Evaluation of Heavy Metal Accumulation in Water and Sediment from Elechi Creek, Port Harcourt, Nigeria

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Abstract
Elechi creek has been known to be one among those receiving quantum of wastes from the surrounding due to its location close to several numbers of companies discharging their effluents directly into it. Accumulation of heavy metals such as Cd, Cr, Pb and Cu in the water and sediment from Elechi creek were studied for twelve months between February 2015 to January 2016 using Atomic Absorption Spectrophotometer in the surface water and sediment collected from four different locations in the laboratory. The result showed that the mean concentrations of Cd, Cr, Pb and Cu in the sediment (µg/kg) were higher than that of the water (µg/l). The order of magnitude of accumulation of heavy metals in sediment and water were respectively, Cu>Cd> Pb> Cr and Cu> Pb> Cr >Cd with the mean values 0.731±0.204, 0.494± 0.203, 0.468±0.205 and 0.457±0.172µg/kg for sediment and 0.682±0.217, 0.420±0.196, 0.387±0.136 and 0.361±0.227µg/l for water respectively. Spatially, station 4 had the highest concentrations of Cu and Cd in both sediment and water. Seasonally, dry seasons' values of all the heavy metals were significantly higher than the wet season values (P≤0.05). There was a weak and positive correlation (0.441) between Chromium and Cadmium in the sediment at P≤0.005 while there was no correlation between all the heavy metals in water studied. The mean values recorded for the various metals studied were all within the permissible limit of the World Health Organisation (WHO), United State Environmental Protection Agency (USEPA,), National Health and Medical Research Council (NHMRC) and Australian and New Zealand Environment and Conservation Council (ANZECC/ARMCANZ). The study therefore concluded that the water and sediment of Elechi creek were not polluted though contaminated. It is therefore recommended that the water and aquatic biota are safe for human consumption since they are safe for habitation by aquatic biota.

Key words: *Heavy metals, Sediment, Water, Elechi creek, Port Harcourt*

Introduction

Elechi creek which lie between longitude $7^0$00' to 7^0 15'' E and latitude 4^0 25'' to 4^0 45' N is one of the tributary of the Bonny Estuary considered to have received considerable amount of effluents of industrial and domestic origins over the years with respect to the ongoing anthropogenic activities in the area. This water body provides the inhabitants of the area with several numbers of services ranging from provision of seafood, water for domestic use, source of water for irrigation activity along the creek, cooling system by the companies along the creek and source of transport for the people. These services therefore make the study of this creek water and sediment very crucial in its effective utilization thereby avoiding consumption of aquatic resources polluted by the existing pollutants especially heavy metals. However, several studies have been carried out to understand the physicochemical and biological characteristics of the environment as well as the extent of pollution in this area

(RPI, 1985; Ajaji and Osibanjo, 1981; IPS, 1990, 1991a,b; Obire *et al*., 2003).

Metals generally enter the aquatic environment through atmospheric deposition, erosion of the geological matrix, or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes (Tarvainen *et al*., 1997; Stephen *et al*., 2000). Some of these metals, such as Cd and Pb are toxic to living organisms even at quite low concentrations, whereas others, such as Zn and Cu, are biologically essential and natural constituents of aquatic ecosystems, and generally only become toxic at very high concentrations. When these metals find their way into the creek, they settle in both the water and sediment which serves as habitat for the aquatic organisms.

Contaminants in general released 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).

The investigations carried out in recent years revealed that the metal ions have a biological significance and show that the living world falls within the realm of organic and biochemistry contrary to the classical concept that inorganic chemistry is limited to non-living systems. Recent researches have revealed that life is as much inorganic and organic, because of the pivotal significance of trace metals which are easily available for uptake by biota continuously inhabiting the water and sediment thereby entering into food chain.

Owing to rapid progress of technological innovations it becomes 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). The possibility of these metals is expected due to geological strata, decay and decomposition of vegetation in and around the area. Since, most industrialized areas of the world are located on the banks of rivers, these waters are particularly at risk from metallic contaminates. 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 interface between freshwater and seawater tends to encourage the transfer of metals from water to sediments. In a special environment like an estuary, the harmful nature of trace elements has to be critically looked into taking into considerations the effectiveness of estuaries where heavy metals became deposited in sediments (Turekian, 1977). Thus rather than being dispersed to the open sea, metal inputs to the estuaries and other restricted areas may become actually be trapped in highly metal sediments. Particulate matter generated by biological productivity may also be important in the supply of suspended sediments in the lower portion of estuaries (Biggs, 1970).

Chemical analysis of the environment matrix such as water and sediment is the most direct approach to disclose the heavy metal pollution status in the environment despite that it cannot afford the powerful evidence on the integrated influence and possible toxicity of such pollution on the organisms and ecosystem.

