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Determination and Evaluation of Heavy Metal Concentration in Surface Water and Sediment from Orashi River in Rivers State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

The research was intended to study the influence of human and industrial activities on the Orashi River. Three groups are observed to have impacted the environment – Oil/gas industries, tyre burning (smokes and ashes) released during roasting of slaughtered animals in abattoir, untreated human and animal waste from settlers and the abattoir. The study was carried out from September 2019 to August 2020. The mean concentrations of the parameters studied in some samples were close to or exceeded World Health Organization (WHO) and Nigerian Federal Ministry of Environment (FMEnv) recommended limits for drinking water and seafood. The results from this study have provided information on the heavy metals profile on the surface water and sediment of the river. Essential heavy metals detected in water were in the range of Cu (1-5.4mg/l), Zn (1-4.4mg/l) and Fe (0.1 – 1.8 mg/l) which were within the WHO (1989), USEPA (1986), FEPA (1999) permissible limit of 3mg/l. The non-essential metals investigated were Cd, Cr and Pb but only Cd was detected. Cd levels (0.1-0.8mg/l) were slightly high, above the permissible limit of 0.01mg/l. Heavy metals in sediment were higher than those in the water body, occurring in the sequence Zn>Cu>Fe >Cd. The ranges were Zn (1.4-5mg/kg), Cu (0.8-3mg/kg), Fe (0.4-4.9mg/kg) and Cd (0.5-1.8mg/kg). All relationship were statistically significant (p=0.05). With regards to seasonal variation, dry season recorded higher values than rainy season. Heavy metals in sediment were higher than those in the water body, occurring in the sequence Zn>Cu>Fe >Cd. The ranges were Zn (1.4-5mg/kg), Cu (0.8-3mg/kg), Fe (0.4-4.9mg/kg) and Cd (0.5-1.8mg/kg). Cd and Fe in water and

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sediment have higher concentration during the dry season while Cu and Zn are higher during the rainy season in both parameters during the study period. Increased level of pollutants in the Orashi River may have significant effect on the ecological balance of the River. Again, long term bioaccumulation through food chain is a major concern as this study had revealed that sediment act as sink of pollutant loads than the water samples.

Keywords: Metal; determination; evaluation; industries; contamination.

1. INTRODUCTION

1.1 Background Information

Water is the most important natural resources and there are many conflicting demand for them. Skillful management of water bodies is required if they are to be used for such diverse purpose as domestic and industrial supply, crop irrigation, transport, recreation, sports, commercial fisheries, power generation and waste disposal. Water bodies are vulnerable to contamination accident and bioterrorism attacks because they are relatively unprotected, easily accessible, often isolated and their various use by human pre-disposes them to contamination [1]. Environmental exposure to toxic metals is a critical issue in environmental and public health.

The modern world is aware of the relationship between water and water borne diseases, as a vital public health issue [2-4].

Heavy metals are well known pollutants in aquatic systems where industrial wastes are discharge, petroleum production and refining, gas flaring, gas processing plants and conveyance pipelines [5-7]. Gas flares are operated in relatively uncontrolled manner in Niger Delta region. These effluents discharge and atmospheric emissions from flow stations and refineries often settle in the aquatic environment. When contamination reaches levels in excess of the assimilative capacity of the receiving waters, they may affect the survival, reproduction capacity, growth and behavioral condition of organisms [6].

In the attempt to define and measure the effect and presence of pollutants on aquatic ecosystems, biomarkers or bio-indicators have attracted a great deal of interest. The increase level of heavy metals in human has often been traced to heavy metal contamination in the aquatic system [8].

The heavy metals of interest in this study include the non-essential trace element Cd, Cr, and Pb) and the essential metals such as Cu, Zn, and Fe which have important biochemical functions to the organism at very low concentration [9]. These heavy metals are blacklisted in EEC Directive as dangerous substances in the aquatic environment [10]. These heavy metals can be hazardous to human, even in very small amount. They are taken up by aquatic organisms and passed up the food chain through the process known as bio-magnification. Species varies in their degree of tolerance with the result that under polluted conditions, a reduction in species diversity is the most obvious effect [11]. The intense industrial activity in Niger Delta region has attracted much research interest but no systematic study has so far been conducted in Orashi River of ONELGA to ascertain its level of metal concentration and the health effects on the inhabitants.

It is therefore very important to conduct this study in view of the rapid growth of population, exploration and exploitation of natural resources, lack of environmental regulations, industrialization, urbanization, clearing of bank vegetations, annual dredging of the river to contain yearly flooding, construction of roads and bridges, drains and embankment walls and Agricultural activities of the inhabitant of Ogba/Egbema/Ndoni LGA (ONELGA) to record the range of the concentration within commercial as well as non-commercial species so that assessment about potential hazardous levels from the human nutritional standpoint can be made.

1.2 Aim

To determine the concentrations of heavy metals in the surface water and sediment from Orashi River. This is to enable the assessment of potential hazardous levels from human nutritional stand point.

2. MATERIALS AND METHODS

2.1 The Study Area

The study area is Ogba/Egbema/Ndoni LGA in Rivers State of Nigeria. (Fig: 1a, b & c). The area has a number of oil wells and major flow stations within the Niger Delta region of Nigeria. Nigerian Agip Oil Company (NAOC) and Total E & P Nigeria Limited explores, exploit crude oil and flare gases indiscriminately in three locations - Ebocha, Obrikom and Obitte.

The inhabitants of the area are predominantly farmers and fishermen which is their basic source of livelihood. The major activity of economic value in the area is exploration and exploitation of crude petroleum oil.

The area has a growing population of 283, 294 in 2006 and a projection of 398,000 in 2016 {National population commission of Nigeria (web), National Bureau of statistics (web)}.

