

Table 8: HPI values using CCME (2005) standard

Stations	HPI Value	Critical Pollution Index	Ratio of HPI to Critical Index	Critical Difference
A	871.13	100	8.71	771.13
B	1447.45	100	14.47	1347.45
C	618.85	100	6.19	518.85
D	2615.23	100	26.15	2515.23
E	1337.72	100	13.38	1237.72

Table 9: HPI values using FMEnv (2007) standard

Stations	HPI Value	Critical Pollution Index	Ratio of HPI to Critical Index	Critical Difference
A	987.57	100	9.88	887.57
B	1668.69	100	16.69	1568.69
C	729.97	100	7.30	629.97
D	2877.11	100	28.77	2777.11
E	1480.33	100	14.80	1380.33

Table 10: HPI values using WHO (2006) standard

Stations	HPI Value	Critical Pollution Index	Ratio of HPI to Critical Index	Critical Difference
A	1118.12	100	11.18	771.13
B	1886.45	100	18.86	1347.45
C	746.28	100	7.46	578.85
D	3294.32	100	32.94	2515.23
E	1681.44	100	16.81	1237.72

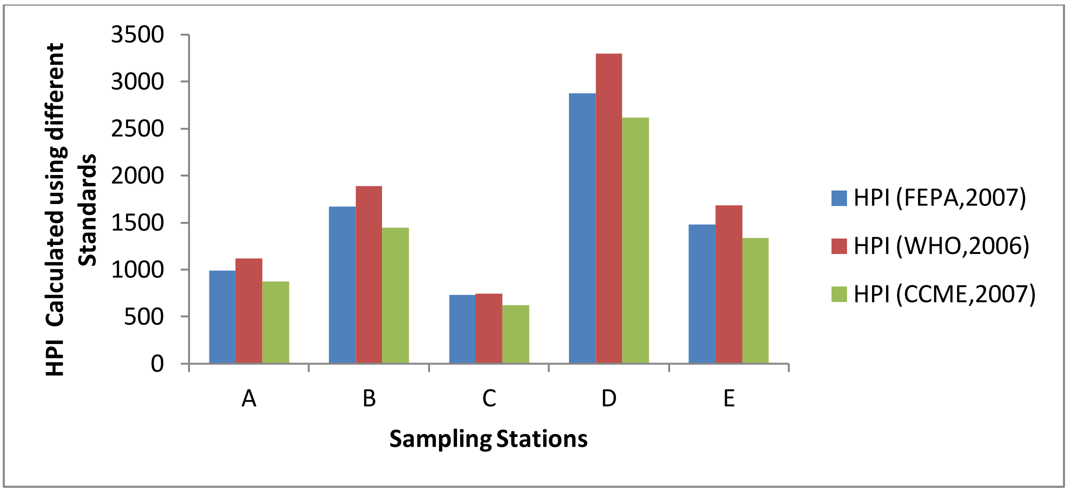

Figure 8: HPI for each sampling station

The individual Metal Pollution Index (MPI) was calculated from Equation (4) using the different water quality standards and then represented in Figures 9 to 11. The results, with respect to FMEnv, (2007) standard show Cd, Pb and Hg with mean MPI values of 29.33, 6.57 and 4.67. Larger values were obtained for Hg, Cd and Cu with respect to WHO (2006) standards having mean MPI's of 46.67, 17.6 and 5.32, respectively. Furthermore, much larger MPI values of 48.89, 26.58, 9.38 and 466.67 for Cd, Cu, Pb and Hg respectively, were obtained with respect to CCME (2005) standards. Based on these results, Abonnema river could be said to be seriously polluted and can be classify as class VI seriously affected, using the criteria set by Lyulko et al. (2001) and Caerio et al. (2005).

