Direct RESEARCH JOURNALS

Direct Research Journal of Chemistry and Material Science
Vol.6 (3), pp. 25-31, November 2019
ISSN 2354-4163
DOI: https://doi.org/10.5281/zenodo.3550983
Article Number: DRJCMS12808486

https://directresearchpublisher.org/drjcm/

Full Length Research Paper

Status of heavy metals contamination in water from the Elelenwo River, Obio-Akpor, Rivers State, Nigeria

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Received 3 October 2019; Accepted 29 October, 2019

Water samples were collected from Elelenwo River between the periods of three months (June – August year) and analyzed for heavy metal content. The concentrations of the metal observed within the period showed the order of concentration as; iron (Fe) > zinc (Zn) > silver (Ag) > chromium (Cr) > copper (Cu) > cobalt (Co) > lead (Pb) > cadmium (Cd) > nickel (Ni) > Arsenic (As). The mean concentrations of the examined metals in mg/Kg within the period were Cd (0.251±0.000), Pb (0.428±0.001), Cr (0.139±0.001), Ag (1.428±0.384), Ni (0.184±0.000), Fe (5.910±0.008), As (undetected), Zn (1.324±0.320), Cu (0.781±0.003) and Co (0.672±0.002). All the examined metals were detected in the Elelenwo River except As. The concentrations of the heavy metals were all above the individual standard limits in drinking water stipulated by WHO except Zn, Cu and As. The values obtained for the different metals examined revealed that the concentrations of the metals were as a result of anthropogenic input sources rather than natural influence. The high values observed for the metals call for proper investigation on the input sources so as to provide preventive measures in order to curb further increase that can lead to fatal conditions in the environment.

Keywords: Elelenwo river, heavy metals and contaminants

INTRODUCTION

Rivers form the major source of surface water for use at homes, engineering and irrigation of farms. The pollution of surface water results mainly from enormous discharges of industrial used water and run-offs from agricultural wastes (Edori and Kpee, 2018). These wastes continuously discharged into surface water bodies constitute potential and emergent jeopardy to the immediate aquatic environment and other adjoining rivers that may receive discharges from the immediate polluted river and water dwelling organism (Hadzi *et al*., 2015). The quality of water is very important to humanity and a cause for daily concern because it is an indispensable factor for the growth and quality of any environment. It is a well-known fact that the aquatic ecologies (rivers, lakes, streams, ponds, oceans, seas, lagoons, estuaries, etc), accomplish important roles in the total well-being and welfare of both countryside and city populations over the world (Bytyçi *et al*., 2018). The process of water contamination or pollution involves both natural routes and anthropogenic activities. These routes of pollution, introduces chemical components such as heavy metals (Ato *et al*. 2010; Naveedullah *et al*., 2014) and other organic constituents into the water, which thus alter the original composition of the water and its natural applications (Marcus and Edori, 2016).

Water have distinguishing characteristics (as a universal solvent) of dissolving a massive variety of substances and transferring them as either suspended particles or dissolved solids. This particular feature or property has significantly turned different water sources into impure forms and in some cases become polluted to undesirable levels (Nizami and Rehman, 2018).

Irrespective of source where water resources are obtained; there is a rising increase in the concentrations of heavy metals in water. This has become a severe hazard to anthropological well-being and those of aquatic ecosystems (Humood, 2013; Naveedullah *et al.*, 2014). As soon as the concentrations of levels of heavy metals in water go beyond environmental acceptance boundaries, its uses in agricultural (irrigation and aquaculture) activities could be detrimental to the aquatic ecosystem and human through the food chain (Wright and Welbourn, 2002).

Heavy metals do not undergo degradation in any environment and with protracted resident period in any location leads to accumulation. Due to the toxic and accumulating characteristics of heavy metals, they have become one of the most important ecological and environmental worries (MacFarlane and Burchette, 2014; Islam *et al.*, 2015; Martin *et al.*, 2015). In Nigeria, there has existed the behaviour of direct discharge of wastes into the river. This particular behaviour by the inhabitants along the shore (coastal communities) has affected the coastal aquatic ecological systems and has posed different pollution challenges to different environmental agencies within the country. Human bound activities can naturally intensify increase in heavy metals input in river water systems (Sánchez-Chardi *et al.*, 2007)**.** Leachates or seepages of agro based chemicals and composts that comprise heavy metals from farmhouses in most cases end up in many rivers. In the process of transportation of heavy metals in the riverine system, they can go through repeated fluctuations in concentration within the water system as a result of suspension, solubility, precipitation and adsorption processes (Adebanjo and Adedeji, 2019).