The site of the study is Orashi river, a non-tidal freshwater of the lower Niger basin that runs through some communities in Imo State, Egbema, Ndoni and Ogba communities in Rivers State. The river is a freshwater swamp forest river with several tributaries and originate from River Niger and empties into Sombrieiro river in Ahoada. The area is tropical with two seasons- the rainy (April – October) and dry season (November – March) with annual average temperature ranges between 29^{0c} during the rainy season and 32^{0c} during the drier months and tidal range of 1.2m which are usually flooded in the rainy seasons. It is a lotic ecosystem with the average flow velocity ranges from 0.1 to 1m/s. The location of the sampling stations is summarized in Table 1.

Fig 1a Map of Nigeria Showing Rivers State

Fig 1b Map of Rivers State Showing Ogba/Egbema/Ndoni L G A

Fig 1c Map of Ogba/Egbema/Ndoni L G A

Fig. 1. Maps showing location of the study area

2.2 Sampling Stations

A reconnaissance survey was carried out in the study area on November 2018 and then sampling stations were established at five locations along the Orashi River, 5km distance from each other using Global positioning system navigator (GPS) as shown in Table 1 and represented by station 1 – 5.

2.3 Field Study

Water and Sediment were collected from the 5 sampling stations monthly beginning from September 2019 during rainy and dry seasons respectively. The sampling of the 5 stations started at about 8.30am each day.

2.4 Field Collection of Water Samples

Water samples were collected from all stations at a depth of 15-25cm with pre-rinsed containers. Duplicate samples of surface water from the five (5) sampling station were collected for twelve (12) sampling periods (September 2019 to August 2020). Water sample were collected with pre-rinsed I00ml plastic container and treated with 2ml concentrated HNO_3 in order to stabilize the oxidation state of the metals and stored in a refrigerator [12].

2.5 Collection of Sediment Sample

Sediment samples were collected at each of the five (5) sampling stations for the specified period using BENTHIC GRAB of about $1.0cm^3$ in replicate for each sampling station for each sampling period. The sample was put in a polythene bag, kept in a cooler and taken to the laboratory deep freezer prior to sediment analysis.

2.6 Laboratory Analysis of Samples

In the laboratory, the following analysis was performed on the duplicate samples collected.

2.7 Heavy Metal Analysis in Surface Water (Fe, Cd, Pb, Cu, Cr And Zn)

Samples previously collected in the field and fixed with 2 drops of concentrated HNO_3 in order to preserve the metals and also to avoid precipitation were used for heavy metals analysis. Metal analysis was performed using Unicam 969 Atomic Absorption spectrophotometer (AAS) in accordance with [13]. This involves direct aspiration of the sample into an air/acetylene or nitrous oxide/acetylene flame through which a light source emitting a narrow spectral line of characteristic energy. A hollow cathode lamp peculiar only to the metal under investigation was used to excite the free atoms of metal of interest in the flame. The concentration of the excited metal atoms calculated by comparison with a standard curve of the metal. Prior to analysis, the AAS.

2.8 Sediment Sample Analysis

The sediment samples were air-dried at room temperature for 5 days and grounded into powdery form.

1 g of each was digested with Aqua-Regia (mixture of distilled water, HCL and HNO_3). The digestates were filtered and the filtrates were stored in clean acid-washed and appropriately labeled 30ml polyethylene sample containers for analysis by Atomic Absorption Spectrometric method using Atomic Spectrometer (Model 210 VGP Buck Scientific, USA).

2.9 Data Analysis

All statistical analysis and presentation of results was done using Microsoft excel and Minitab 16 software.

Raw data was subjected to a two way analysis of variance (ANOVA).

Table 1. Geographical positioning system (GPS)

Stations	Locations	Coordinates	Elevation
Station 1	Okwuzi	N05^{0}29'08.3" E006^{0}42'26.3"	21M
Station 2	Ebocha	N05^{0}27'49.3" E006^{0}42'06.6"	24M
Station 3	Ndoni	N05^{0}27'24.6" E006^{0}40'27.8"	12M
Station 4	Obrikom	N05^{0}23'31.0" E006^{0}39'03.0"	22M
Station 5	Omoku	N05^{0}20'18.7" E006^{0}38'34.6"	16M

3. RESULTS OF HEAVY METALS IN SURFACE WATER

The following heavy metals were monitored during the study period – Chromium (Cr), Cadmium (Cd), Lead (Pb), Copper (Cu), Zinc (Zn) and Iron (Fe). Of all these metals, chromium and lead was not detected during the sampling period.

3.1 Cadmium (Cd) in Surface Water

The mean values recorded in appendix 1 are station 1(0.35 mg/l), station 2(0.53 mg/l). Station 3 (0.4 mg/l), Station 4(0.46 mg/l) and station 5(0.27 mg/l) and represented in Fig 1. The values recorded show that it ranged from 0.1 to 0.8 mg/l.

Seasonal variations in cadmium levels in water are presented in Table 3 and showed that dry seasons has higher value (0.43 mg/l) than Rainy season (0.37 mg/l).

The analysis of variance (ANOVA) result showed that there was significant difference ($P<0.05$) observed for the water sample during the monitoring period ($P=0.000$).

3.2 Copper in Surface Water

The mean levels of Cu is presented in appendix 1- station 1(2.73 mg/l), station 2(4.08 mg/l), station 3(1.2 mg/l), station 4(1.4 mg/l) and station 5(0.91 mg/l) and represented in Fig. 2. The value ranged from 1.0 to 5.4mg/l. The highest value recorded was in February and March in station 2.

Seasonally, the result in Table 3 showed that Rainy season (2.24 mg/l) recorded a higher value while the Dry season recorded a lower value (1.89 mg/l) during the sampling period.

The analysis of variance (ANOVA) results showed there is significant difference ($P< 0.05$) for copper concentration in the water sampled and the locations during the monitoring period ($P= 0.000$).

