University of Tehran Press

Pollution

Print ISSN: 2383-451X
Online ISSN: 2383-4501

https://jpoll.ut.ac.ir/

Ecological and Health Risk Assessment of Trace Metals in Waters from North-West Zone of Akwa Ibom State, Nigeria

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Article Info

Article type:
Research Article

Article history:
Received: 19.07.2022
Revised: 04.10.2022
Accepted: 27.11.2022

Keywords:
Trace metals
Pollution indices
Humans
Health risk
Assessment

ABSTRACT

Metals contamination in water is becoming a threat to human health. The studies ecological and health risk assessment of trace metals was conducted in seven water bodies in Akwa Ibom State, between May 2021 and April 2022 (twelve months), to evaluate the levels of trace metals contaminant and suitability of the waters for human consumption. Six trace metals were assessed in the water samples; using atomic absorption spectrophotometer after digestion. Pollution indices such as heavy metal pollution index, comprehensive pollution index, contamination index and health risk assessment for non-carcinogenic were employed. The findings were compared with Nigerian Standard for Drinking Water Quality. The mean concentration of some metals (Pb, Cd, Cr, and Cu) in some stations were exceeded the standard limits, while Fe and Ni exceeded the acceptable limits in all the stations, due to anthropogenic activities. The values for HPI in stations I, II, IV and VII were exceeded the threshold of 100, ranging between 61.4 and 743.5; CPI ranged from 1.05 to 3.72, while Cd ranged from 0.94 to 16.3, indicated that the water bodies are highly contaminated. The CDI and HQ values for Fe, Cd, Cr and Cu exceeded the oral toxicity reference dosage of contaminant and stipulated threshold (1) for HI in some stations both in children and adult, indicated that the water bodies are not suitable for human consumption. The findings call for concern regarding their effects on human health, which could be detrimental to the people drinking from these water.

Cite this article: Effiong Jonah, U., Friday Mendie, C., & Gregory Asuq, U. (2023). *Ecological and Health Risk Assessment of Trace Metals in Waters from North-West Zone of Akwa Ibom State, Nigeria.* Pollution, 9(1): 271-285. http//doi.org/10.22059/poll.2022.345817.1538

 Publisher: University of Tehran Press.
DOI: http//doi.org/10.22059/poll.2022.345817.1538

INTRODUCTION

Water has always been the most important component of the earth. It is essential in the sustenance of life (Howladar et al., 2021). Streams are sources of water for the domestic and other uses for rural community dwellers. Anthropogenic activities such as sand mining, extraction of mineral resources, agricultural activities, and couple with increased in human population, urbanization and industrialization usually imposed toxic pollutants into the water body including trace metals, which may turn become a threat to the environment and aquatic organisms (Wieczorek- Dabrowska et al., 2013; Nasrabadi et al., 2016; Hashem et al., 2017; Slaveykova & Cheloni, 2018 & Okoro et al., 2020). Trace metals contamination in aquatic system is one of the major quality issues in many fast growing cities, because maintenance of water quality, sanitation did not increased along with population and urbanization growth (Karbassi

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et al., 2007; Akoto et al., 2008; Reza & Singh, 2010 & Ahmed et al., 2010). Studies reported that the greater concentrations of trace metals in aquatic environment are linked with anthropogenic activities and surface run-offs (Singh, 2007; Obaroh et al., 2012; Nasrabadi et al., 2016 & Okon et al., 2019). About 1.5 billion of people in the world are suffering from drinking of metals contaminated water (WHO, 2017). Acute exposure to metallic pollutants have been reported associated with various health challenges such Cardiovascular, Kidney, and Bone diseases (Reilly, 1991; Sanchez-Castillo et al., 1998; Steenland & Boffetta, 2000). Human exposure to lead toxicity is known to cause constipation and anemia (Bolger et al., 2000), while in children, it causes noxiousness and dysfunction of central nervous system. Higher exposure to Nickel could leads to hypoglycemia, asthma, nausea, headache and epidemiological symptoms like cancer of nasal cavity and lungs (Rattan et al., 2005). Trace metals pollutants have turn into an attractive issue in the world because of its high diligences toxic and carcinogenic character (Sengupta & Agrahari, 2017) and persistency in the environment with ability to accumulate in the biota (Morillo et al., 2002; Baghvand et al., 2010; Rajaei et al., 2012 & Ali et al., 2019), which more attention should be given. Water quality and its suitability for drinking purpose can be examined by determining its quality index (Mohan et al., 1996; Prasad & Kumari, 2008; Prasad & Mondal, 2008). However, several published research studies have employed the use of pollution indices and health risk assessment approach to interprets the overall quality of water in respect of trace metals pollution (Agneta et al., 2006; Muhammed et al., 2011; Liu et al., 2012; Ekere et al., 2014; Moses & Etuk, 2015; Nasrabadi, 2015; Majhi and Biswal, 206; Balakrishnan & Ramu, 2016; Onyele & Anyanwu, 2018; Dibofori-Orji et al., 2019; Anyanwu and Umeham, 2020b; Anyanwu et al., 2020). Therefore, the study of ecological and health risk assessment of trace metals in waters from North-West zone of Akwa Ibom State will help to understand the overall water quality status in respect of trace metals contamination. The selected water bodies are subjected to various anthropogenic activities, and they served as the only source of water for irrigation and drinking for the nearby communities. Hence, this study seeks to evaluate the concentrations of some trace metals and associated health risk of waters from north-west zone of Akwa Ibom State, Nigeria vis-à-vis its suitability for human consumption.