In studies conducted on the concentrations of heavy metals in the surface water matrix of Oginigba and Bomu Rivers (which fall within the same environment as the Elelenwo River) showed that the concentrations of heavy metals such as Cu, Cr, Ni and Pb were higher than the WHO requirement for drinking, while Zn was lower than the standard and Cd undetected (Marcus and Edori, 2016). In another study, Marcus and Edori (2017), observed that in Ekerekana River, Rivers State heavy metals namely Ni, V, Cd and Pb were higher than the recommended values for drinking water. Adesiyan *et al.* (2018), observed seasonal variations of heavy metals in Asejire and Dandaru Rivers, with higher concentrations recorded in the dry season. They further observed that the concentrations of Cd, Cr, Pb, Mn and As were either higher or lower than the WHO standard requirement for drinking water. This work therefore investigated the concentrations of heavy metals in Elelenwo River, Obio-Akpor, Rivers State, Nigeria.

MATERIALS AND METHODS

Three sample stations were selected due to the closeness of the communities and associated anthropogenic activities to the river. The samples were collected between the periods of June to August, 2019. In each of the sampling months, 3 composite samples were taken from the rivers from 12 sample points. The composite samples were collected from a distance of 50 m sideways from a chosen point of sampling at the centre of the river. The samples were collected in 1.0 L cellophane vials previously washed in a detergent and rinsed in dilute solution of concentrated nitric acid. Before collection of the samples, the vials were rinsed with the water from the river and the samples were taken. The samples were acidified by the addition of nitric acid and tightly capped with a plastic cover. The samples were immediately transported to the laboratory in ice filled ice chest containers. In the laboratory, the samples were stored in the refrigerator at 4°C until further analysis. The investigation of water samples from Elelenwo River was done without further laboratory treatment. The analysis was done at the Analytical Laboratory, Woji, Port Harcourt, Rivers State. The concentrations of the heavy metals were determined using Atomic Absorption Spectrophotometer (AAS). Commercially prepared standards of the various metals were used as quality check on the determined concentrations of the heavy metals (Marcus and Edori, 2016). Statistically, the calculations in this article were done using Excel package to obtain the means and standard deviations of the various measurements. The results were interpreted based on the data obtained and compared with given international standards.

RESULTS AND DISCUSSION

The result of the heavy metals in the various stations between June and August along the Elelenwo River is given in (Tables 1-3). The mean values in the different stations with the associated standard deviations are shown (Table 4). The general mean concentration of the heavy metals in the river is shown in (Figure 1). The concentrations of Cd within the period of assessment varied from 0.216 – 0.277 mg/L. The mean concentration of Cd within this period was 0.25±0.02 mg/L. The values of Cd detected in the river in all the stations within the period of analysis were higher than the WHO value of 0.03 mg/L for drinking water. The concentrations of Cd observed in the Elelenwo River were higher than those of Banzi *et al.* (2015) in Mkuju River in Tanzania and those of Adebanjo and Adedeji, (2019) in Osun River, Osogbo, Nigeria. Effluents from industries and ore wastes are some of the ways Cd is discharged into the river. Galvanized products and batteries also contain Cd. Basically, Cd exist in the +2 oxidation state in water and behaves similar to Zn. In nature, it is found combined with Sulphur as CdS and also found in ore deposits of Pb and Zn. Cd poisoning is associated with food intake and at

Table 1. Concentrations of heavy metals in Elelenwo River in the month of June.

Heavy Metals (mg/L)	Stations			Mean±SD
	A	B	C	
Cd	0.258	0.259	0.257	0.258±0.00
Pb	0.447	0.437	0.457	0.447±0.01
Cr	0.174	0.176	0.172	0.174±0.00
Ag	1.16	1.13	1.19	1.16±0.02
Ni	0.170	0.172	0.168	0.170±0.00
Fe	5.21	5.18	5.24	5.21±0.02
As	<0.002	<0.002	<0.002	-
Zn	2.73	2.72	2.74	2.73±0.01
Cu	0.685	0.696	0.674-0.844	0.685±0.00
Co	0.805	0.801	0.809	0.805±0.00

Table 2. Concentrations of heavy metals in Elelenwo River in the month of July.