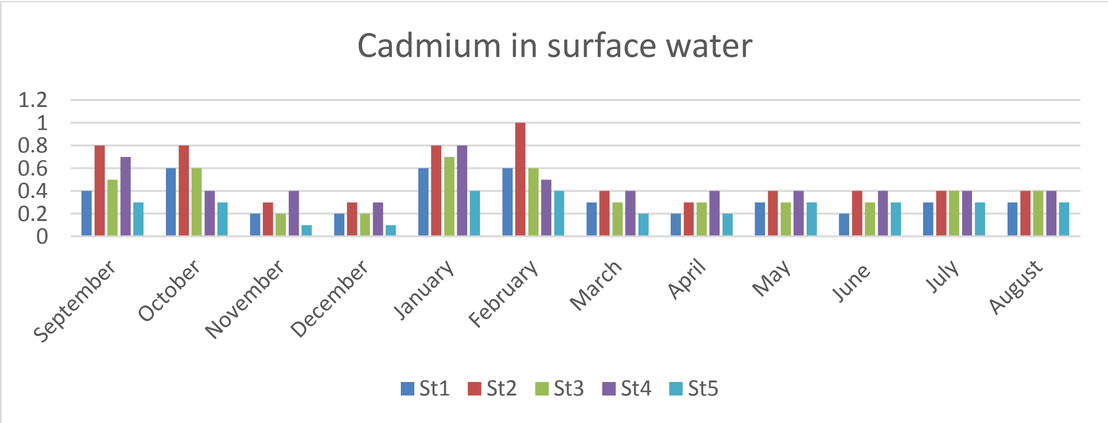

Fig. 2. Cadmium (Cd) in surface water (mg/l)

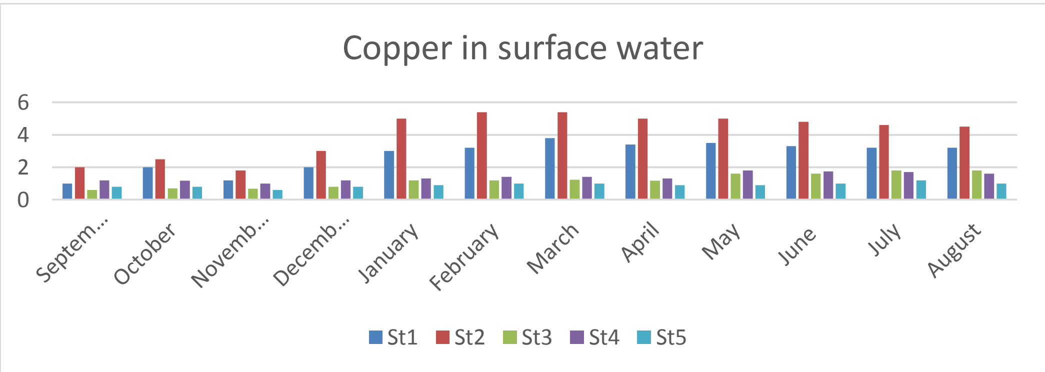

Fig. 3. Copper (Cu) in surface water (Mg/l)

3.3 Zinc in Surface Water

The mean concentration of zinc in water during the study period is in appendix 1 thus station1 (2.16), station 2(1.67), station 3(3.52), station 4(2.2) and station 5(1.35 mg/l) and represented in fig 3. The result indicates that zinc range from 1.0 to 4.4mg/l in the surface water. The highest level of zinc was observed in the month of March followed by February.
Seasonally, higher values were recorded for rainy season (2.31 mg/l) while lower values (1.97 mg/l) were recorded for dry season.

The analysis of variance (ANOVA) showed that there was significant difference ($P< 0.05$) between location and time.

3.4 Iron (Fe) In Water

The result obtained for iron is presented in appendix 1 and represented in Fig 4. The result indicates that iron range from 0.1 to 1.8. The mean value levels were station 1(0.49), station 2(0.75), station 3(0.55), station 4(1.08) and station 5(1.25).

Seasonally, higher values (0.86 mg/l) were recorded for dry season while lower levels (0.79mg/l) were recorded for rainy season. The highest level of iron was observed in the month of March followed by April, February and January.

The analysis of variance (ANOVA) shows that there is significant difference ($P< 0.05$) between locations and time. P=0.00).

3.5 Heavy Metals in Sediment

The following heavy metals were sampled from the 5 stations and analyzed during the monitoring period:

3.6 Cadmium (Cd) in Sediment

The concentration of Cadmium recorded in sediment is presented in appendix 2 and shown in fig. 5. The results indicate that Cadmium level in this study ranged from 0.5 to 1.8 mg/kg in all the stations. The mean values obtained were station 1(0.805), station 2(1.42), station 3(1.04), station 4(0.83) and station 5(0.73 mg/kg).

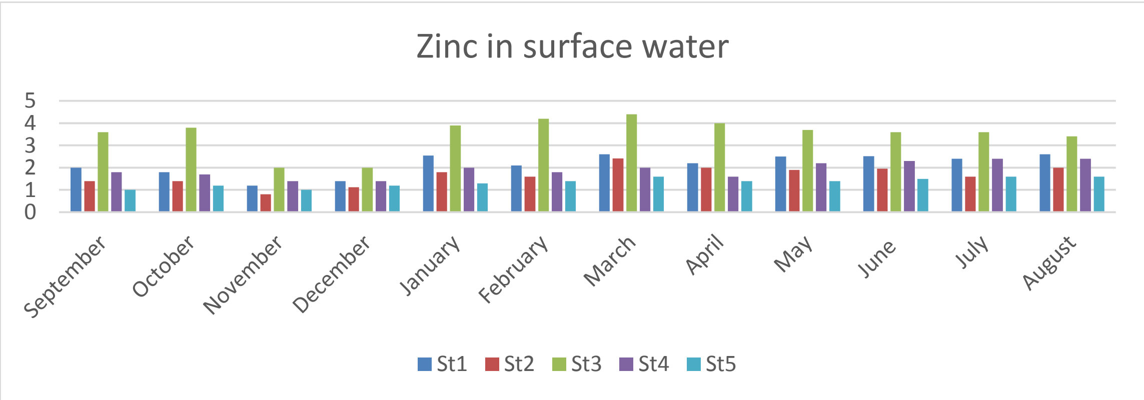

Fig. 4. Zinc in Surface water. (Mg/l)

