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Impacts of human activities on trace metals of Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom State, Nigeria

Nsima A. Akpan *, Rosemary B. Udombeh, Mfon B. Ukpong and Iboroakam E. Udosen

Department of Chemical Sciences, Ritman University, P.O.Box 1321, Ikot Ekpene, Akwa Ibom State, Nigeria.

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Abstract

Water, whether used for the purpose of drinking, irrigation, domestic purposes, has an important impact on health. Although pollution can occur naturally, it is the anthropogenic (man-induced) pollution that crates more problems. These activities include agriculture, fishing, sand mining, boating and a host of other activities carried out by man capable of polluting water bodies significantly (Akpan *et al.,* 2024). The assessment of impacts of human activities on levels some trace metals (Cd, Cr, Pb, Cu and As) in water samples from Qua Iboe River, Ikot Ekpene stretch, Akwa Ibom State, was carried out using atomic absorption spectrometry (AAS). The levels of trace metals obtained across the sampling locations were significantly higher in location (Afaha Ikot Ebak) with tremendous human activities and lowest at location (Uwa) with least human activities. The trend of the levels of trace metals obtained across all the sampling locations in both seasons indicated Cu > Cr > Cd > Pb > As. The levels of the trace metals obtained across the sampling locations showed significant positive relationship with levels of human activities across the sampling locations. Although the levels of all the trace metals determined were within WHO (2011) permissible limits, they were significantly higher at locations with tremendous human activities. The results of this study indicated that the studied river could be sustained for use by the present and future generations through routine monitoring to prevent escalation in levels of these pollutants beyond tolerability limits given by regulatory bodies.

Keywords: Trace metals; Levels; Analysis; River water; Qua Iboe River.

1. Introduction

Water pollution may be said to occur when toxic substances resulting in certain activities enter water bodies such as lakes, rivers, oceans and so on, getting dissolve in them, suspended in the water as colloids or deposited on the bed. This degrades the quality of water and the pollutants also seep through and reach the ground water, which might end up in our household as contaminated water we use in our daily activities, including drinking (Ayanwu, 2012; Nsi *et al.*, 2020). As man continues to advance technologically, industrially and socially, water is likely to remain the most highly polluted environment unless efficient treatment and/or recovery plants are installed in all industries and factories to remove or convert pollutants to useful items prior to discharge to bodies of water (Udosen *et al.,* 2005).

Water pollution can result in a number of ways, one of the most polluting sources being city sewage and industrial waste discharge. Indirect sources of water pollution include contaminants that enter the water supply from soils or groundwater systems and from the atmosphere via rain (Abowei and George 2010). Water pollutants include contaminants due to domestic wastes, insecticides and herbicides, food processing wastes, pollutants from livestock operations, volatile organic compounds (VOCs), trace metals, chemical wastes and others (Adefemi *et al.*, 2007).

Humans are the main cause of water pollution, which is triggered in many ways. Dumping of industrial waste; due to temperature rise that causes the attractions of water by reaching the oxygen in its composition or due to deforestation,

* Corresponding author: Nsima A. Akpan

which causes sediment and bacteria to appears under the soil and therefore contaminate groundwater. Trace metals and other chemicals find their ways into water bodies through many sources. These include natural occurring biogeochemical cycles (Ajibade, 2004).

Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom state is an important source of water for various purposes to urban and riverine communities. It flows through densely populated and farming regions. Predominant human activities within the section of the river under study with potentials to pollute the river with trace metals and other kinds of pollutants include sand mining, farming, fishing, transportation including run off from automobile workshops, domestic wastes, municipal waste dumpsites, washing, boasting etc Ikpe, *et al*., (2019). The presence of these pollutants at elevated levels in the river can affect vital fish population (Etuk *et al*., 2020). Hence there is need for quantification of these pollutants (trace metals) in the river to assess the levels of impact of human activities around the study area.

By definition, trace metals are defined as members of a subset of elements that have density above 5.0 g/cm^{-3} exhibiting metallic properties and are chemically toxic to plants and animals (Asonye *et al.,* 2007). Examples of trace metals include Cadmium (Cd), Copper (Cu) Arsenic (As), Chromium (Cr), Lead (Pb), Nickel (Ni) Vanadium (V) among others.

