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Determination of heavy metal levels in surface water and sediment of *Mini-Ezi* Stream, Elele-Alimini, Rivers State, Nigeria.

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ABSTRACT

Mini-Ezi Stream is one stream of significant importance in Elele-Alimini area of Rivers State, Nigeria, receiving array of wastes bearing heavy metals, which originate from household, agricultural and other anthropogenic activities. Consequently, this study evaluated the levels of heavy metals (Fe, Pb, Zn, Cu, Cd, Cr, Mn and Ni) in water and sediment samples of *Mini-Ezi* Stream. Samples were collected monthly for 12 months (to cover both wet and dry seasons), preserved, digested and analyzed using Perkin Elmer Analyst 300 Atomic Absorption Spectrophotometer (AAS). Data obtained showed that the level of Fe, Pb, Cr, Cu, Cd, Zn, Ni and Mn were 0.78 ± 0.09 mg/l, 0.01 ± 0.01 mg/l, 0.02 ± 0.01 mg/L, 0.01 ± 0.01 mg/L, 0.001 ± 0.00 mg/l, 0.015 ± 0.01 mg/l, 0.005 ± 0.01 mg/l and 0.012 ± 0.01 mg/l in water and sediments 5.98 ± 2.43 mg/kg, 0.01 ± 0.01 mg/kg, 0.05 ± 0.02 mg/kg, 0.09 ± 0.03 mg/kg, 0.03 ± 0.01 mg/kg, 1.52 ± 0.69 mg/kg, 0.03 ± 0.01 mg/kg and 0.89 ± 0.23 mg/kg respectively. The results obtained revealed that all metals tested for water, were present in this order of decreasing concentration: Fe > Cr > Zn > Mn > Cu ≈ Pb > Ni > Cd, while in sediment, the sequence was: Fe > Zn > Mn > Cu > Cr > Cd ≈ Ni > Pb. Generally, the mean concentrations of the metals were within the National and International permissible limits in both water and sediments, except for Fe (0.78 ± 0.09 mg/L) in water that exceeded the limit. The concentrations of the metals were generally higher in dry season than in wet, though there was no significant difference (p>0.05). The presence of all the metals in water and sediment indicate potential danger, hence there is need for routine monitoring.

Keywords: Heavy metal levels, *Mini-Ezi*, Sediment, Stream.

INTRODUCTION

The advent of industrialization and urbanization in most Nigerian communities has heralded activities which have brought about an increase in production of commodities and exploitation of the available natural resources directly or indirectly. These myriads of activities have caused diverse interferences on the environmental compartments, particularly the aquatic ecosystem, thereby leaving an unbearable stress that has resulted in deterioration and debasement of biological and physicochemical sanity of both water and sediment qualities (Tony *et al.*, 2018). And one agent of such environmental distortion is the heavy metal.

Heavy metal is one of the most pronounced aquatic pollutants that threatens both flora and fauna functionality in an ecosystem (Withanachchi *et al.,* 2018). The environmental red alertness of the heavy metal could be attributed to its persistence, non-biodegradable nature, bioaccumulation, and toxicity when found in water and sediments, thereby causing harm to plants and benthic organisms (Huang *et al.*, 2020; Nti *et al.*, 2021). Unfortunately, surface waters like stream, river, lagoon and lake have been at the receiving end of the array of indiscriminate and untreated discharges of industrial effluents, agricultural wastes, household wastes and other substances of anthropogenic activities, bearing different degrees of heavy metals (Nwankwoala and Angaya, 2017), thereby inflicting unimaginable damages to the surface water and sediments. These waste materials have the potentiality to deteriorate water and sediment qualities, thus, posing inimical health challenge to human via the food chain (Kar *et al.,* 2008).

Streams are of significant importance to man in most Nigerian communities, and one stream of such importance is the *Mini-Ezi* Stream. This aquatic ecosystem serves as a source of potable water for rural dwellers, provides irrigation and a fishing point for artisanal fishermen (Okey-Wokeh *et al*., 2020). The *Mini-Ezi* Stream is strategically located along the old Ahoada-Elele road, which makes it prone to different anthropogenic activities that expose the stream to pollution. In spite of these arrays of activities that could expose this water body to environmental pollution, there is still a paucity of information regarding the levels of heavy metal in both water and sediment of the *Mini-Ezi* Stream, considering the prominence of oil and gas explorations in the Niger Delta region where the stream is located.

Therefore, this study was conducted to determine the levels of heavy metal in both surface water and sediment samples of the *Mini-Ezi* Stream in order to assess the water quality of the stream for the purposes of human consumption and agricultural use. Also, data obtained from the study will serve as background information for government, water management agencies and research scholars.