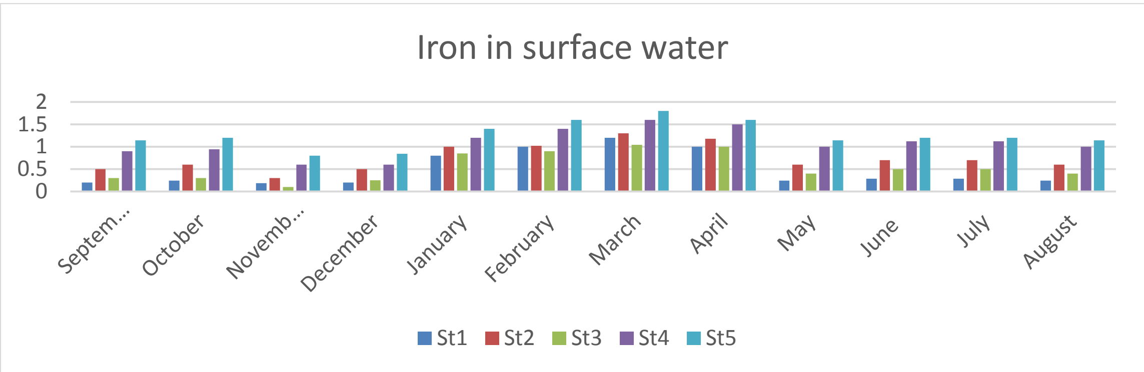

Fig. 5. Iron (Fe) in Surface water. (Mg/l)

Seasonal variations as presented in Table 4 show that total Cadmium level was higher during the dry season (1.14 mg/kg) than the rainy season (0.99 mg/kg).

The analysis of variance (ANOVA) result showed that there is significant difference ($p < 0.05$) in time (P=0.00).

3.7 Copper (Cu) in Sediment

The concentration of Copper recorded in sediment is presented in appendix 2 and shown in Fig. 6. The results indicate that Copper level in this study ranged from 0.8 to 3 mg/kg in all the stations. The mean values observed for copper was station 1(1.93), station 2 (2.70), station 3(1.24), station 4(1.48) and station 5(1.24 mg/kg).

Seasonal variations show that Copper level was higher during the rainy season (1.90 mg/kg) than the dry season (1.8 mg/kg).

The analysis of variance (ANOVA) result showed that there was significant difference ($p < 0.05$) between locations and time (P=0.00).

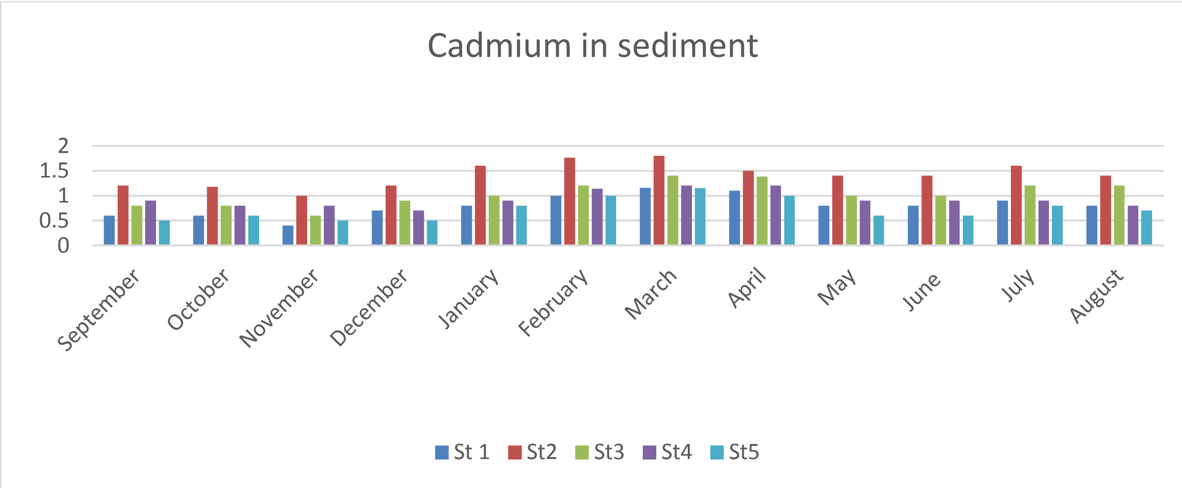

Fig. 6. Cadmium (Cd) in Sediment (Mg/kg)