Aquatic ecosystem naturally contains some trace metals essential for growth of aquatic organisms but raised levels of these metals due to anthropogenic inputs of domestic, chemical and industrial wastes often dumped indiscriminately into the aquatic environment result in water pollution (Nnaji *et al.,* 2011). The increased levels of these trace metals in the rivers and lakes also affect aquatic organisms. There is a considerable concern in levels of trace metals in aquatic environment and marine organisms due to their toxicity effects particularly on man. Trace metals that are essential nutrients include Ca, Fe, Cu, Zn, etc., while those that are toxic at elevated level include Hg, Pb and Cd and are not useful at all (Udosen, 2000).

Qua Iboe River, Ikot Ekpene stretch studied, passes through an urban area highly populated where several human activities such as farming, road construction, sand mining, fishing, transportation, boasting including several automobile workshop activities are carried out. The studied river is located down gradient to residential areas around it. It is a truism that after rain the end products and after effects of these activities are usually washed into the river thereby polluting the river with all kinds of trace metals and other pollutants. Although many studies have been carried out on trace metals quantification in the studied river by other researchers, there is every need for periodic research to quantify the levels of these trace metals especially those that are toxic even at low concentrations such as Cd, Cr, Pb and As to prevent escalation in levels beyond tolerability range given by world Health Organization (WHO) as the Riverine communities depend on it for food, domestic and other purposes.

The research was carried out to determine the impacts of human activities on trace metals in water samples from Qua Iboe River, Ikot Ekpene Stretch, Akwa Ibom State, Nigeria and comparison of the levels with standards set up by UNICEF and WHO (2008) for human consumption.

2. Materials and Methods

2.1. Study Area

The study area is Qua Iboe River, Ikot Ekpene stretch, Akwa Ibom State, Nigeria. It is one of major rivers with tributaries streams that drain through Akwa Ibom State.

2.1.1. Description of sampling locations

2.1.2 Uwa (upstream): The location is in semi urban area. Around that location, inhabitants are few and they are living in isolation with least level of human activities when compared to other locations. The activities carried by the few riverine dwellers around the location include subsistence farming and fishing. The location is not susceptible to heavy load of agrochemicals due to peasant farming carried out by the riverine dwellers.

2.1.3 Nto Nsek Afaha (NNA-Midstream)

The location is an urban area and is densely populated than Uwa sampling location. Levels of human activities around the location are tremendous and include agriculture, roads construction, industrial and automobile works and the river is used for fishing, boating, washing among others. The river is also impacted by run-off from agricultural farmlands, automobile workshops and waste dumpsites.

