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COMPARATIVE EVALUATION OF HEAVY METAL ACCUMULATION IN WATER AND SEDIMENT OF ELELE-ALIMINI STREAM, PORT HARCOURT, NIGERIA.

Otene, B.B[1] and Iorchor, S.I[2]

[1]Department of Fisheries and Aquatic Environment, Rivers State University, Port Harcourt
[2]Dept of Fisheries, Akperan Oshi College of Agriculture, Yandev, Gboko, Benue State.
Corresponding Author: Otene, B.B (benjaminotene56@yahoo.com)

Abstract

Heavy metal concentrations in water and sediment of Elele-Alimini Stream were studied between April and June, 2019. Surface water samples were collected from three stations and analyzed using Atomic Absorption Spectrophotometer following standard method. The results showed that the mean concentration of Cd, Cr, Pb, Ni and Cu in water (mg/l) were respectively 0.0368± 0.035, 2.044± 0.201, 0.194± 0.064, 1.159± 0.166 and 0.423± 0.253 while that of sediment(mg/kg) were 0.069± 0.048, 2.089± 0.223± 0.115, 1.289± 0.114 and 1.289± 0.114 respectively. Metals concentrations in sediment were higher than that of water with station 2 values consistently higher than stations 1 and 3 for both sediment and water with only copper showing significant difference across the stations at $P< 0.05$. The order of magnitude of metal concentrations in water and sediment were Cr> Ni Pb> Cu Cd and Cr > Ni > Cu> Pb>Cd respectively. The results Showed that the concentration of all the metals investigated in this study except Cu were slightly above the respective MPl/WHO, WPCL and CMC,CCC and USEPA recommended limits for natural water. Also the metal concentrations in the sediment were also above the oral reference dosage (RFD). The prolonged presence of these heavy metals in this water body might affect aquatic life and eventually threaten the life of the inhabitants of the area. It is therefore recommended that continuous monitoring need to be carried out to determine the long term impact of anthropogenic activities in the area to ensure the safety of health of man and that of aquatic life.

Introduction

It is an established fact that rapid progress of technological innovations made it virtually impossible to do without the use of metals and therefore the environment is inundated with excess of metals either biologically essential or non-essential which has led to the present age of ecological fright. Now-a-days, the concentrations of heavy metals are high in the lotic and lentic water due to the release of waste water and agricultural runoff (Sahu, 1991 in Otene & Alfred-Ockiya,2019). The possibility of these metals is expected due to geological strata, decay and decomposition of vegetation in and around the area. Since, most technologically industrialized areas of the globe are located on the banks of rivers, these waters are particularly at risk from metallic contaminants. The metals introduced into the system do not remain in water column and sediment but get precipitated or adsorbed by suspended particulate matters in the form of dissolved metallic ions. Trace metals transported by rivers to the coastal, creek and estuarine systems are in dissolved colloidal and particulate forms.

The ability of a water body to support aquatic life as well as its suitability for other uses depends largely on many of these trace elements, which naturally through precipitation and atmospheric deposition, have significant amounts entering the hydrological cycle through surface waters (Marian,1991, Robinson *et al.*,1996 and Adekoya *et al.*,2006). The most worrisome is the anthropogenic releases from industrial and domestic wastewater sources, the burning of fossil fuels, land run-off, oil spill, gas leaks, blow outs, canalization and discharge from oil and gas operations into surface water bodies or release from industrial operations such as mining, canning and electroplating.

The protection of water and aquatic ecosystem from adverse effects of pollutants such as heavy metals is central to environmental risk management (Bere and Tundisi, 2011). Evaluation and understanding the sources and impact relationship of the effects of heavy metals in water bodies and biological species is important for effective water management, and the preservation of the aquatic ecosystem. This is because trace amounts of such metals can accumulate in the food chain, eventually causing diseases (Gulson et al., 1996; ATSDR, 1999; Windham, 2000). The assessment of water quality is therefore a vital tool to manage land and water resources within a particular catchment (Petts and Calow, 1996).

It is pertinent to note that monitoring the concentration of heavy metals in water, sediment and even in aquatic fauna is important since knowledge of heavy metal levels in these matrices especially sediment gives vital information concerning their sources, distribution and degree of pollution (Adefemi *et al*, 2004; Oyakhilome *et al*, 2013). Contaminants in general discharged into aquatic systems, generally show a large propensity to bind to suspended matter, and thus, through sedimentation, accumulate in aquatic sediments (Wong *et al*., 2006; Kelderman and Osman, 2007; Saygi and Yiğit, 2012). Although this will lead to a provisional improvement of the overlying water quality, the potential release of sediment bound contaminants to the overlying water column may still pose a concealed threat to ecosystem health (Simpson *et al*., 2005; Kelderman and Osman, 2007). Consequently, sediments are extremely important in understanding geochemical cycling and bioavailability in aquatic ecosystems (Birch, 2003).