MATERIALS AND METHODS

The study was conducted within the north-west district of Akwa Ibom State, south-south geopolitical zone of Nigeria (Figure 1). The area covered about 6,858km^2 lands mass, with an estimated population of 5,482,200 million, 799.3/km^2 population density (NPCN, 2016). The region is characterized by tropical humid climate with distinct dry season (November - March) and wet season (April - October), with a mean annual rainfall of 2200mm. The region experience rapid urbanization, industrialization and agricultural activities. For the purpose of this study, seven (7) freshwater bodies were selected based on the level of perturbation by anthropogenic activities and geo-morphological features of the area. The freshwater bodies are within low land area where runoffs from communities are high, and receive wastes from different anthropogenic sources. The location and geo-coordinates of the stations are presented in Table 1. The anthropogenic activities observed during the study period in station I, II and VII were bathing, intense agricultural activities, domestic waste discharge and laundering. The inhabitants of the area and other nearby villages always extract water from this station for domestic uses, including drinking. Station 1 received effluents from oil mile factory near the water body. Intense sand mining, farming, bathing and domestic waste disposal were observed in station III, IV and V. Station III, IV and V received waste from municipal run-off, while station VI constantly received waste from the nearby settlement directly and indirectly, municipal and urban run-off.

Water samples for the trace metals evaluation were collected between May 2021 and April 2022 with 500mL polyethylene bottles and acidified with Nitric acid (HNO_3) immediately after