Due to the toxicity of heavy metals, accurate information about their concentration in the aquatic ecosystems especially in Elechi creek is needed (Janssen *et al*., 2000). Therefore, the objective of this study is to evaluate the accumulation of Cu, Cr, Cd and Pb in the water and sediment of the creek so as to monitor and regulate the influx of toxicants into the aquatic ecosystem.

Materials and Methods

Study Area

The creek is brackish in nature and surrounded by different companies discharging their effluents indiscriminately into it. Elechi Creek is within the upper reaches of the Bonny Estuary which lies between longitude 6^{0}58'10.83'' to 00'23.64''E and latitude 4^{0} $4^{6'}$11.34' to 4^{0} $4^{7'}$ 43.33''N and it receives indiscriminate effluents discharges from the heavily industrialized and highly populated Port Harcourt Metropolis (figure1). It is characterized by high sea inflow and low freshwater input from adjoining swamp forest and municipal sewers within the Diobu area of Port Harcourt.

Sediment and water samples were collected from four different locations of the creek on monthly basis for twelve months to cover dry and wet seasons respectively. The locations were chosen to represent different degrees of activities in the areas (figure 1). The top 20 cm of the bottom sediment samples were collected from each sampling station using the Eckman bottom sampler (Topouoglu *et al*., 2002; ATSM, 1990) and kept in glass bottles (at least 80 g). The samples were subjected to triacid digestion and filtered (Chester and Huges, 1967). The filtrate was made up to 25 ml using metal free double distilled water and the concentration of the heavy metals (Cd,Cr, Pb and Cu) were determined using an Atomic Absorption Spectrophotometer (Varian Spectr AA 220, Australia). Water samples were collected at various stations at a depth of 50 cm below the water surface. They were treated and analyzed for heavy metals using appropriate methods (Lau *et al*., 1998). Two-way ANOVA was employed to find the significant differences of heavy metal concentrations in water and sediment with regard to sites and seasons (Bailey, 1982) with the significant level set at $P < 0.05$.