In the aquatic environment, sediments have been widely used as environmental indicators for the assessment of metal pollution in the natural water (Islam *et al*.,2015a). The principal comportment of metals is a function of the suspended sediment composition and water chemistry in the natural water body (Mohiuddin *et al*.,2012).Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity (Islam, *et al*.,2015, Ahmed *et al*.,2015b). The assessment of the potential risk of heavy metals contamination was proposed as a diagnostic tool for water pollution control purposes as a result of the increasing content of heavy metals in sediments and their subsequent release into the water, which could threaten ecological health.

In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair (Wang and Shi 2001). Many researchers opined that metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis (Kasprzak, 2002, . Beyersmann and Hartwig,2008). Several studies have also confirmed that reactive oxygen species (ROS)

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production and oxidative stress play an essential role in the toxicity and carcinogenicity of metals such as arsenic (Tchounwou *et al.*,(2004a)], cadmium (Tchounwou *et al.*, 2001), chromium (Patlolla *et al*.,(2009b), lead (Tchounwou *et al.*,2004a, Tchounwou *et al.*,2004b) and mercury (Sutton and Tchounwou.,2007). Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals are also classified as either "known" or "probable" human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals.

Elele-Alimini Stream is an important water body running across parts of Rivers state emptying into the New Calabar River through Iwofe axis. During its course particularly around the study area, it receives huge quantities of sewage both agricultural and industrial runoffs as well as arrays of anthropogenic impacts from the residents which could impact significantly on the physiochemical characteristics of the Stream. Thus the health and/or sustainability of the water could be doubtful since these activities cause the water quality to decrease and affect the biotic and abiotic components of the water. There is therefore the need for constant monitoring of this important water body to determine its heavy metal concentrations and to know if they still within permissible limit.

There have been studies in this water body based on plankton and physicochemical properties (Amadi,2018) but to the best of my knowledge detailed work has not been carried out on the heavy metal concentrations of both the water and sediment. The essence of the study was therefore to assess the heavy metals concentrations in water and sediment of the Stream by estimating mean values of metals in respective stations.

Materials and Methods
Study Area
This Study Was Carried Out In Elele-Alumini Stream (New Calabar River), Emohua Local Government Area Of Rivers State Which Lies Between Longitudes 5° 3'0" North And Latitudes 6° 44'0" East (Figure 1). However, the entire river course is situated between longitude 7° 60'E and latitude 5° 45'N in the coastal area of the Niger Delta and empties into the Atlantic Ocean. There are industries, dredging sites; weekly market and fishing activities ongoing alongside numerous other human activities. It has an annual rainfall between 2000-3000 mm (Abowei, 2000) and is a rare tidal freshwater body.