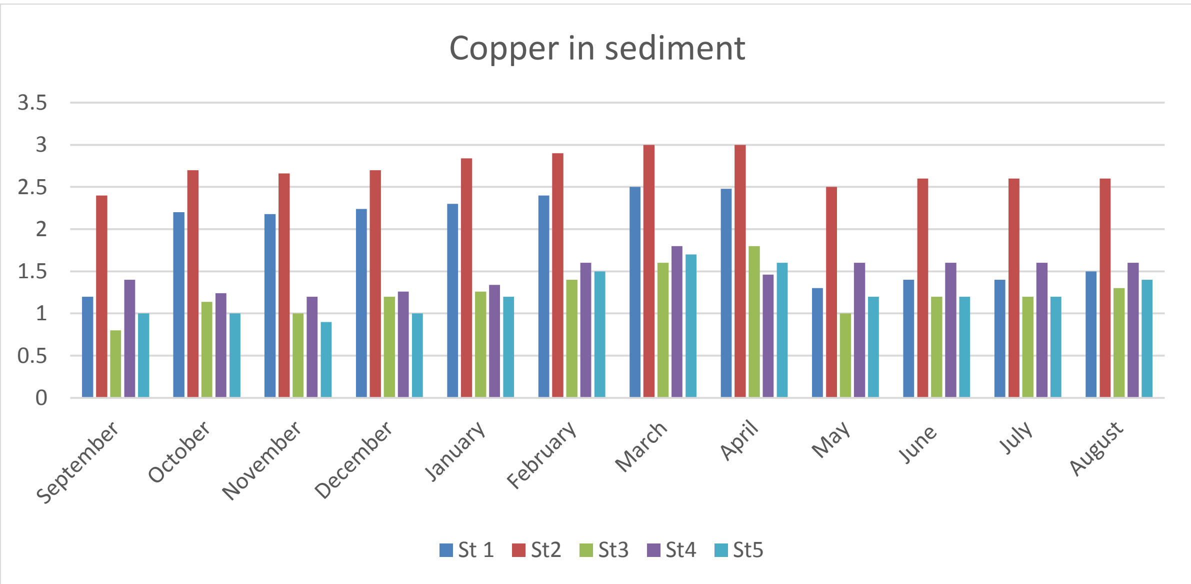

Fig. 7. Copper in sediment (Mg/kg)

3.8 Zinc (Zn) in Sediment

The concentration of Zinc recorded in sediment is presented in appendix 2 and shown in fig.7. The results indicate that Zinc level in this study ranged from 1.4 to 5mg/kg in all the stations. The mean values observed for Zinc was station 1(3.68), station 2(2.24), station 3(4.49), station 4(2.42) and station 5(1.91 mg/kg).

Seasonal variations recorded in Table 4 show that Zinc level was higher during the rainy season (2.74 mg/kg) than the dry season (2.72 mg/kg).

The analysis of variance (ANOVA) result showed that there was significant difference ($p < 0.05$) between locations and time ($P=0.00$).

3.9 Iron (Fe) in Sediment

The concentration of Iron recorded in sediment is presented in appendix 2 and shown in fig. 8. The results indicate that Iron level in this study ranged from 0.4 to 4.9mg/kg in all the stations. The mean values observed for Iron was station 1(1.37), station 2(1.39), station 3(2.17), station 4(1.84) and station 5(1.62).

Seasonal variations show that Iron level was higher (1.91 mg/kg) during the dry season than the rainy season (1.41 mg/kg).

The analysis of variance (ANOVA) result showed that there was significant difference ($p < 0.05$) between locations and time ($P=0.005$).

4. DISCUSSION

4.1 Heavy Metals in Water

The essential heavy metals detected in the surface water in the present study were copper (Cu), Zinc (Zn) and Iron (Fe) and the non-essential heavy metals is cadmium (Cd).

The values obtained from the 5 stations for the 4 heavy metals detected vary in composition in different station and at different time (month).

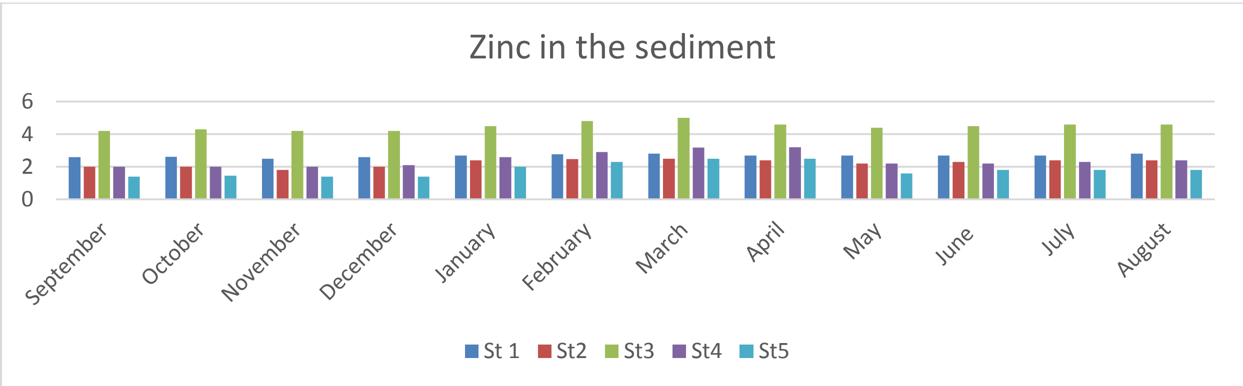

Fig. 8. Zinc in Sediment(Mg/kg)

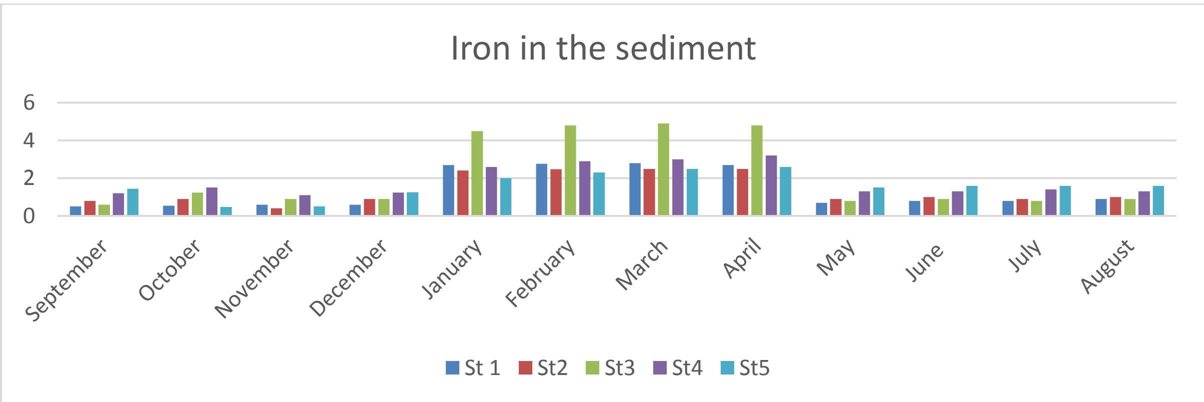

Fig. 9. Iron (Fe) in Sediment(Mg/kg)

4.2 Cadmium (Cd) in Water

Cadmium (Cd) was widely distributed in low levels in the environment. The mean value recorded ranged from 0.29 – 0.8 with specific mean record of station 1 (0.55), station 2 (0.53), station 3 (0.4), station 4 (0.46) and station 5 (0.29). These values of Cd are high compare to Nigerian FMEnv, WHO/USEPA limit of 0.1mg/l. This high cadmium concentration differs from the low metal concentration reported by earlier workers which include Obire et al. [14] on Elechi creek, Omoigherale and Ogbeibu, [15] on Osse River, Southern Nigeria and Ekweozor and Agbozu [16].