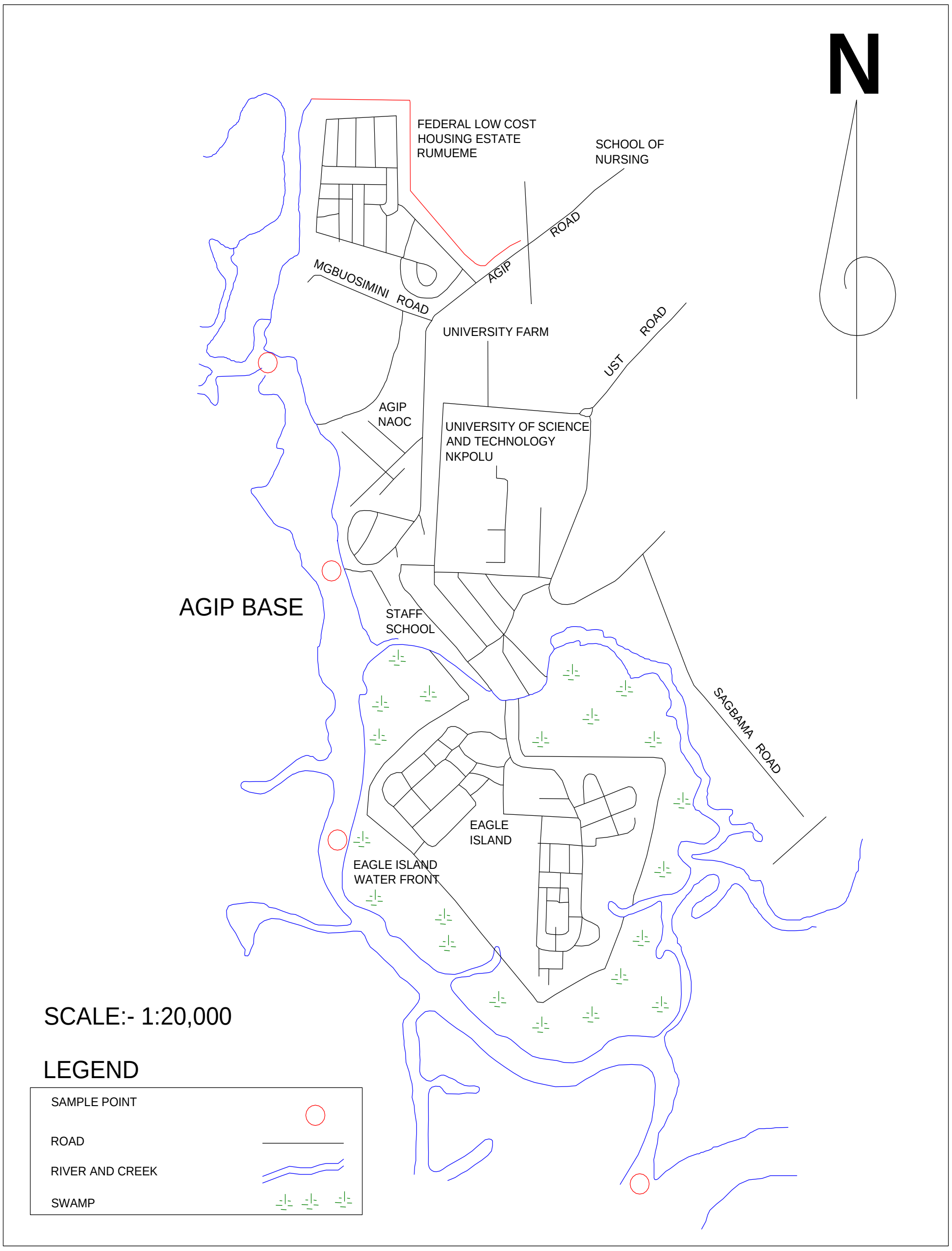

Figure1: A Sketch Map of the Study Area Showing Sampling Stations

Results and Discussion

Table 1 showed that the mean concentrations of Cd, Cr, Pb and Cu were respectively 0.494± 0.203, 0.457±0.172, 0.468±0.205 and 0.731µg/kg for sediment and 0.361±0.227, 0.420±0.196, 0.387±0.136 and 0.682±0.217µg/l for water. The range of Cd, Cr, Pb and Cu for sediment and water are as represented in table 1. The result showed that the concentrations of all the heavy metals studied except Cu are higher in the sediment than that of the water (Table 2 and 3). The mean values recorded for the various metals studied were all within the permissible limit of the World Health Organisation (WHO) and United State Environmental Protection Agency (USEPA, 2009), NHMRC(2004) and ANZECC/ARMCANZ (2000). The result of this study is in agreement with the finding of

Davies *et al*., (2006) in Elechi Creek where heavy metal concentrations in sediment was higher than that of the water. This result is also in agreement with the assertion that sediment acts as sinks and sometimes considered as potential sources of various contaminants in aquatic systems (Christophoridis *et al*., 2008). According to Odiete (1999) sediment is the major depository of metals in some cases, accounting for or holding more than 99 percent of total amount of a metal present in the aquatic system. The higher value of copper in both sediment and water is in line with the finding of Nwoko *et al., (*2014) which was attributed to anthropogenic activities arising from solid and liquid wastes discharged by cottage industries located around the area of study. The observed low concentrations of Cr, Cd and Pb in this present study is in conformity with the findings of Obire *et al.* (2003) who also reported similar range of values in this creek but contrary to the reports of Chindah and Braide (2003) who reported higher values of Cd and Pb in this aquatic body.
The temporal values of heavy metals in the study area showed that the heavy metal concentrations in the months of April, May and June were consistently lower than the other Months except copper (Table 1).

Spatially and seasonally, there were significant differences among the metals in both sediment and water except lead (Table2 and 3). The higher concentration of all the heavy metals studied in the sediment than the water and fluctuation in values across the stations and seasons observed in this study could be associated with difference in environmental factors and variation in the level of urbanization and industrialization in the various areas studied. The order of magnitude of accumulation of heavy metals in sediment and water were respectively, Cu>Cd> Pb> Cr and Cu> Pb> Cr >Cd. Spatially, station 4 had the highest concentrations of Cu and Cd in both sediment and water. In general, there is fluctuation in the sequence of heavy metal concentration in both sediment and water. This observation could be attributed to the presence of different anthropogenic and petrogenic activities in the various stations coupled with difference in environmental factors. This phenomenon could also be attributed to the pH, sediment texture and level of organic matter in the sediment which all together constitutes the non- anthropogenic activities in the area. Santschi *et al*., (2001) opined that many factors such as grain size, mineralogy, concentration of organic carbon, Al, Fe and Mn play a role in the concentration of heavy metals in sediments. Ghrefat and Yusuf,2006) also reported several physico-chemical parameters that affect the adsorption process which include pH, inorganic and organic carbon content, dissolved oxygen, oxidative -reductive potential and the presence of certain anions and cations in a water phase.
There was a weak and positive correlation (0.441) between Chromium and Cadmium in the sediment at $P \leq 0.005$ while there was no correlation between all the heavy metals in water studied at either $P \leq 0.001$or $P \leq 0.005$.

Conclusion/Recommendation
The study therefore concluded that the water and sediment of Elechi creek were not polluted though contaminated. It is therefore recommended that the water and aquatic biota are safe for human consumption since they are safe for habitation by aquatic biota but there should be no further indiscriminate introduction of waste into the creek.