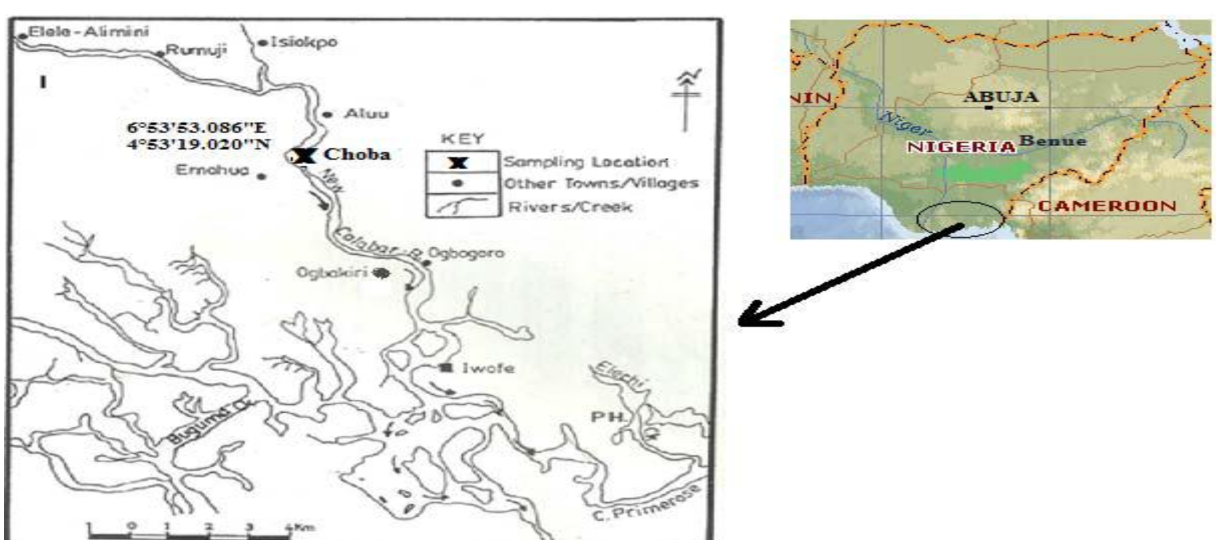

Fig. 1: Map of the study area
(Source: Nzeako *et al.*, 2014)

Sampling Stations

The three sampling stations carefully selected 500m apart along the stream course (fig 1) for their closeness to facilities, structures or human activities that could have potential impact on the water quality thus aggravating pollution as follows:

Station 1 This is the upstream section of the Stream

Station 2 Midstream

Station 3 Downstream

The areas have diversities of vegetation with different anthropogenic activities such as fishing, car washing, slaughter/ abattoir and oil activities.

The Ogbogoro region of the New Calabar River creek creates ready incentives for capture fisheries, transportation, fuel wood production, domestic waste disposal, small-scale aqua-culture. The margins of the study area is dominated by red mangrove, *Rhizophora racemosa* with presence of the white mangrove, *Avicennia africana* , black mangrove (*Laguncularia racemosa*), mangrove sedge (*Paspalum vaginatum*), and nypa palm (*Nypa fructicans*). On the upper shore limits, the vegetation is dominated by mango (*Mangifera indica*), coconut (*Cocos nucifera*) and raffia palm (*Raffia vinifera*).

Sample Collection

The collections of water and sediment samples were done with the aid of plastic sampler previously prewashed with an acid while sediment sample was collected in polythene bag and transported to the laboratory for heavy metals analysis. Sample containers were tightly sealed immediately after sample collection. Sampling was carried out three times between April, 2018 and June, 2018.

Heavy Metal Analysis

The determination of heavy metals was performed with a bulk scientific 205 atomic absorption spectrophometer (AAS). The instrument's setting and operational conditions were done in accordance with manufacturer's specifications. The instrument was calibrated with analytical-grade metal standard stock solutions (1 mg/L) in replicate. 150 ml of sample was transferred to a beaker, 5 ml concentrated HNO_3 was added and the mixture evaporated almost to dryness on a hot plate. 1-2 ml of concentrated HNO_3 was added to dissolve the residues on the walls of the beaker. The distilled, digested samples were filtered and made up to 50 ml and analyzed using AAS. Blank was prepared by carrying distilled deionized water through the whole procedure above. Water and heavy metal samples were prepared for analysis, following the standard methods (APHA,1998). 150 ml of water samples in 5 ml concentrated HNO_3 was used.

Statistical Analysis

Obtained data from the chemical measurements were subjected to descriptive statistical analysis, Pearson correlation coefficient and Duncan Multiple range Test (DMRT) to determine the mean, level of significant difference at $p \leq 0.05$ and the Pearson correlation coefficient ($P < 0.01$) was used to establish relationship trend between parameters. The mean values were compared with the water quality criteria of World Health Organization (WHO), Criterion Maximum Concentration (CMC) and Environmental Protection Agency (EPA).

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Results

Table 1 showed the mean values and ranges of metals in water and sediment. The mean concentration of Cd, Cr, Pb, Ni and Cu in water and sediment in mg/l were respectively 0.0368± 0.035, 2.044± 0.201, 0.194± 0.064, 1.159± 0.166 and 0.423± 0.253 while that of sediment were 0.069± 0.048, 2.089± 0.223± 0.115, 1.289± 0.114 and 1.289± 0.114 respectively. Metal concentrations were higher in sediment than water. Ranges are as shown in Table 1.