This may be attributed to intense oil exploration and exploitation in the area which ranked ONELGA as the highest oil producing LGA in Nigeria. These activities involved the use of dynamites, chemicals; effluent discharges in the area which will incidentally washed into the river during rain.

4.3 Copper (Cu) in Water

The values of copper ranged from 0.1 – 5.4mg/l with specific mean record of 2.73, 4.08, 1.2, 1.4 and 0.91mg/l for station 1, 2, 3, 4 and 5 respectively. The results also show that dry season recorded a higher value than the rainy season. Copper is an essential element observed in low levels in stations 3, 4 and 5. Notwithstanding, the discharge of waste containing copper should be discouraged since its presence in the environment is hazardous, as copper salts are poisonous. Station 2 recorded high level (4.08 mg/l) which is above the 3 mg/l NFMEnv (1999) maximum permissible limit. The low copper concentration in some stations is in agreement with low metal concentration reported by Obire et al. [17] on Elechi creek, Ekweozor and Agbozu [18] in Azuabie creek.

4.4 Zinc (Zn) in Water

The concentration of Zinc in surface water ranged from 1 – 4.4 mg/l during the study period with specific mean values of station 1(2.16), station 2(1.67), station 3(3.52), station 4(2.2) and station 5(1.35) mg/l.

Rainy season recorded higher values (2.31 mg/l) than dry season (1.97 mg/l) with the highest value (3.5 mg/l) in March followed by February and January in station 3. The low zinc concentration in stations 1, 2, 4 and 5 is below the international standards – WHO [19] USEPA [20] and FEPA [21] permissible limit of 3mg/l. The high level of Zn (3.52 mg/l) in station 3 may be attributed to the tyre ash in abattoir located near the Shore of Orashi River in station 3. Zinc makes up 51.48% of tyre ash (Bay *et al,* 2005). This indicates an impact from runoff of tyre ash and animal blood which is rich in zinc and Iron [22].

4.5 Iron (Fe) in Water

The concentration of Iron in surface water ranged from 0.1 – 1.8mg/l during the study period with specific mean values of station 1(0.49), station 2(0.75), station 3(0.55), station 4(1.08) and station 5(1.25) mg/l.

Dry season recorded higher values (0.86 mg/l) than rainy season (0.79 mg/kg) with the highest value observed in the month of March in station 5. The low Iron concentration in all stations is below international standards – WHO [20], USEPA [21] and FEPA [22] permissible limit of 3mg/l. The presence of Iron in the stations may be attributed to the tyre ash in abattoir located near the Shore of Orashi River and other anthropogenic activities in the area. Iron makes up 6.33% of tyre ash. This indicates an impact from runoff of tyre ash and animal blood which is rich in Iron [23].

4.6 Sediment Analysis in Sediments

Sediment is an important component of aquatic ecosystem because it provides a habitat for a wide range of benthic and epi-benthic organisms [24] and act as sink to contaminants and pollutants. The exchange between sediments and the overlying water depends on the chemical characteristics of both phases [24].

Therefore, exposure to certain substances in sediments represents a potentially significant hazard to the health of these organisms. An assessment of this hazard would require an understanding of the relationships between concentration of chemicals in sediment and occurrence of adverse biological effects. Bioaccumulation is a long time effect of heavy metals which endanger organism that are higher on the food-chain.

The heavy metals analyzed for in the sediments are Cadmium, Copper, Lead, Zinc and Iron.

4.7 Cadmium (Cd) in Sediment

The results obtained in this study showed a range of 0.5 – 1.8 mg/kg and mean values of station 1(0.805), station 2(1.42), station 3(1.04), station 4(0.83) and station 5(0.73) mg/kg.
The level recorded in sediment is higher than that recorded in water and exceeded the maximum level of 0.01mg/l allowed for discharge into inland waters [25]. The levels were higher than the reported values of below detection limit (BDL) and 0.080mg/kg in Taylor creek [26].

Cadmium is toxic even at trace level and has been identified as one of the trace metals contained in crude oil in varying concentrations and has been shown to be capable of accumulating in food chain [27].

Seasonally, Cadmium level where generally higher in the dry season (1.14 mg/kg) than rainy season (0.99 mg/kg) and exceeded sediment toxicity guideline value.

Cadmium has both long and short term effects on specific tissues/organs of the body of aquatic organisms and mammals that feed on them. Kidney and ocular damages are long term effects while testicular damage is short term [28].

4.8 Copper (Cu) in Sediments

The level of copper recorded in this study were relatively high and ranged from 0.8 – 3.0mg/kg and mean values of stage 1(1.93), stage 2(2.70), stage 3(1.24), station 4(1.48) and stage 5(1.24) mg/kg. The level recorded in sediment is higher than that recorded in water but is within the FMENV recommended limit of 3mg/kg allowed in sediment.

Copper is not often considered a threat to human health except when present at abnormal values.

Seasonally, the levels were slightly higher in the rainy season (1.90mg/kg) than dry season (1,8mg/kg) and are within sediment guideline value [29].