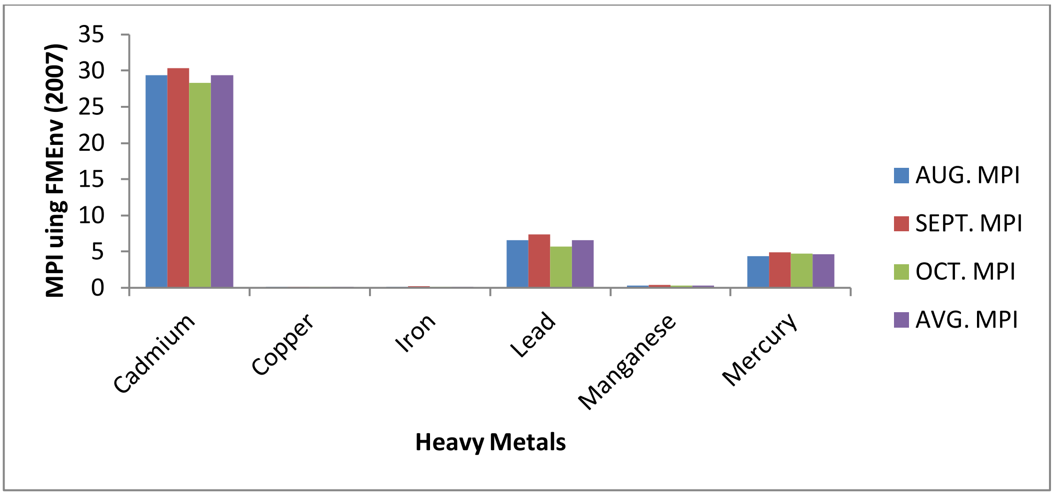

Figure 10: MPI using FMEnv (2007) guideline

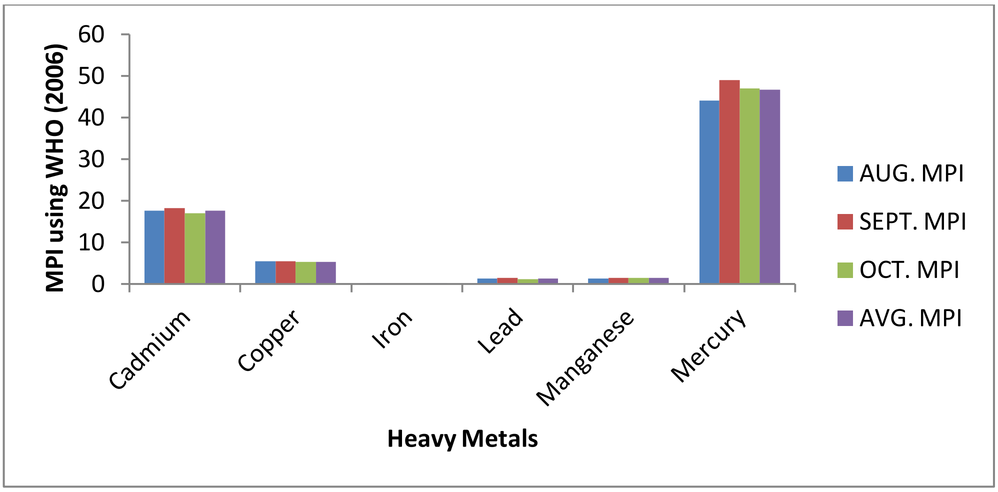

Figure 11: MPI using WHO (2006) guideline

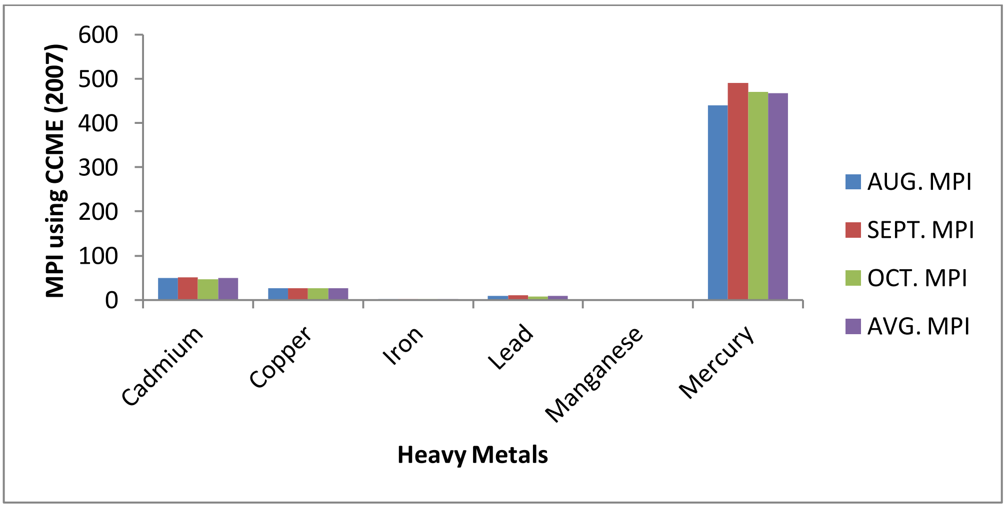

Figure 12: MPI using CCME (2005) guideline

IV. Conclusion

Based on this study, the Abonnema River could be seriously affected by acute concentrations of priority heavy metals which led to increase in both the individual metal pollution index (MPI) and heavy metal pollution index (HPI) far above the recommended critical pollution index. Also, the acute concentrations observed for these heavy metals exceeded the standard maximum allowable concentrations set by the FMEnv (2007), CCME (2005) and WHO (2006) standards.

The critical findings from the Metal Pollution Index (MPI) calculation revealed the presence of Cd, Pb and Hg in very high concentration especially in Station D. Furthermore, Heavy Metal Pollution Index (HPI) calculated using both national and international standards gave very high values which are far above the recommended values (2877.11 for FMEnv), (3294.32 for WHO) and (2615.23 for CCME).

The Abonnema River, though not utilised by the community as a source of drinking water, is used for some domestic and recreational purposes and serves as a major source for fishing activities. Also, as the community largely depends on the groundwater sources, there is a likelihood that a considerable heavy metal pollutants can gain access into the groundwater, since there is a link between surface water and groundwater. Thus, this study is an indication of a well polluted water with respect to heavy metal pollutants and as such the level of anthropogenic activities especially from industrial effluents need to be checked.

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