Table 1. Mean Values and Ranges of Heavy Metals in Water and Sediment of the Area

Mean Value (mg/l)	Cd	Cr	Pb	Ni	Cu
Water	0.037±0.035	2.044±0.201	0.194±0.064	1.159±0.166	0.423±0.253
Range	0.001-0.090	1.600-2.300	0.100-0.300	0.900-1.320	0.100-1.000
Sediment	0.069±0.048	2.089±0.238	0.223±0.115	1.289±0.114	1.289±0.114
Range	0.015-0.106	1.900-2.00	0.10-0.240	1.100-1.450	1.100-1.450

Table 2. Spatial Mean Values of Heavy Metals in Water (mg/l) and Sediment(mg/kg)

Metal/Station	1		2		3	
	Water	Sediment	Water	Sediment	Water	Sediment
Cd	0.024±0.032[a]	0.052±0.045[a]	0.075±0.018[a]	0.080±0.063[a]	0.011±0.016[a]	0.074±0.016[a]
Cr	1.878±0.27[a]	2.033±0.160[a]	2.200±0.100[a]	2.300±0.300[a]	2.053±0.045[a]	1.933±0.057[a]
Pb	0.179±0.064[a]	0.157±0.129[a]	0.250±0.050[a]	0.333±0.058[a]	0.153±0.050[a]	0.180±0.072[a]
Ni	1.099±0.131[a]	1.300±0.100[a]	1.307±0.012[a]	1.383±0.076[a]	1.070±0.207[a]	1.183±0.076[a]
Cu	0.256±0.140[b]	1.300±0.100[a]	0.607±0.341[b]	1.183±0.076[a]	0.407±0.168[b]	1.183±0.076[a]

Difference in superscript across the column shows significant difference

Table 3: Acceptable level (mg/l) of Heavy Metals in Natural Waters (Water Guideline)

Heavy Metal	**Cd**	**Cr**	**Pb**	**Cu**
Maximum Permissible Limit (MPL	0.003	0.05	0.01	NA
Threshold Concentration for aquatic lifeTC	0.01	0.05	0.10	NA
Bureau of Indian Standards BIS	0.01	0.05	0.05	NA
World Average of trace element in unpolluted rivers (WA)	0.001	NA	0.04	NA
Turkish Standard,2006) (TSE-266)	0.005	0.05	0.01	2.0
Water Pollution Control (WPCL,2004)	0.003	0.02	0.01	0.02
Annonymous Criterion of the Irrigation Water (CIW,1997)	0.01	0.10	5.0	0.20
World Health Organisation (WHO,2006)	0.01	0.05	0.05	2.00
European Community (EC)Water Guideline	5	50	10	2.00
Environmental Protection Agency (EPA)	0.01	0.05	0.05	1.30
Fresh Water Quality Criteria				
Criterion Maximum Concentration (CMC) (USEPA,2006)	0.002	0.016	0.07	NA
Criterion Continous Concentration (CCC) (USEPA,2006)	0.0003	0.011	0.003	NA

NA=Not available

Table 4. Temporal Mean Values of Heavy Metals in Water and Sediment of Elele-Alimini Stream.

M	Cd		Cr		Pb		Ni		Cu	
	W	**S**	**W**	**S**	**W**	**S**	**W**	**S**	**W**	**S**
April	0.019±0.03	0.043±0.05	2.215±0. 15	2.213±0.36	0.212±0.10	0.28±0.1	1.29±0.0	1.33±0.1	0.36±0.1	1.33±0.1
May	0.057±0.03	0.092±0.05	2.067±0.I5	2.137±0.15	0.183±0.02	0.18±0.2	1.12±0.2	1.27±0.2	0.57±0.5	1.27±0.2
June	0.035±0.04	0.071±0.05	1.917±0.28	1.917±0.08	0.187±0.07	0.20±0.1	1.07±0.2	1.27±0.2	0.35±0.1	1.27±0.1

M= Month, W= Water, S=Sediment

Table 2 and 3 showed the Spatial mean concentrations of heavy metals in water and sediment and the permissible limits. Metals concentrations in sediment were higher than that of water with station 2 values consistently higher than stations 1 and 3 for both sediment and water with only copper showing significant difference across the stations at $P< 0.05$. The order of magnitude of metal concentrations in water and sediment were Cr> Ni Pb> Cu Cd and Cr > Ni > Cu> Pb>Cd respectively. The results also showed that the concentration of all the metals investigated in this study except Cu were slightly above the respective MPl/WHO, WPCL and CMC recommended limits for natural water. Also the metal concentration in the sediment was above the oral reference dosage (RFD) of metals in the sediment.

Table 4 showed the temporal mean values of metal concentration in water and sediment. Metal concentrations fluctuate consistently across the months as shown.