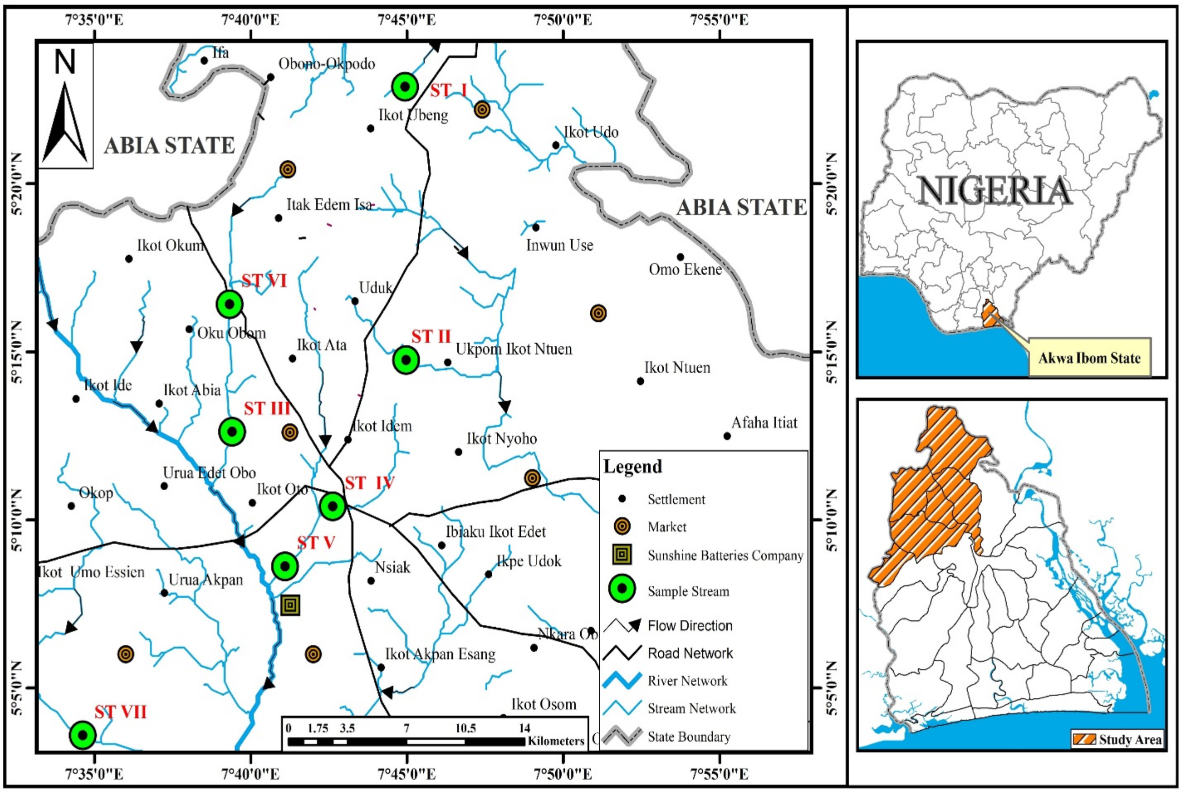

Fig. 1. Map of Nigeria indicating Akwa Ibom State with reference to the study area

Table 1. Details of surface water sampling location along with their longitude and latitude

Stations	Location	Co-coordinates
I	Ini Local Government Area.	Latitude 5.3732; Longitude 7.75742
II	Ikono Local Government Area	Latitude 5.2461; Longitude 7.74946
III	Ikot Ekpene Local Government Area	Latitude 5.2105; Longitude 7.65677
IV	Ikot EkpeneLocal Government Area	Latitude 5.1735; Longitude 7.71045
V	Essien UdimLocal Government Area	Latitude 5.1438; Longitude 7.68498
VI	Obot AkaraLocal Government Area	Latitude 5.2737; Longitude 7.65546
VII	Ika Local Government Area	Latitude:5.0600; Longitude 7.57713

collection. The water samples were digested as described by Akan et al. (2009) and Moses & Etuk (2015) using concentrated Nitric acid and heavy metals concentration in each water sample were determined with atomic absorption spectrophotometer (UNICAM 939/959 model). All data were summarized in Microsoft excel and subjected to statistically analysis using single factor ANOVA, while Tukey Pairwise Posthoc was used to compare the means between the stations with significant difference set at $P<0.05$.

The analyzed trace metals were subjected to ecological risk assessment, to evaluate the impact of trace metals contaminant in the water using pollution indices (heavy metal pollution index, comprehensive pollution index and contamination index). The heavy metal pollution index (HPI) method is based on weighted arithmetic mean as described by Prasad & Bose (2001) using the formula developed by Mohan et al. (1996). The index indicates the overall quality of water in respect to trace metals contaminant (Horton, 1965 & Mohan et al., 1996). To compute HPI, unit weightage (Wi) is considered as a value inversely proportional to the recommend standard (Si) for the investigated trace metals (Prasad and Bose, 2001). The HPI was determined using the formula below:

$$\mathbf{HPI} = \frac{\sum \mathbf{Qi \times Wi}}{\sum \mathbf{Wi}} \tag{1}$$

Where, Qi is the sub-index of *i*-th parameters, while Wi is the unit weightage of the *i*-th parameters. The Qi is calculated with the equation below:

$$\mathbf{Qi = 100 \times \frac{Ci}{Si}} \tag{2}$$

Where, Ci is the mean value of *i*-th parameter and Si is the acceptable standard limit of *i*-th parameter. The acceptable limit for HPI is 100 for drinking purposes; values above 100 are not fit for consumption (Prasad and Bose, 2001). All the parameters were considered in computing HPI and the weightage (Wi) was taken as the inverse of standard permissible limit (SON 2015). The comprehensive pollution index (CP1) method employed was to evaluate the water quality for aquatic life sustainability and human consumption. The index provides vital information about the water quality for effective management and control of metal pollution. The CP1 was calculated using the formula below:

$$\mathbf{CP1} = \frac{1}{\mathbf{n}} \sum_{i=0}^{n} \mathbf{Pli} \tag{3}$$

Where, *n* is the number of considered parameters and *P1i* is the pollution index number *i*. The Pli is calculated using the equation below:

$$\mathbf{P1i} = \frac{\mathbf{Ci}}{\mathbf{Si}} \tag{4}$$

Where, *Ci* is the concentration of each parameter and *Si* is the acceptable limit of Nigerian Standard for Drinking Water Quality (SON, 2015). The values were compared with the water quality rating of CPI, where value > 0.21 is clean water, from 0.21 to 0.40 is a sub-clean water, while values from 0.41 to 1.00 is slightly polluted, between 1.01 and 2.00 is moderately polluted water, and value > 2.01 is an indication of heavy polluted water as reported by Imneisi & Aydin (2018) and Matta et al. (2018). The Contamination index (C_d) has been employed by many researchers, to evaluate the level of contamination in water body (Talalaj, 2014; Brraich & Jangu2015; Anyanwu et al., 2020; Tomasz & Dominika, 2021), using the formula developed by Backman et al. (1997). The index reveals the relative contamination of different metals separately and manifests the sum of generated components as a representative (Backman et al., 1997). The index was calculated using the equations below:

$$C_d = \sum_{i=0}^{n} C_{fi} \tag{5}$$

Where, $\mathbf{Cf_i} = \left(\frac{\mathbf{CA_i}}{\mathbf{CN_i}}\right) \mathbf{-1}$

Cfi is the contamination factor for i-th component, C_{AI} is the mean value for i-th component and C_{Ni} is the upper permissible concentration of i-th parameter, while N denotes the normative value.

Health risk assessment was carried out for non-carcinogenic for children and adults using Chronic Daily Intake (CDI), Hazard Quotient (HQ) and Hazard Index (HI) approach as described by USEPA (2011), Muhammad et al. (2011), Caylak (2012) and Naveedullah et al. (2014). The CDI of trace metals was calculated by the equation below (USEPA 2021):

$$\mathrm{CDI} = \frac{\mathrm{Cw} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{Bw} \times \mathrm{AT}} \tag{6}$$

Where, CDI is the daily doses intake of trace metal (mg/kg/day) to which consumers could be exposed to; Cw is the concentration of trace metals in the water samples (mg/L), IR represent the ingestion rate; EF is the exposure frequency; ED represent the exposure period; Bw is the body weight of the exposed person and AT represent the averaging time in days. The parameters for the evaluation of CDI are shown in Table 2. The Hazard Quotient for non-carcinogenic health risk was calculated using equation below (USEPA, 1999):

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RFD}} \tag{7}$$

Where, CDI is the daily dose intake value of trace metals (mg/kg/day) and RfD is oral toxicity reference dose of the contaminant (mg/kg/day). 1f HQ value > 1, it indicates adverse non-carcinogenic effects, while value < 1 represent acceptable level with no effect. The hazard index (HI) of the trace metals was calculated with equation below (Onyele & Anyanwu, 2018 and Moses & Etuk (2015):

$$\mathrm{HI} = \sum_{i=1}^{n} \left(HQ \right) i \tag{8}$$

Where, HI is the hazard index for the overall toxic risk and n is the total number of considered trace metals. The non-carcinogenic adverse effect can be considered to be insignificant if HI value is <1, value greater than 1 should of concern (Ayantobo et al., 2014). The HI is treated as the arithmetic sum of HQ Value (USEPA, 2011).

Table 2. Accessible parameter used for the calculation of chronic daily intake (CDI)

Parameters	Symbol	Units	Adult	Children
Ingestion rate	IR	Litre / Day	2 L	1 L
Exposure frequency	EF	Days / Years	365	365
Exposure duration	ED	Years	70	6
Body weight	BW	Kg	70.0	15.0
Average time	AT(ED ×EF)	Days	2555	2190