STUDY AREA

The *Mini-Ezi* Stream is one of the major essential surface waters in Alimini area of the Niger Delta region, Nigeria. The Stream is non-tidal fresh water that rises from the Orashi River in Onelga area of Rivers State, serving as a headwater of the New Calabar River, from where it flows down to Aluu (Okey-Wokeh *et al.,* 2020). *Mini-Ezi* tream is connected by smaller affluent rivers that originates from Ogbodo-Isiokpo in Ikwerre Local Government and then empties into some lagoon and creek bordering the Atlantic Ocean. This aquatic ecosystem is located within the Elele Alimini area, which lies between Latitude 5°45°N and Longitude 7°60°E in the coastal area of Niger Delta (Figure 1). *Mini-Ezi* Stream became a stream of research interest because of some anthropogenic activities going on within the area.

METHODOLOGY

Sampling and sample collection

The sampling was done monthly for 12 months to cover both dry and wet seasons. Prior to sampling, the vial bottles and other sampling equipment were washed and dried. Samples of water were collected using 120 ml vial bottle and drops of concentrated HNO_3 were added to the samples for preservation until analysis, while samples of sediments were collected by scooping with plastic spoon into cellophane bags where fine materials accumulate with little or no water. The samples were encoded for easy identification.

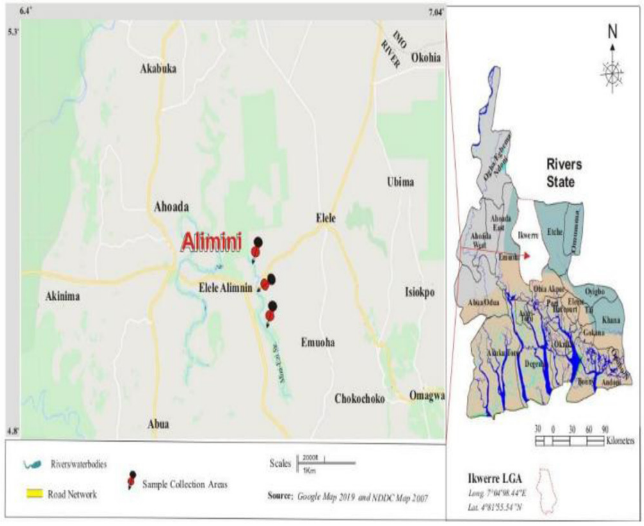

Figure 1: Map of study area showing the sampling points

Analysis of water and sediment samples

Samples of water collected were preserved and digested thus: 100 ml of water was transferred into a beaker and 5 ml of concentrated HNO_3 acid added to it. The beaker that had the content was placed on a hot plate and evaporated down to about 20 ml, the beaker was covered with a watch glass and returned to the hot plate for heating. Heating of the content continued and small portion of HNO_3 added to a point that the solution appeared colourless. The beaker and watch glass used to cover the beaker were washed with reagent water and the sample filtered to remove some insoluble materials that could clog the Atomizer. Then the filtrate was poured into a container and the volume made up to 100 ml with reagent water. The concentrations of eight potentially toxic metals (Cd, Cr, Fe, Cu, Pb, Mn, Zn, and Ni) were determined using Perkin Elmer Analyst 300 Atomic Absorption Spectrophotometer (AAS) with appropriate lamps and standards, according to the analytical procedures by (APHA, 1998).

The samples of sediment that was collected were air dried in the laboratory, ground, and sieved with a 2mm mesh and then preserved in brown paper in order to prevent it from being contaminated by any parameter of interest until analysis was carried out in the Laboratory. For digestion, 0.5g of the sediment sample was weighed out into the acid washed glass beaker and the sample digested by adding $20cm^3$ of aqua ragia (being mixture of HCl and HNO_3 in a ratio of 3:1), and $10cm^3$ of 30% H_2O_2. To avoid overflow, which will possibly lead to loss of material from the beaker, Hydrogen Peroxide (H_2O_2) was added in small portions. The beaker was then covered with a watch glass and heated over a hot plate at 90 °C for 2 hours before washing the beaker wall and watch glass with reagent water, while the mixture was filtered into a 100 ml volumetric flask. The volume was made up to 100 ml mark with reagent water. Blanks solution was handled the same way as the samples, and thereafter, each metal (Fe, Pb, Cr, Cu, Cd, Zn, Ni, and Mn) concentration was determined using the Perkin Elmer Analyst Atomic Absorption Spectrometer (AAS) with appropriate lamps and standard.