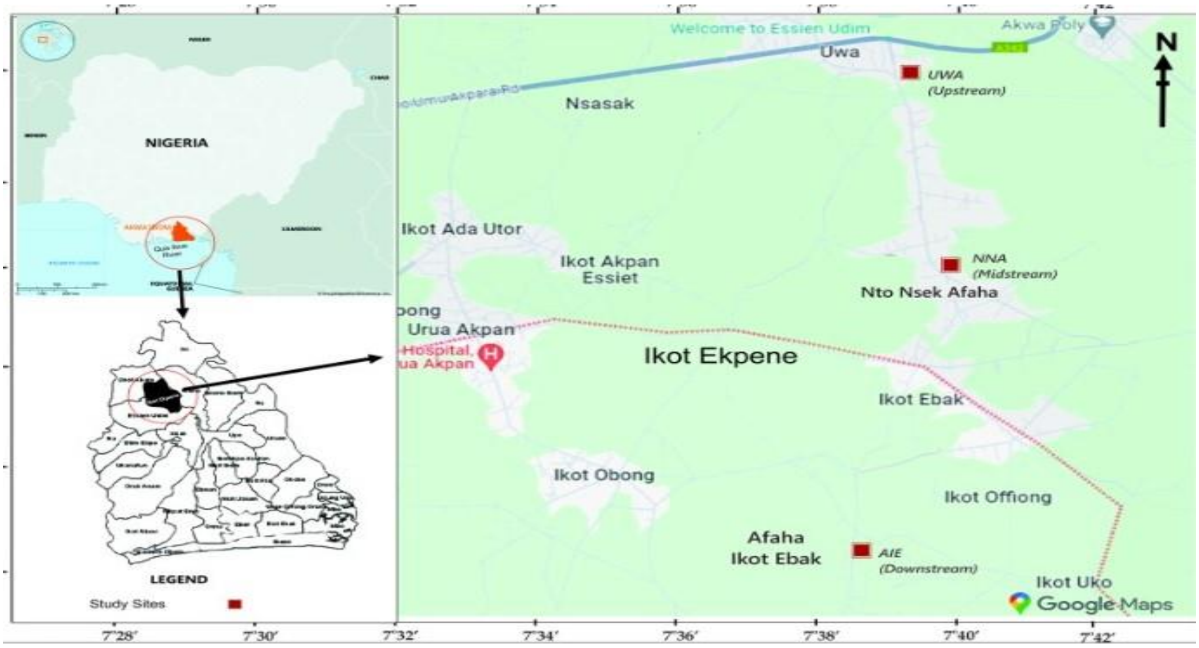

Figure 1 Study area

2.1.4 Afaha Ikot Ebak (AIE-downstream)

This location is urban area and densely populated with all kinds of human activities around it. Predominant human activities include industrial works, roads construction, agriculture, sand mining, fishing and transportation. The river is also used for washing and due to slope gradient; the location is susceptible to run-off from domestic, industrial, agricultural and automobile areas.

2.2 Samples Collection and Methods of Analysis

Sampling is an essential step in any analysis. It is one of the factors that determine the validity of the results (Udosen, *et al.,* 2005). It is essential to carry out samples collection using suitable methods and apparatus. Samples were collected from three sampling locations namely; Uwa, Nto (upstream), Nsek Afaha (midstream) and Afaha Ikot Ebak (downstream) for four months covering both wet and dry seasons. The bottles for sample collection were washed, sum dried prior to the day of collection. In the field, the bottles were pre-rinsed many times with water from the different sampling points. Water samples were collected with one litre (IL) polyethylene bottles with caps.

The samples for trace metals analysis were collected with $HN0_3$ pre-rinsed (IL) containers and 5 mL of concentric acid $HN0_3$ to a pH < 2 was added to maintain the oxidation state of the metals, to prevent the metals from adhering to inner walls of the container and to reduce microbial action

2.2.3 Determination of trace metals.

Trace metals analysed in this study were copper (Cu), cadmium (Cd), lead (Pb), Chromium (Cr) and Arsenic (As). The analysis of each parameter was performed in triplicates. Trace metals in water samples were determined using UNICAM Solar 969 Atomic Absorption Spectrometer (AAS). The water samples were filtered using suitable filter paper (filter paper No.1). The filtrate was acidified with HNO_3 (10 mL) and HCl solution (10 mL). It was evaporated to near dryness on an electric hot plate. The solution was transferred to 100 mL volumetric flash and made up to mark with distil water. A blank was also prepared the same way with the omission of the sample using deionized water (Ihenyen and Agbimien, 2002). The samples were aspirated into the AAS.

2.2.4 Determination of nitrate (NO_3^-).

Each water sample (10 mL) was transferred into different 25 mL standard flasks and 2 mL of Brucine reagent was added; then 10 mL of conc. H_2SO_4 was also added rapidly. It was mixed for about 30 seconds and allowed to stand for 5 minutes. The flasks were set in cold water for about 5 minutes and then made up to volume with deionized water. The absorbance was read at 470 nm with Unicam 8626 UV/VIS spectrometer (Ekiye and Zejiao, 2010).

2.2.5 Determining of phosphate (PO_4^{3-}).

Each water sample (25 mL) was measured into 50 mL volumetric flasks. 10 mL of vanadate-molybdate reagent was added and diluted to volume with deionized water. A reagent blank was prepared by making up 20 mL of reagent to volume in a 50 mL volumetric flask. The solutions were mixed and allowed to stand for about 10 minutes for colour development. The absorbance was read at 470 nm with Unicam 8625 UV/VIS spectrometer (Durubi *et al.,* 2007).