Table 1. Temporal, Overall Mean Values and Ranges of Heavy Metals in Sediment (µg/kg) and Water (µ/l) in Elechi Creek.

Month/Heavy metal	**Cd**		**Cr**		**Pb**		**Cu**	
	Sediment	**Water**	**Sediment**	**Water**	**Sediment**	**Water**	**Sediment**	**Water**
January	0.475±0.467	0.425±0.13	0.525±0.096	0.425±0.13	0.425±0.126	0.250±0.10	0.725±0.096	0.750±0.10
February	0.458±0.301	0.155±0.14	0.513±0.155	0.513±0.10	0.488±0.118	0.425±0.03	0.800±0.071	0.754±0.10
March	0.488±0.170	0.450±0.19	0.528±0.123	0.350±0.13	0.488±0.202	0.400±0.18	0.825±0.050	0.725±0.15
April	0.350±0.058	0.300±0.07	0.375±0.126	0.313±0.03	0.400±0.082	0.413±0.09	0.750±0.129	0.625±0.24
May	0.338±0.095	0.325±0.05	0.300±0.082	0.163±0.08	0.275±0.096	0.175±0.10	0.803±0.144	0.775±0.15
June	0.350±0.208	0.350±0.17	0.225±0.050	0.160±0.09	0.700±0.469	0.475±0.05	0.388±0.343	0.425±0.25
July	0.475±0.150	0.400±0.16	0.500±0.216	0.475±0.29	0.438±0.048	0.388±0.09	0.525±0.250	0.500±0.34
August	0.728±0.061	0.675±0.06	0.633±0.538	0.613±0.05	0.525±0.150	0.358±0.09	0.850±0.129	0.845±0.30
September	0.425±0.171	0.235±0.12	0.250±0.186	0.308±0.17	0.268±0.209	0.313±0.11	0.688±0.063	0.575±0.09
October	0.413±0.246	0.248±0.21	0.588±0.131	0.645±0.18	0.525±0.171	0.488±0.09	0.072±0.142	0.600±0.16
November	0.800±0.082	0.625±0.10	0.525±0.150	0.575±0.03	0.550±0.192	0.550±0.17	0.850±0.129	0.800±0.14
December	0.625±0.096	0.513±0.06	0.520±0.054	0.500±0.09	0.538±0.095	0.413±0.09	0.850±0.252	0.825±0.17
Mean Value	0.494±0.203	0.361±0.23	0.457±0.172	0.420±0.20	0.468±0.205	0.387±0.139	0.731±0.204	0.682±0.22
Range	0.050-0.900	0.06-0.70	0.060-0.800	0.10-0.90	0.110-1.400	0.20-0.60	0.200-1.200	0.30-1.00
WHO/USEPA LIMIT (mg/l)	0.01		0.1		0.05		0.05	

Table 2: Spatial Mean Values of Heavy Metals in Water (µg/l) and Sediment (µg/kg) from Elechi Creek, Port Harcourt

Station/Heavy Metal	Cd		Cr		Pb		Cu	
	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
1	0.462±0.241[b]	0.361±0.23[b]	0.387±0.145[b]	0.418±0.24[a]	0.551±0.325[a]	0.398±0.12[b]	0.755±0.251[a]	0.661±0.22[b]
2	0.583±0.20[a]	0.335±0.22[b]	0.459±0.175[a]	0.403±0.18[a]	0.438±0.153[b]	0.375±0.14[a]	0.707±0.206[b]	0.619±0.22[b]
3	0.617±0.16[a]	0.408±0.17[a]	0.512±0.165[a]	0.472±0.21[a]	0.479±0.250[a]	0.417±0.14[b]	0.713±0.210[b]	0.699±0.21[a]
4	0.625±0.15[a]	0.463±0.13[a]	0.475±0.198[a]	0.386±0.16[b]	0.413±0.157[b]	0.358±0.16[a]	0.779±0.144[a]	0.750±0.23[a]

Means of similar superscript across the vertical row are not significantly different at P≤0.05

Table 3: Seasonal Mean Values of Heavy Metals in Sediment (µg/kg) and Water (µg/l) of Elechi Creek, Port Harcourt

Season/Heavy Metal	Cd		Cr		Pb		Cu	
	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
A	0.533±0.202[a]	0.411±0.19[a]	0.498±0.122[a]	0.446±0.13[a]	0.481±0.138[a]	0.408±0.13[a]	0.800±0.131[a]	0.745±0.15[a]
B	0.455±0.199[b]	0.372±0.20[b]	0.416±0.206[b]	0.394±0.25[a]	0.455±0.258[a]	0.366±0.13[a]	0.662±0.241[b]	0.620±0.25[b]

Mean with similar superscript across the same vertical row are not significantly different at P≤0.05
NB: A= Dry Season. B= Wet season.

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