Statistical analysis

Data obtained were analyzed, using Microsoft Excel spreadsheet and Statistical Package for Social Sciences (SPSS version 21). T-test was used to compare the significance level of the wet and the dry season samples at 95% intervals.

Pollution index models

To determine the extent of contamination in samples of the sediment collected, data obtained were used to calculate the CF (Contamination Factor) and PLI (Pollution Load Index) of the samples. CF was used to review the extent of metal enrichment of sediment samples, which was calculated as the ratio between the levels of metals content and the reference value of the metal. This was expressed as:

$$CF = \frac{Ci}{Bi}$$

Where:
Ci – Concentration of metal in the sediment
Bi – Concentration of metal in the background

Pollution Load Index (PLI): This tool was used to determine the quality of sediment in a polluted study area, which was obtained as a product of the measured contamination factor of the different metals in the sample.

$$PLI = (CF1 \, x \, CF2 \, x \, CF3 \, x \ldots CFn)^{1/n}$$

Where;
n = Number of metals considered in the study
CFi = Contamination factor for each individual metal

The significance of intervals of contamination factor/ pollution load index showed that when *CF* is less than 1, it indicates low contamination of the sample, when *CF* ranges from 1-3, it indicates moderate contamination, when it ranges from 3-6, it indicates considerable contamination, while when *CF* is more than 6, it indicates very high contamination (Otene and Alfred-Ockiya, 2019).

RESULTS

The summary of the heavy metal concentrations in surface water of the *Mini-Ezi* Stream covering both dry and wet seasons is presented in Table 1. All the potentially toxic metals in the surface water showed values that were below the FMEnv and WHO permissible limits for surface water except for Fe. The mean values of Fe, Cr, Zn, Cu, Pb, Mn and Cd were higher in dry than in wet seasons, although there was no observable significant difference (p>0.05). There was no observable change in the mean value of Ni in the two seasons. The mean concentration of heavy metals in the water revealed that the eight heavy metals tested occurred in this sequence: Fe > Cr > Zn > Mn > Cu ≈ Pb > Ni > Cd.

While, the mean values of heavy metal in sediment samples of the *Mini-Ezi* Stream as shown in Table 2, revealed that the concentration of heavy metals in sediment samples were higher than in the surface water samples. The values were also higher in dry when compared with that of wet seasons, although there was no observable significant difference (p>0.05). The levels of metals in the sediment samples occurred in following order: Fe > Zn > Mn > Cu > Cr > Cd ≈ Ni > Pb. All the metals were below National and International standard limits except Mn. The values of the contamination factor (CF) and the Pollution Load Index (0.0013) as shown in Table 3, are <1

DISCUSSION

Assessment of heavy metal levels of an aquatic ecosystem is vital in determining the sanity and stability of water quality for both domestic and industrial uses. The study of potentially toxic metals known as heavy metals has gained significant attention by different scholars, Environmental managers and policy makers in the last two decades, because of their toxicity, non-biodegradable nature, persistence in the environment and high accumulation in the food chain (Badr *et al.,* 2020). The result of metals analysis in the *Mini-Ezi* Stream showed that the mean value of iron (Fe) in water was above international standard for domestic water, while the mean value of Fe recorded in sediment fell below FMEnv (2011) and WHO (2011) set standards. Fe is naturally found in an elevated concentration in the earth's crust, and its abundance in soil that discharges as run-off may have a significant impact on surface water (Asare *et al.,* 2018). High concentration of Fe in surface water as recorded in this work is typical of a tropical aquatic ecosystem as reported by Davies and Ekperusi (2021). The mean concentration of Fe obtained in this study is in consonance with the findings of Nwankwoala and Ekpewerechi (2017) in Aba River. The sources of Fe in this water body could be attributed to domestic wastes, air particles, vehicular emissions, and refuse from dumpsites which were carried into the stream as runoff during the

Table 1: Descriptive summary of heavy metal concentration in surface water of *Mini-Ezi* Stream.

Metal (mg/l)	Mean± SD (Dry)	Mean± SD(Wet)	Mean of both Wet and Dry	WHO (2011)	FMEnv (2011)
Fe	0.92 ± 0.12	0.64 ± 0.005	0.78 ± 0.09	0.30	1.00
Pb	0.016 ± 0.02	0.006 ± 0.011	0.01 ± 0.01	0.01	0.04
Cr	0.029 ± 0.011	0.013 ± 0.005	0.02 ± 0.01	0.05	0.05
Cu	0.022 ± 0.014	0.001 ± 0.00	0.01 ± 0.01	2.0	1.0
Cd	0.01 ± 0.00	0.001 ± 0.00	0.001 ± 0.00	0.003	0.003
Zn	0.023 ± 0.02	0.002 ± 0.001	0.015 ± 0.00	3.0	1.0
Ni	0.006 ± 0.005	0.005 ± 0.004	0.005 ± 0.01	0.02	0.02
Mn	0.013 ± 0.012	0.007 ± 0.002	0.012 ± 0.01	0.05	0.05

Table 2: Descriptive statistics for sediment samples of *Mini-Ezi* Stream.