Table 5 showed levels of correlations between the metals studied both in water and sediment. There were weak and strong, positive and negative correlations between the metals studied. There were strong positive and significant correlation between chromium in sediment (Cr_s) and chromium in water (Cr_w), lead in water (pb_w) and chromium in water (Cr_w) and copper in sediment (Cu_s) as well as Nickel in sediment (Ni_s).

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Table 5. Correlation Coefficient of Heavy Metals in Water and Sediments in the Study Area

	Cdw	Cds	Crw	Crs	Pbw	Pbs	Niw	Nis	Cuw	Cus
Cdw	1.00									
	0.00									
Cds	0.109	1.00								
	0.339									
Crw	0.447	-0.41	1.00							
	0.133	0.462								
Crs	0.465	0.305	0.841	1.00						
	0.123	0.231	0.004							
Pbw	0.488	0.008	0.854	0.743	1.00					
	0.110	0.492	0.003	0.017						
Pbs	0.325	0.163	0.560	0.605	0.488	1.00				
	0.216	0.350	0.074	0.056	0.110					
Niw	0.414	-0.356	0.643	0.552	0.386	0.694	1.00			
	0.154	0.193	0.043	0.078	0.172	0.028				
Nis	0.605	-0.304	0.622	0.640	0.693	0.304	0.643	1.00		
	0.056	0.232	0.05	0.044	0.028	0.232	0.043			
Cuw	0.461	0.520	0.423	0.392	0.168	0.546	0.361	0.424	1.00	
	0.126	0.093	0.148	0.168	0.346	0.081	0.190			
Cus	0.605	-0.304	0.622	0.640	0.693	0.304	0.643	1.000	-0.082	1.00
	0.056	0.232	0.050	0.044	0.028	0.232	0.043	0.000	0.424	

$P<0.05$. Key: Cd= Cadmium, Cr= Chromium, Pb= Lead, Ni= Nickel, Cu= Copper, W= Water, S= Sediment

Discussion

The mean concentration of Cd, Cr, Pb and Cu observed in this study were higher than the values reported by Otene and Alfred-Odaiya (2019) in Elechi creek. The values were also higher than the values reported by Eletta (2007) in Asa River but in agreement with the values reported for Cd, Cr, Pb Ni and Cu from public water supply in Kaduna Metropolis by Kazaure *et al* (2015). The values were also in line with the finding of Joseph *et al* (2012) in Lake Chad, Baga, North Eastern Nigerian except chromium value which was completely contrary to this result.

The higher values of metal concentration in sediment than water observed in this study is in line with the finding of Davies *et al* (2009) in Elechi Creek where all the metals studied concentrated in sediment than the water. This result is also in conformity with that of Otene and Alfred-Ockiya (2019) with sediment metal concentration higher than that of the water.

The high concentration/accumulation of metal in the water and sediment above the required or permissible limit of WHO (1993,2006), WPCL (2004) ,CCC(USEPA,2006) and CMC (USEPA,2006) is also in line with the finding of Joseph *et al* (2012) in Lake Chad, Baga, North Eastern Nigerian. This observation is also in agreement with the finding of Maitera *et al* (2011) in River Gongola, Adamawa state Nigerian where metals such as Cr, Cd and Pb were present above the required / permissible limit of WHO (2006). According to Maitera *et al* (2011) higher concentration of heavy metals in sediment than water is normal since sediments are considered to be metal reservoirs. Ademoroti (1996) opined that higher presence of heavy metals in sediment than water is normal because metals are originally found to reside in sediment. According to Mason (2002), higher levels of Cd and Pb in any water body could be attributed to huge agricultural and industrial discharge into the area. Hardman *et al* (1994) also opined that high concentration of Pb in water could be attributed to spill of leaded petrol in automobile cars and heavily traveled roads running along the lake while Banat *et al* (1998) attributed it to proximity of water body to highways and large cities due to gasoline combustion. Hamed, (1998) and Nguyena *et al* (2005) also reported higher accumulation of metals in sediment than water owing to the fact that sediment acts as reservoirs for all containments and dead organic matter descending from the ecosystem above.

Conclusion/ Recommendation

Considering the result of this study Elele-Alimini stream is contaminated by the heavy metals Cd, Cr and Pb since their concentrations in both water and sediment exceeded the WHO, EU, CCC and CMC permissible limits for natural water and Oral reference Dosage (RFD) for sediment. The prolonged presence of these heavy metals in this water body might affect aquatic life and eventually threaten the life of the inhabitants of the area. It is therefore recommended that continuous monitoring need to be carried out to determine the long term impact of anthropogenic activities in the area to ensure the safety of health of man and that of aquatic life.

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