2.2.6 Determination of sulphate (SO_4^{2-}).

Sulphate determination was carried out as thus: Each water sample (10 mL) was measured into different 25 mL volumetric flask, 10 mL of deionized water was added. 1 mL of gelatin-$BaCl_2$ reagent was also added in each case and mixed thoroughly, made up to volume with deionized water (Asonye, *et al.,* 2007).

It was allowed to stand for about 30 minutes. The absorbance was read at 420 nm with Unicam 8625 UV/VIS spectrometer

3 Results and Discussion

The results of analysis of trace metals (Cd, Cr, Pb, As and Cu) in water samples from the three sampling locations are discussed in this section. Tables 1 and 2 show levels of trace metals obtained in water samples across the sampling locations in dry season. Tables 3 and 4 show the levels of trace metals in water samples across the three sampling locations in wet season.

Trace metals determined in this study include cadmium (Cd), Chromium (Cr), Lead (Pb), Arsenic (As) and Copper (Cu).. Results in Tables 1 and 2 representing dry season show levels of the trace metals studied across the three sampling locations.

Levels of Cadmium obtained in water samples across the three sampling locations in dry season presented in Tables 1 and 2 ranged from 1.87±0.03 - 1.95±0.05 and 1.87±0.04 to 2.01±0.41 mg/L, respectively. The levels obtained increased gradually from Uwa sampling location (upstream) to Afaha Ikot Ebak sampling location (downstream) in line with levels of human activities across the sampling locations among other causal factors. This reveals that sections of the river with higher levels of human activities are more susceptible to higher level pollution with these trace metals than section with less human activities.

Tables 1 and 2 present levels of chromium obtained from water samples across the three sampling locations in dry season, presented in Tables 1 and 2 and ranged from 0.89±0.05 to 1.52±0.02 mg/L and from 1.01±0.01 - 1.53±0.02 mg/L respectively. Chromium levels obtained follow the same trend of increase with cadmium levels obtained and were similar to levels recorded by Udosen *et al.,* (2005). The levels obtained were below maximum permissible limit recommended by regulatory bodies for drinking water.

Levels of lead obtained in water samples across the sampling locations in dry season presented in Tables 1 and 2 ranged from 2.68±0.05 - 2.80±0.05 and from 2.72±0.06 - 2.91±0.07 mg/L respectively. Levels of lead in water samples were notably observed by determination to increase also from Uwa sampling location (upstream) to Afaha Ikot Ebak (downstream). This could also be attributed to factors explained for other metals studied.

Levels of arsenic obtained in water samples across all sampling locations in dry season presented in Tables 1 and 2 below detection limit.

Levels of copper obtained in water samples across the sampling locations in dry season presented in Tables 1 and 2 ranged from 0.33±0.02 to 0.47±0.02 mg/L and from 0.35±0.05 to 0.49±0.05 mg/L respectively. Similar to results of other trace metals obtained, level of copper also increased from Uwa sampling location (upstream) to Afaha Ikot Ebak (downstream). This trend could also be attributed to variations in levels of anthropogenic activities within the study area.

Table 1 Trace metals concentration in water samples Of Qir, Ikot Ekpene Strtch In January, 2023

Metals					**Anions**				
Location	Cd	Cr	Pb	As	Cu	NO_3^-	SO_4^{2-}	PO_4^{3-}	Cl^-
Uwa	1.87±0.033	0.98±0.005	2.68±0.005	<0.00±0.005	0.33±0.002	28.44±0.04	52.93±0.01	1.17±0.02	19.88±0.05
Nto Nsek Afaha	1.90±0.04	1.43±0.010	2.77±0.004	<0.001±0.003	0.45±0.005	26.44±0.02	37.55±0.03	0.78±0.01	28.40±0.03
Afaha Ikot Ebak	1.95±0.05	1.52±0.015	2.81±0.005	<0.001±0.001	0.47±0.004	27.51±0.03	42.65±0.04	0.80±0.02	29.35±0.04

Table 2 Trace metals concentration in water samples of Qir, Ikot Ekpene Stretch In February, 2023