4.9 Zinc (Zn) in Sediments

The level of Zinc recorded in this study ranged from 1.4 – 4.5 mg/kg and mean values of station 1(3.68), station 2(2.24), station 3(4.49), station 4(2.42) and station 5(1.91) mg/kg. The level recorded in sediment is higher than that recorded in water and are within the FMENV recommended limit of 3mg/kg allowed in sediment except in station 4 (4.49 mg/kg) which exceeded sediment toxicity guideline value. This could be attributed to effluents from abattoir with tyre ash and residue as well as animal blood waste which have high percentage of Zinc. Zinc is not often considered a threat to human health except when present at abnormal values.

Seasonally, the values were slightly higher in the rainy season (2.79mg/kg) than observed in dry season (2.72mg/kg).

4.10 Iron (Fe) in Sediments

The concentration of Iron recorded in sediment ranged from 0.4 – 4.9mg/kg and mean values of station 1(1.37), station 2(1.39), station 3(2.17), station 4(1.84) and station 5(1.62) mg/kg.

These values recorded in sediments are within the NFMENV recommended limit of 3mg/kg allowed in sediment. It is interesting to note that Iron is one of the beneficial metals and can become toxic if optimum level of 3 mg/kg is exceeded.

Seasonally, Iron levels were generally higher during the dry season (1.91mh/kg) than observed in rainy season (1.41mg/kg). This could be attributed to sedimentation of pollutants from continuous leaching of rusty iron fragment from pipeline, tyre burning sites in abattoir, residue and animal blood waste.

Statistically, there is significant difference ($p< 0.05$) between locations and time ($p= 0.005$).

4.11 Comparism of Heavy Metals in Water and Sediment

The concentration of heavy metals in water and sediment were compared to show a clear picture of the level of concentrations of different heavy metals in Orashi River. The mean occurrence of heavy metals recorded in this study showed that the concentration of different heavy metals decreases thus: sediment > water. The heavy metals observed were highest in the sediment and lowest in the surface water. Sediment which is the sink for heavy metal pollutant had higher concentration of heavy metals than the surface water. Heavy Metal concentration in sediment decreases in the following order; Zn > Cu > Fe > Cd with mean value of 8.636 mg/kg. Heavy metals are known to accumulate in the sediments which act as sink for these pollutants [30]. The sequence of heavy metal concentration in water is Zn > Cu >Fe > Cd. Heavy metal concentration was lowest in water with a mean value of 6.734mg/l. Although the water column first received any input, the low levels of metals determined could be as a result of dilution, sedimentation and continuous water exchange [28]. Higher water temperature especially in the dry season could also contribute to its low level. A slow flow condition of the study river enhances sedimentation thus sedimentation is mechanism for removing heavy metals and other pollutants from the water column during the dry season when the influx of freshwater is very minimal.

5. CONCLUSION

The research was intended to study heavy metal concentration as a result of the influence of human and industrial activities on the Orashi River and to provide information on the heavy metals profile of the river. The average mean concentrations of the heavy metals studied in some samples were close to or exceeded World Health Organization (WHO) and Nigerian Federal Ministry of Environment (NFMEnv) recommended limits for drinking water and seafood. Essential heavy metals detected in water were Copper (Cu), Zinc (Zn) and Iron (Fe) and were low when compared with international standard [30] recommended limits of 3 mg/l. The non-essential metals detected were Cadmium (Cd) which exceed the international standard of 0.01mg/kg but do not constitute health risk. Heavy metals concentration was generally elevated at and around abattoir and gas flare sites. The high level of Heavy metals in the water calls for concern as prolonged exposure can have some health – risk implication on the biota and humans who are the final consumers.

Heavy metals showed longtime bioaccumulation, which have been taking place before the study. This may pose serious health hazards to the inhabitants in the area over time if the discharge of untreated and partially treated effluents into the surface water is allowed to continue unabated. The high levels have been encouraged by the dry season rather than the rainy season.

6. RECOMMENDATION

This study has shown that Heavy metals may have accumulated for some time within the Orashi aquatic ecosystem. Observation during the study showed that Orashi River has been the major source of domestic water supply, bathing, cassava fermenting and protein supplement to the indigenous community who are exposed to the hazardous effects of these pollutants. It is therefore recommended that:

(i) The companies operating in the area should adopt improved waste management plans to reduce the levels of the pollutants discharge in the environment.

(ii) Comparative studies in other biota of the environment would be useful in monitoring the rate and mechanism of uptake of the metals in the food. This will provide data for informed decision on uptake of what is available in a polluted environment.

(iii) The local communities should be enlightened about the adverse effects of anthropogenic activities and other activities that could cause pollution and fire out-break along oil installations.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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APPENDIX 1. RAW DATA OF HEAVY METALS OBTAINED IN WATER SAMPLES

Cd	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	0.4	0.6	0.2	0.2	0.6	0.6	0.3	0.2	0.3	0.2	0.3	0.3
St 2	0.8	0.8	0.3	0.3	0.8	1	0.4	0.3	0.4	0.4	0.4	0.4
St 3	0.5	0.6	0.2	0.2	0.7	0.6	0.3	0.3	0.3	0.3	0.4	0.4
St 4	0.7	0.4	0.4	0.3	0.8	0.5	0.4	0.4	0.4	0.4	0.4	0.4
St 5	0.3	0.3	0.1	0.1	0.4	0.4	0.2	0.2	0.3	0.3	0.3	0.3

Cu	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	1	2	1.2	2	3	3.2	3.8	3.4	3.5	3.3	3.2	3.2
St 2	2	2.5	1.8	3	5	5.4	5.4	5	5	4.8	4.6	4.5
St 3	0.6	0.7	0.68	0.8	1.2	1.2	1.24	1.18	1.6	1.6	1.8	1.8
St 4	1.2	1.18	1	1.2	1.3	1.4	1.4	1.3	1.8	1.74	1.7	1.6
St 5	0.8	0.8	0.6	0.8	0.9	1	1	0.9	0.9	1	1.2	1