Metal (mg/kg)	Mean ± SD (Dry)	Mean ± SD (Wet)	Mean of both Dry and Wet ± SD	WHO (2011)	FMEnv (2011)
Fe	11.11±1.61	0.85±0.92	5.98±2.43	20.00	20.00
Pb	0.01±0.008	0.003±0.003	0.01±0.01	2-20	0.50
Cr	0.06±0.021	0.033±0.008	0.05±0.02	0.50	0.05
Cu	0.11±0.03	0.069±0.014	0.09±0.03	2.00	-
Cd	0.06±0.01	0.001±0.001	0.03±0.01	0.30	0.03
Zn	1.85±0.78	1.18±0.39	1.52±0.69	3.00	-
Ni	0.05±0.03	0.002±0.001	0.03±0.01	0.80	0.05
Mn	1.73±0.49	0.039±0.009	0.89±0.23	0.40	0.40

Table 3: Assessment models for sediment samples in the study area.

Metals	Fe	Pb	Cr	Cu	Cd	Zn	Ni	Mn
CF	0.0002	0.0001	0.0005	0.0035	0.038	0.011	0.0008	0.001
PLI	**=0.0013**							

rainy season (Mgbemena, 2014). Higher concentrations of Fe were observed during the dry season than in the wet both in surface water and sediment samples, and this could be attributed to concentration factor and evaporation. The analysis of water and sediment samples in the *Mini-Ezi* Stream revealed the presence of Lead (Pb) in both water and sediment, with mean values that are below both National and International standard limits. Lead is a non-essential metal and no amount of it is safe in aquatic ecosystem due to its negative effects on living cells (Mgbemena, 2014). The low concentration of Pb observed in the *Mini-Ezi* Stream is typical of area with low anthropogenic activities, like automobile mechanics, oil and gas exploration and other sources of Pb pollution. The low concentration of Pb observed in this study is similar to the finding of Bhuyan *et al.* (2019) in Old Brahmaputra River, Bangladesh, but is in variance with the report of Otene and Alfred-Ockiya (2019) in Elechi Creek. The Pb concentration obtained in the dry season was higher than that of wet, attributed to dilution of the surface water during the wet season that lowers the metal concentration (Edokpayi *et al.,* 2017). The low concentrations of Pb observed in water and sediment of the *Mini-Ezi* Stream, located within the Niger Delta region, negates the view of many that the entire aquatic ecosystem of the area is badly polluted with toxic metals like Pb.

The concentrations of Chromium (Cr) as shown in Tables 1 and 2, revealed that the mean values obtained in surface water and sediments were within WHO (2011) and FMEnv (2011) set standard limit. This is in conformity with the findings of Ighariemu *et al.* (2019) in Ikoli Creek and Nwankwoala and Angaya (2017) in New Calabar River, Eastern Niger Delta. Cr is one potentially toxic metal with mutagenic effects on human and other living organisms. The increase in value of Cr above the recommended limits can lead to damage of sensitive organs like liver, kidney and brain (Bazrafshan *et al.*, 2015). The low Cr levels observed in both surface water and sediment samples are an indication that the stream is not polluted with Cr ion, attributed to fewer anthropogenic activities within the water course.

The levels of Cadmium (Cd) obtained in water and sediment in this study were significantly low compared to National and International permissible limits for water and sediment. Although, the presence of Cd in the aquatic system (water and sediment) is of great concern due to its non-biodegradable and persistent nature in an ecosystem (Badr *et al.*, 2020). Cd is a non-essential element for living organisms, and even in minute deposit, it sends a wrong signal such as causing food poisoning that results in inimical changes in kidney and human arteries (Hussain *et al.,* 2021). Therefore, it is good to avoid food or water that contains Cd (Ipeaiyeda and Onianwa 2011). The presence of Cd in the *Mini-Ezi* Stream could be attributed to fertilizer applied in the nearby farm lands which may have been washed into the water body since the Alimini people, are agrarian in nature. The low concentration of Cd as observed in both surface water and sediment samples of the *Mini-Ezi* is similar to the values reported by Ighariemu *et al.* (2019) in Ikoli Creek, Bayelsa State, but varies from the higher Cd levels observed by Howard *et al.* (2006) in an oilfield in Niger Delta.