Heavy Metals (mg/L)	Stations			Mean±SD
	A	B	C	
Cd	0.218	0.216	0.220	0.218±0.00
Pb	0.424	0.434	0.414	0.424±0.00
Cr	0.111	0.112	0.110	0.111±0.00
Ag	1.05	1.03	1.07	1.05±0.02
Ni	0.188	0.186	0.190	0.170±0.00
Fe	7.34	7.33	7.35	7.34±0.01
As	<0.002	<0.002	<0.002	-
Zn	1.09	1.07	1.11	1.09±0.02
Cu	0.816	0.816	0.816	0.685±0.00
Co	0.674	0.673	0.675	0.805±0.00

Table 3. Concentrations of heavy metals in Elelenwo River in the month of August.

Heavy Metals (mg/L)	Stations			Mean±SD
	A	B	C	
Cd	0.276	0.275	0.277	0.276±0.00
Pb	0.413	0.410	0.416	0.413±0.00
Cr	0.132	0.132	0.132	0.132±0.00
Ag	1.30	1.27	1.33	1.300±0.02
Ni	0.194	0.193	0.195	0.194±0.00
Fe	5.17	5.18	5.16	5.170±0.01
As	<0.002	<0.002	<0.002	-
Zn	1.51	1.52	1.50	1.510±0.01
Cu	0.843	0.842	0.844	0.843±0.00
Co	0.538	0.535	0.541	0.538±0.00

acute levels of poisoning, presents serious health challenges in the form of hypertension, kidney damage and also causing potential prostate cancer (Durmishi *et al*., 2016). The very high concentration of Cd in the river is an indication of human influence rather than natural causes.

The concentrations of Pb in the period of investigation varied from 0.410-0.457 mg/L. The mean concentration of Pb within this period was 0.428±0.02 mg/L. The observed values of Pb in the present work are higher than the WHO required value for domestic water. The measured values of Pb in this work were higher than the values obtained in water elsewhere in Rupsha River, Bangladesh (Sabbir *et al*., 2018) and those of Hadzi *et al*., (2015) in surface Water from virgin environments and main quarrying parts in Ghana. Lead (Pb) is non biological important metal. It has not been known to perform any positive metabolic function in both plants and animals in the environment (Brochin *et al*., 2008). In any environment, both natural and anthropogenic factors contribute to the concentration of Pb. However, the major contributions of Pb in any surrounding environment arise from human input or output sources (Adebanjo and Adedeji, 2019). The presence of Pb in water is mostly in the +2 oxidation state. It is a toxic metal and its presence in human systems is associated with kidney function

Table 4. Mean concentrations of heavy metals at the various stations during the sampling period compared with Standards.

Heavy Metals (mg/L)	Stations			WHO (2011)
	A	B	C	
Cd	0.251±0.02	0.250±0.03	0.251±0.02	0.03
Pb	0.428±0.01	0.427±0.01	0.429±0.02	0.01
Cr	0.139±0.03	0.140±0.03	0.138±0.03	0.05
Ag	1.170±0.10	1.143±0.10	1.97±0.11	0.05
Ni	0.184±0.01	0.184±0.01	0.184±0.01	0.15
Fe	5.910±1.01	5.900±1.01	5.920±1.01	0.3
As	-	-	-	
Zn	1.777±0.70	1.095±0.34	1.100±0.34	5.0
Cu	0.781±0.07	0.785±0.06	0.778±0.07	2.0
Co	0.672±0.11	0.670±0.11	0.675±0.11	0.05