Metals						**Anions**			
Location	Cd	Cr	Pb	As	Cu	NO_3^-	SO_4^{2-}	PO_4^{3-}	Cl^-
Uwa	1.89±0.040	1.01±0.06	2.72±0.006	<0.00±0.004	0.35±0.003	28.54±0.005	53.01±0.01	1.21±0.82	19.84±0.05
Nto Nsek	1.95±0.05	1.52±0.010	2.82±0.004	<0.001±0.003	0.45±0.004	27.51±0.004	38.01±0.003	0.81±0.02	29.14±0.04
Afaha Ikot Ebak	2.01±0.41	1.52±0.020	2.91±0.007	<0.001±0.002	0.49±0.005	29.0±0.003	43.05±0.04	0.81±0.03	30.01±0.05

Table 3 Trace metals concentration in water samples of Qir, Ikot Ekpene For June, 2023

Metals						**Anions**			
Location	Cd	Cr	Pb	As	Cu	NO_2^-	SO_4^{2-}	PO_4^{3-}	Cl^-
Uwa	1.72±0.03	0.91±0.05	1.91±0.05	<0.00±0.05	0.22±0.02	26.11±0.04	51.01±0.01	1.05±0.01	17.34±0.05
Nto Nsek Afaha	1.73±0.02	0.92±0.05	1.92±0.05	<0.00±0.04	0.28±0.03	22.01±0.04	51.50±0.01	1.01±0.02	17.51.±0.04
Afaha Ikot Ebak	1.25±0.01	0.95±0.04	1.93±0.05	<0.00±0.04	0.24±0.03	22.50±0.03	52.40±0.01	1.09±0.03	18.01±0.03

Table 4 Trace metals concentration in water samples of Qir, Ikot Ekpene For July 2023

Metals						**Anions**			
Location	Cd	Cr	P6	AS	Cu	NO_3^-	SO_4^{2-}	PO_4^{3-}	Cl^-
Uwa	1.76±0.01	0.95±0.03	1.91±0.02	<0.00±0.00	0.21±0.01	27.50±0.02	50.01±0.01	1.10±0.01	18.01±0.02
Nto Nsek Afaha	1.78±0.02	0.92±0.03	1.92±0.01	<0.00±0.00	0.22±0.01	27.40±0.02	49.01±0.01	1.11±0.01	18.00±0.02
Afaha Ikot Ebak	1. 17±0.02	0.91±0.01	1.93±0.02	<0.00±0.00	0.20±0.02	26.11±0.01	48.56±0.01	1.12±0.01	18.05±0.02

Levels of nitrate obtained in water samples across the sampling locations in dry season presented in Tables 2 and 4 ranged from 28.44±0.04 to 27.51±0.03 and from 28.54±0.05 to 29.52±0.03 mg/L respectively. Levels recorded were similar to levels reported by Uwah *et al.,* (2013) and were below maximum permissible limits of 50 mg/L for drinking water given by Nigeria Industrial Standard.

Results of levels of sulphate obtained in water samples across the sampling locations in dry season presented in Tables 1 and 2 ranged from 52.93±0.01 to 42.63±0.04 and from 53.01±0.01 to 43.03±0.04 mg/L respectively. The levels obtained follow the same trend of increase with other trace metals studied. This could also be attributed to high level of pollution induced human activities among other factors along the coast.

Levels of phosphate obtained in water samples across the sampling locations in dry season presented in Tables 1 and 2 ranged from 1.17±0.02 - 0.80±0.02 and from 1.21±0.02 - 0.81±0.03 mg/L respectively. According to World Health Organization (WHO), levels of phosphate obtained were below maximum permissible limit of 250 mg/L.

Tables 1 and 2 show levels of chloride obtained in water samples in dry season and ranged from 19.88±0.05 to 29.35±0.04 mg/L and from 19.84±0.05 to 30.01±0.05 mg/L respectively. Chloride levels also increased from Uwa sampling location (upstream) to Afaha Ikot Ebak location (downstream) which could also be ascribed to variations in levels of human activities across the sampling locations. The levels obtained were below allowable limit of 250 mg/L recommended by WHO.

Results in Tables 3 and 4 show levels of trace metals (Cd, Cr. Pb, As and Cu) determined in surface water in wet season.