The concentrations of Zinc (Zn) as shown in Tables 1 and 2 revealed that the metal was below WHO and FMEnv permissible limits in both surface water and sediment of the *Mini-Ezi* Stream. Zn is of biological importance to living organisms having many physiological functions of cells, but has adverse effects on man and other organisms when it is elevated beyond the set standard (Edokpayi *et al.*, 2017). The values of Zn obtained in both surface water and sediment samples of the *Mini-Ezi* Stream, do not pose any form of danger since it is within the threshold required for surface water. Similar observations of low Zn concentration in an aquatic ecosystem located in the Niger Delta region, also was reported by (Otene and Ukwe, 2018), attributed to be typical of areas with little impacts of anthropogenic activities.

The values of Copper (Cu) obtained in this study revealed that the concentrations in surface water and sediment samples are below National and International standard limits for freshwater. The levels of Cu observed in surface water and sediment samples, were higher in the dry season than that of the wet season. This could be attributed to evaporation and concentration effects of heavy metals. Similarly, Islam *et al.* (2015) asserted that concentrations of metals are expected to be low in the wet season due to dilution effects of runoffs. The low Cu concentration obtained in water and sediment samples of the *Mini-Ezi* Stream is similar to the finding of Mgbemena (2014) in Aba River. The concentration of Cu in most tropical freshwater has been reported to be low in surface water (Babatunde *et al.,* 2013). Cu is one of the essential metals needed for metabolic processes in human but consumption of water or food elevated in Cu above the permissible limits, causes negative impacts on both the nervous and the circulatory systems (Hussain *et al.*, 2021).

Mean values of Nickel (Ni) recorded in surface water and sediment samples of the *Mini-Ezi* Stream as shown in Tables 1 and 2, clearly showed that the concentration of Ni was generally low in the aquatic ecosystem of the study area, and fell below the set standard for water. The presence of Ni in both water and sediment showed no significant elevation in both the dry and the wet seasons.

The finding in terms of Ni levels in this study, agrees with Mahurpawar (2015) who asserted that Ni occurs in the environment at very low level, and as well found naturally in foodstuffs in small quantity. Ni is a major alloy used in production of stainless steel and discharges of this metal into water in an elevated concentration can be dangerous since it is carcinogenic (Bazrafshan *et al.*, 2015).

Meanwhile, the results of this study also revealed that the mean value of Manganese (Mn) in the surface water was below recommended standard for water, while higher mean concentration that was above both FMEnv and WHO standards was observed in sediment samples. Similar observation was reported by Dapam *et al.* (2016). Higher concentration of Mn observed in sediment of this water body, could be attributed to the washing of top soil, cans and leaching of dry cell batteries which emptied into the stream as runoffs (Nwankwoala and Ekpewerechi, 2017). Mn is an essential element for all living organisms and occurs naturally in soil, water and plants (Ljung and Vahter, 2007). Elevated concentration of Mn in an aquatic ecosystem can constitute a nuisance in domestic water, having characteristic metallic taste and staining properties (Edokpayi *et al.*, 2017).

Generally, in this study, the levels of heavy metals observed in sediments were significantly higher than that of surface water in all the metals except Pb that was within the same range in surface water. This is in conformity with the assertion that sediments act as sink that absorb and accumulate heavy metals (Vincent-Akpu and Babatunde, 2013). Apart from sediment serving as sink for pollutants, it also reflects the history of human impacts on the pollutants into the aquatic environment (Devesa-Rey *et al.,* 2010; Edokpayi *et al.*, 2017).

The results of pollution index models (CF and PLI) revealed that there is low degree of contamination of metals in the sediment samples (CF and PLI < 1). The trend of accumulation in terms of the heavy metals as shown in (Table 3) was in this sequence: Cd > Zn > Cu > Mn > Ni > Cr > Fe > Pb.

CONCLUSION

This study has shown low levels of heavy metals accumulation in both water and sediment samples of the *Mini-Ezi* Stream, which clearly indicates that the stream has low levels of metal pollution, except for Fe that exceeded the international standard for domestic water. The presence of all the metals tested in both water and sediment samples, portrays potential danger on the aquatic ecosystem if care is not taken to safeguard the stream against anthropogenic activities that could possibly increase the levels of heavy metals in the stream. Therefore, it is pertinent to closely monitor the activities that go on around the *Mini-Ezi* Stream.

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CONFLICTS OF INTEREST

No observable conflicts of interest amongst the authors were recorded.

ETHICAL APPROVAL

There was no direct or indirect use of human or animal samples in the course of this research. The research was carried based on institutional guidelines provided by the Rivers State University for Postgraduate studies**.**

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