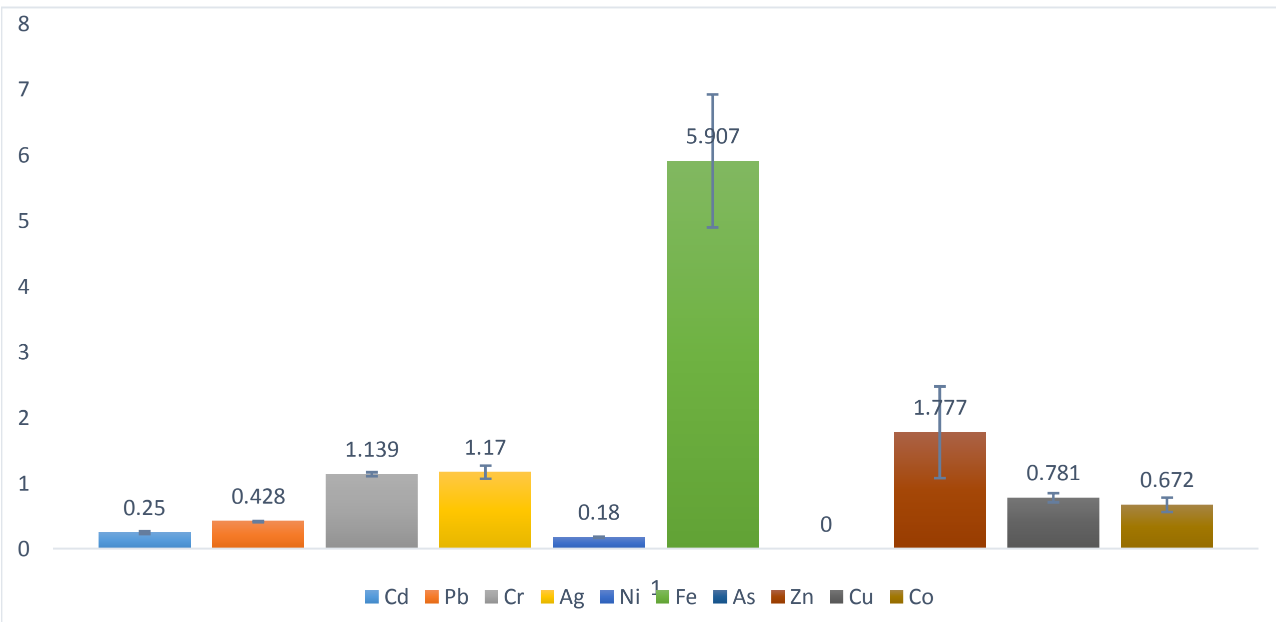

Figure 1. Mean concentrations of heavy metals in Elelenwo River.