Zn	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	2	1.8	1.2	1.4	2.54	2.1	2.6	2.2	2.5	2.52	2.4	2.6
St 2	1.4	1.4	0.8	1.12	1.8	1.6	2.42	2	1.9	1.95	1.6	2
St 3	3.6	3.8	2	2	3.9	4.2	4.4	4	3.7	3.6	3.6	3.4
St 4	1.8	1.7	1.4	1.4	2	1.8	2	1.6	2.2	2.3	2.4	2.4
St 5	1	1.2	1	1.2	1.3	1.4	1.6	1.4	1.4	1.5	1.6	1.6

Fe	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	0.2	0.24	0.18	0.2	0.8	1	1.2	1	0.24	0.28	0.28	0.24
St 2	0.5	0.6	0.3	0.5	1	1.02	1.3	1.18	0.6	0.7	0.7	0.6
St 3	0.3	0.3	0.1	0.25	0.85	0.9	1.04	1	0.4	0.5	0.5	0.4
St 4	0.9	0.94	0.6	0.6	1.2	1.4	1.6	1.5	1	1.12	1.12	1
St 5	1.14	1.2	0.8	0.84	1.4	1.6	1.8	1.6	1.14	1.2	1.2	1.14

APPENDIX 2. HEAVY METAL IN SEDIMENT

Cd	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	0.6	0.6	0.4	0.7	0.8	1	1.16	1.1	0.8	0.8	0.9	0.8
St 2	1.2	1.18	1	1.2	1.6	1.76	1.8	1.5	1.4	1.4	1.6	1.4
St 3	0.8	0.8	0.6	0.9	1	1.2	1.4	1.38	1	1	1.2	1.2
St 4	0.9	0.8	0.8	0.7	0.9	1.14	1.2	1.2	0.9	0.9	0.9	0.8
St 5	0.5	0.6	0.5	0.5	0.8	1	1.15	1	0.6	0.6	0.8	0.7

Cu	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug
St 1	1.2	2.2	2.18	2.24	2.3	2.4	2.5	2.48	1.3	1.4	1.4	1.5
St 2	2.4	2.7	2.66	2.7	2.84	2.9	3	3	2.5	2.6	2.6	2.6
St 3	0.8	1.14	1	1.2	1.26	1.4	1.6	1.8	1	1.2	1.2	1.3
St 4	1.4	1.24	1.2	1.26	1.34	1.6	1.8	1.46	1.6	1.6	1.6	1.6
St 5	1	1	0.9	1	1.2	1.5	1.7	1.6	1.2	1.2	1.2	1.4

Zn	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	2.6	2.62	2.5	2.6	2.7	2.76	2.8	2.7	2.7	2.7	2.7	2.8
St 2	2	2	1.8	2	2.4	2.48	2.5	2.4	2.2	2.3	2.4	2.4
St 3	4.2	4.3	4.2	4.2	4.5	4.8	5	4.6	4.4	4.5	4.6	4.6
St 4	2	2	2	2.1	2.6	2.9	3.18	3.2	2.2	2.2	2.3	2.4
St 5	1.4	1.46	1.4	1.4	2	2.3	2.5	2.5	1.6	1.8	1.8	1.8

Fe	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
St 1	0.5	0.54	0.6	0.6	2.7	2.76	2.8	2.7	0.7	0.8	0.8	0.9
St2	0.8	0.9	0.4	0.9	2.4	2.48	2.5	2.5	0.9	1	0.9	1
St3	0.6	1.24	0.9	0.9	4.5	4.8	4.9	4.8	0.8	0.9	0.8	0.9
St4	1.2	1.5	1.1	1.24	2.6	2.9	3	3.2	1.3	1.3	1.4	1.3
St5	1.44	0.48	0.5	1.26	2	2.3	2.5	2.6	1.5	1.6	1.6	1.6

APPENDIX 3. SEASONAL VARIATION IN HEAVY METAL CONCENTRATION IN WATER

Heavy Metal	DRY SEASON							RAINY SEASON						
	OCT	NOV	DEC	JAN	FEB	MAR	$\bar{x}$ conc.	APR	MAY	JUN	JUL	AUG	SEP	$\bar{\bar{x}}$ conc.
Cd	0.54	0.24	0.22	0.66	0.62	0.32	**0.43***	0.28	0.34	0.32	0.36	0.36	0.34	**0.37**
Cu	1.44	1.07	1.56	2.28	2.44	2.57	**1.89**	2.36	2.56	2.49	2.5	2.42	1.12	**2.24***
Zn	1.98	1.28	1.42	2.31	2.22	2.60	**1.97**	2.24	2.34	2.37	2.32	2.6	1.96	**2.31***
Fe	0.66	0.4	0.48	1.05	1.18	1.39	**0.86***	1.26	0.68	0.76	0.76	0.68	0.61	**0.79**

APPENDIX 4. SEASONAL VARIATION IN HEAVY METAL CONCENTRATION IN SEDIMENT

Heavy Metal	DRY SEASON							RAINY SEASON						
	OCT	NOV	DEC	JAN	FEB	MAR	$\bar{x}$ conc.	APR	MAY	JUN	JUL	AUG	SEP	$\bar{\bar{x}}$ conc.
Cd	0.78	0.66	0.8	1.02	1.22	1.34	**1.14***	1.2	0.94	0.94	1.08	0.98	0.8	**0.99**
Cu	1.66	1.59	1.68	1.79	1.96	2.12	**1.8**	3.65	1.52	1.6	1.6	1.68	1.36	**1.90***
Zn	2.40	2.38	2.46	2.84	3.05	3.20	**2.72**	3.08	2.62	2.7	2.8	2.8	2.44	**2.74***
Fe	0.93	0.7	0.82	2.84	3.05	3.14	**1.91***	3.16	1.02	1.12	1.1	1.14	0.91	**1.41**

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