Results of levels of cadmium obtained in water samples across all sampling locations in wet season presented in Tables 3 and 4 ranged from 1.72±0.03 to 1.75±0.01 mg/L and from 1.76±0.01 to 1.77±0.02 mg/L respectively. The results show that there were no significant differences in levels across the sampling locations and seasons. In both seasons, highest levels of cadmium were obtained in Afaha Ikot Ebak (downstream) while lowest levels were recorded in Uwa location (upstream). In general, levels recorded in wet season were all below maximum permissible limits given by UNICEF/WHO (2008).

Results of Chromium levels obtained in water samples in wet season across all sampling locations presented in Tables 3 and 4 ranged from 0.91±0.05 to 0.93±0.05 mg/L and from 0.95±0.05 to 0.91±0.01 mg/L respectively. In both seasons, the levels of cadmium gradually increased from Uwa sampling location (upstream) to Afaha Ikot Ebak sampling location downstream in line with population, levels of human activities among other factors across the sampling locations.

Levels of lead obtained in water samples across sampling locations in wet season presented in Tables 3 and 4 ranged from 1.91±0.05 to 1.93±0.05 mg/L and from 1.91±0.02 to 1.93±0.02 mg/L respectively. Levels of lead obtained in this study were similar to levels reported by Udosen *et al.,* (2005). Levels of lead in both seasons showed the same trend of gradually increase from Uwa to Afaha Ikot Ebak sampling location in accordance with levels of anthropogenic activities across the sampling locations. Levels obtained in both seasons were all within safe limits recommended by regulatory bodies.

Arsenic levels determination in water samples from the study area in wet season were <0.00±0.01 across all the sampling locations. Similar levels were also obtained in dry season. In both seasons, the levels of arsenic in water samples from the study area were below detection limit.

Levels of copper obtained in water samples from the sampling location in wet season presented in Tables 3 and 4 and ranged from 0.22±0.02 to 0.24±0.03 mg/L and from 0.21±0.01 to 0.20±0.02 mg/L respectively. In both seasons, the levels of copper were below maximum permissible limits of 2.0 mg/L recommended by WHO (2011) for human consumption.

Levels of nitrate obtained in water samples from the study location in dry season presented in Tables 3 and 4 ranged from 26.11±0.04 to 27.50±0.03 mg/L and from 27.50±0.02 to 26.11±0.01 mg/L bespectively. Levels of cadmium obtained in this study were similar to levels reported by Uwah *et al.,* (2013). In both seasons, levels obtained were not significantly different and were within permissible limits given by regulatory bodies.

The levels of sulphate obtained in water samples from the sampling location in wet season presented in Tables 3 and 4 ranged from 57.01±0.01 to 52.40±0.01 mg/L and from 50.01±0.01 to 48.56±0.01 mg/L respectively. These levels obtained in both seasons were within permissible levels recommended by WHO (2011) for healthy aquatic biota and plants.

Phosphate levels obtained in water samples from the sampling locations in wet season presented in Tables 3 and 4 ranged from 1.05±0.01 to 1.09±0.03 mg/L and from 1.10±0.01 to 1.12±0.01 mg/L respectively. In both seasons, phosphate levels showed the same trend of increase from location of less human activities (Uwa) to a location of tremendous human activities (Afaha Ikot Ebak) but were all within allowable limits given by WHO (2011) to support aquatic lives.

Results of levels of chloride determination in water samples from the study area in wet season are shown in Tables 3 and 4 and indicated that the chloride levels followed the same trend of increase with other trace metals studied and were all below maximum permissible limit of 250 mg/L.

4 Conclusion

The levels of trace metals studied in water samples varied across sampling locations and seasons. With exception of arsenic which was not detected across the sampling locations, other trace metals studied showed similar trend of increase from a location less human activities to a location with tremendous human activities. Highest levels of trace metals were obtained in Afaha Ikot Ebak, a location with tremendous human activities while lowest levels were recorded in Uwa, a location with least human activities. The levels of trace metals obtained in water samples showed positive relationship with levels of human activities across the sampling locations in the study area. The levels of the trace metals obtained in water samples from the river studied were higher in locations with tremendous human activities though were all below maximum permissible limits set by WHO (2011).

Compliance with ethical standards

Disclosure of Conflict of Interest

The author has no conflict of interest in this research.

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