disorder, disruption in the normal functions of liver, nervous system and the reproductive system (Puri *et al*., 2015). Exposure to environmental Pb causes numerous health challenges or issues such as impedance in the intellectual capacity of children, anaemia, and decreases enzyme activities, causes breakdown in redox reactions within the cell and protein production and disturbance in other body biochemical reactions (Tirkey *et al*., 2012). Industrial and home based Pb originated from Pb in fuels, plastic materials, batteries, paints, alloys, pesticides, radiation prevention material, PVC pipes, cable covers etc (Bytyçi *et al*., 2018). The concentrations of Cr within the months of analysis varied between 0.110 and 0.176 mg/L in the stations. The mean level of Cr within this period was 1.139**±**0.03 mg/L. These values were all higher than the WHO stipulated maximum value for Cr in portable water. The values observed for Cr in the present work is either within the values or lower than those of Syed and Naushad, (2014) in Allahabad river basin in India, but higher than those of Bytyçi.*et al*., (2018) in Lepenci River Basin, Kosova, but lower than the values obtained by Edori and Kpee (2018) in effluent contaminated points along the New Calabar River. Chromium (Cr) is an indispensable micronutrient for animals and plants, but has dual significance in the environment, both as a biological important element and as a pollutant in the environment at higher than required concentrations (Rajappa *et al*., 2010). Normally, the concentration of Cr in the natural environment that has not been interfered with by human activities is very low except when geological conditions of the rock types may be rich in Cr deposits. At high level of Cr, it has been found to affect fishes but the effect in most cases does not lead to death of the fishes affected. High concentration of Cr in the environment is the resultant effect of industrial and mining discharges (Krishna *et al*., 2014). The concentrations of Ag in the water samples from the Elelenwo River ranged from1.03-1.33 mg/L. The mean value for Ag within the period of analysis was 1.170±0.10 mg/L. The values observed in the stations within the period were all higher than the 0.05 mg/L WHO limit for drinking water. The dissolution of silver in water is through a complex formation process with chloride ions and organic material (Whitlow and Rice, 1985).In an environment, Ag naturally exist as insoluble and immobile oxides, sulfides and some salts. The WHO guiding standard for domestic water do not stress any specific concentration of silver that may be toxic to consumers and values of Ag as high as 0.1 mg/L do not pose any health risk to human health (WHO, 2004). In situations of immediate need for portable water, Ag is infused with water to prevent bacterial growth (Jennings, 2010). Ag is not common in the earth's crust. Silver (Ag) is a component of photographic plate, coins, jewelleries, silver plating, mirrors, dental materials and electronic equipment, by-product of mining for Pb, Zn, Cu and Au (CCREM 1987; USEPA, 1987). Silver (Ag) occurs in aqueous systems principally as monovalent element, Ag^{+}. The toxic effect of Ag is manifested when it is in the +1 oxidation state but when other environmental factors change the concentration of the +1 state, it toxicity is compromised (Hogstrand and Wood, 1998; NSW EPA, 2000). In freshwater fish, Ag seems to impair the gills. The observed concentrations of Ni in the Elelenwo River ranged from 0.168 - 0.195 mg/L. The mean value for the months was 0.18±0.01 mg/L. These values observed in the stations within the months were higher than the WHO requirement for drinking water. The observed values in this work are higher than those of Okegye and Gajere, (2015) in river water from Udege, North Central Nigeria and those of Aghoghovwia *et al*. (2018) in River Nun, Bayelsa State, Nigeria. Nickel (Ni) sources in the environment can either be natural or of anthropogenic input sources. In natural aquatic environments, Ni is usually present as $Ni(H_2O)_6^{2+}$ complex (WHO, 2007). Nickel (Ni) undergoes translocation from one point to the other in rivers by adhering to particles which are associated with organic matter and have the capacity to readily accumulate in biological organisms such as aquatic plants e.g phytoplankton (Cempel and Nikel, 2006). The presence of Ni in water is toxicologically lethal to plant life even at very low concentrations as 500 µg/L (USEPA, 1976) and its capacity as possible carcinogens to animals and humans is known but without adequate information on the mechanism of it carcinogenicity (Cempel and Nikel, 2006). The concentrations of Fe in the present work varied from 5.16-7.35 mg/Kg in the examined months with an average value of 5.907±1.01 mg/L. The concentrations of Fe in the present work are higher than the WHO value for drinking water. The observed concentrations of Fe in the surface water of the Elelenwo River is higher than the observed values of Fe in Silver River, Bayelsa State, Nigeria (Ekpete *et al*., 2019) and those of Aghoghovwia *et al*. (2018) in River Nun, Bayelsa State, Nigeria, but lower than the values obtained in rivers in Penang,Malaysia (Alsaffar *et al*., 2016).The importance of Fe as a metal lie in the fact that it is very essential in human biochemical functions. Despite the numerous enzyme enhancing activities that is facilitated by the presence of Fe, it is also a poison at very high concentrations in human tissues. The very high values of Fe observed in the present work will constitute toxicity if taken in by humans (Abbaspour *et al*., 2014). In fish gills, Fe is known to be deposited as Fe^{3+}oxide, which damages or reduces the uptake of oxygen through the gills (Ogaga *et al*., 2018) thus disrupting normal respiratory processes of the animal concerned. One major benefit of Fe to man is the formation of some biomolecules and hemoglobins thereby activating the natural functions of the blood. The existence of different forms or oxidation states of Fe has been established as Fe^{2+} or Fe^{3+}. The two different forms possess different stability and solubility which then determines the rate of absorption of the different species into organism tissues (Sundaray *et al*., 2012; Acton, 2013). The values or concentrations of As in this study were not detected in any of the samples within the months of investigation in the Elelenwo River. This observation agrees with the observation of Sabbir *et al.* (2018) in water of Rupsha River, Bangladesh, where As was not detected in surface water, but disagrees with the observation of Mortuza and Al-Misned, (2017) in surface water from Red Sea coast of Saudi Arabia and the observation of Gafur *et al*., (2018) in water of Bone River, Indonesia. In each of the referenced work above, the authors emphasized that the As sources originated from quarrying activities within the area, which may have transferred As to the water. The undetected nature of As in the present work can be attributed to absence of As in the rock formation and in the different effluent types discharged into the river by the different industries within the area. The concentrations of Zn in the surface water from the Elelenwo River varied between 1.07 and 2.74 mg/L within the months in the various stations. The mean value of Zn as observed within the period was 1.777±0.696 mg/L. The observed values were lower than the WHO recommended value for Zn which is 5.0 mg/L. The values observed for Zn in the water were higher than the values obtained by Asonye *et al*. (2007) in selected rivers within southern Nigeria and those of N'garam *et al*., (2017) in water from Chari River, Chad. The major input sources of Zn into rivers as observed in this work arise from effluents from associated Industries. Zn is very indispensable to humans due to its metabolic functions for normal body and cell development.

Drinking water polluted with elevated levels of Zn could lead to abdominal irritation, nausea, despair, disorder and cough, nonetheless these effects are not permanent (Rodier, 2009)]. However, there have not been any proven harmful physiological effects when Zn is consumed at concentrations beyond 5 mg/L, but at higher levels, it has been observed to introduce bitter taste to water and opalescence in high pH drinking water (N'garam *et al*., 2017).

The concentrations of Cu in Elelenwo River within the different stations within the months of analysis varied from 0.674 - 0.844 mg/L. The mean concentration within the period was 0.781±0.069 mg/L. The values obtained for Zn is lower than the WHO limit of 0.05 mg/L for portable water. The concentrations of Cu observed in the Elelenwo River is higher than the values obtained in water from Lepenci River Basin, Kosova (Bytyçi *et al*., 2018), but lower than the values of Cu observed in Red Sea (Mortuza and A Al-Misned, 2017). The findings of this research corroborates the observation of Rahman and Islam, (2009) that observed increased Cu presence in any river is associated with used water discharges from industries, power generating stations and homes, which were transported through runoffs to rivers. Copper (Cu) is an indispensable component of plant and animals and is naturally ubiquitous (Turnland, 1988).

In the water surroundings, Cu notably may exist in one of these forms; soluble, colloidal or particulate. In the preparation of pipes for use in tanks, Cu is prepared in the form of Cu (II) sulphate to prevent algal growth. Its toxicity to aquatic animals has been established, but, despite that its functions in enhancing the metabolic processes of many enzymes and synthesis of haem has been observed and well documented (Tirkey *et al*., 2012). Toxicity of Cu in water is dependent on the pH of the media and the concentrations of organic matter present. High content of these parameters decreases its toxicity and concentration (Tirkey *et al*., 2012).

High doses may also cause anaemia, liver and kidney damage, stomach and intestinal irritation. The concentrations of Co in the stations within the months in Elelenwo River varied from 0.535 - 0.809 mg/L. The mean concentration observed within the period was 0.672±0.109 mg/L.

The values of Co observed in the river during the period of analysis were higher than the 0.05 mg/L value of WHO for portable water. The values observed for cobalt in the present work disagrees with the observation of Lim *et al*., (2012) in water samples from Langat River, whose values ranged from 0.06 – 6.22 µg/L, and those of Mohiuddin *et al*., (2011) in Buriganga river system. In water, there are two possible oxidation states of Co that can be found. However, the +3 oxidation state is unstable, therefore quickly precipitates and adheres to the loamy fraction of sediments, hydroxides components of the sediments or phytoplankton (Campbell and Stokes, 1985).

Conclusion

The study showed that the concentrations of heavy metals in the Elelenwo River are above the required standard for human consumption in all the months of analysis except Zn, Cu and As. The observed values indicated an aquatic environment that has been influenced by anthropogenic activities. The present content of heavy metals in the water though high for most of the heavy metals, yet the input sources remained unchecked, a situation that if allowed to continue will lead to regrettable consequences in the long run or near future. Therefore, the legal aspect of the government should be put to use to cub this anticipated near future danger among the users of the river water in the area.

Authors' declaration

We declared that this study is an original research by our research team and we agree to publish it in the journal.

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