RESULTS AND DISCUSSION

The mean and range values of trace metals investigated and pollution index values are presented in Table 3. The mean value of all the investigated trace metals were exceeded the acceptable standard limit in some stations. Statistical analysis showed significant differences between the mean values (P <0.05). Lead (Pb) values varied between 0.001 and 0.08 mg/L; higher mean value was recorded in station IV (0.03 mg/L), while the lowest (0.002 mg/L) was recorded in stations V and VI respectively. The values recorded in stations I, III and IV were exceeded 0.01mg/L which is the standard limit set by SON (2015). The poor mental and physical retardation in children are associated with high intake Pb contaminated water (WHO, 2015). The value recorded in stations I, III and IV could suggest to runoff from contaminated soil, couple with anthropogenic activities. The mean values of Iron (Fe) showed significant variation, with higher mean value in station IV (1.42 mg/L) and the lowest was in station V (0.66 mg/L). The mean values recorded were higher when compared with the standard limit (0.3 mg/L) stipulated by SON (2015). The findings were not deviated from the reports of other studies (Asaolu & Olaofe, 2004; George & Edak, 2018; Anyanwu & Umeham, 2020a), attributed to the fact that Fe is the most abundant transition trace metal on earth (Kendrick et al., 1992). However, Zheng et al. (2003) reported that high exposure to Fe contaminated water could leads to neurological dysfunction. The elevated values recorded in stations III, IV and VI are attributed to accumulation of domestic wastes rich in Fe at the banks of the water and runoff from the underlying soil rich in Fe oxide. Nickel (Ni) values had similar trend with Fe, ranging from 0.007 to 0.09 mg/L, with the highest mean value recorded in station I (0.05 mg/L). The mean value recorded in all the stations were slightly exceeded 0.02 mg/L fixed as limit by SON (2015) for drinking water. High concentration Ni in drinking water when consume may leads to loss of hair in the body, cardiovascular, lung and kidney diseases (Salem et al., 2000). The mean values recorded were similar with the report of Jonah et al. (2015). Cadmium (Cd) had it ranged values between 0.001 and 0.09 mg/L, with higher mean value (0.03 mg/L) in station IV. The mean value recorded in stations I and IV were above the standard limit (0.003 mg/L), suggested to unregulated and intense application of pesticide and other related agrochemical at the farmland near the water body which suddenly get into the water through runoff process. The findings affirm the report of Ileperuma (2000) that high content of cadmium in aquatic ecosystem linked to agricultural activities with intense application pest control chemical in a farm near water bodies. Chromium (Cr) had it ranged values from 0.001 to 0.09 mg/L, with the highest mean value recorded in stations IV and VI (0.06 mg/L) respectively, while the lowest value of 0.001 mg/L was recorded in station II. The slightly observed value in stations IV and VI above the 0.05 mg/L recommended by SON (2015), attributed to domestic waste discharge and leaching from waste on the hinterlands during raining season. Strachan (2010) reported that kidney, liver and tissue dysfunctions could be associated with long-term exposure of chromium. Copper (Cu) is considered as an essential nutrient for human, the hazardous nature to human is when the intake is high. In children, kidney failure and brain dysfunction are associated with acute exposure to copper. The ranged values of Cu in this study is between 0.12 and 2.63 mg/L, with the highest mean values (1. 35 and 1.83 mg/L) in stations IV and II, exceeded (1.00 mg/L) recommended by Standard Organization of Nigeria. The significant values recorded in these stations may attribute to impact of precipitation and human activities around the stations.

The values of heavy metal pollution index (HPI), contamination index (Cd) and comprehensive pollution index (CPI) are shown in Table 3. The HPI values varied between the stations, ranging from 61.4 to 743.5. Station IV recorded the highest value (743.5), followed by station I (288.2), station III (166.8) and the least value of 61.4 was observed in station VI. The values recorded in some stations are greater when compared with the ranged values (25.696 to 64.286) reported by Nasrabadi (2015) from Haraz River, Iran and the 17.3504 to 54.5964 reported by Majhi and

Table 3. Summary of Trace Metal Characteristics and Pollution Index of Water from Akwa Ibom North-West Zone

Trace metals (mg/L)	Station I X±S.E.M	Station II X±S.E.M	Station III X±S.E.M	Station IV X±S.E.M	Station V X±S.E.M	Station VI X±S.E.M	Station VII X±S.E.M	SON (2015)
Lead	0.02 ± 0.00^{a}	0.005 ± 0.02^{b}	0.02 ± 0.04^{a}	0.03 ± 0.01^{a}	0.002 ± 0.03^{a}	0.009 ± 0.02^{c}	0.002 ± 0.00^{a}	0.01 mg/L
(Pb)	(0.001- 0.06)	(0.002–0.08)	(0.01 – 0.05)	(0.01 – 0.05)	(0.001 – 0.06)	(0.001 – 0.08)	(0.001–0.007)	
Iron	0.92 ± 0.36^{a}	0.76 ± 0.61^{a}	1.30 ± 0.41^{b}	1.42 ± 0.56^{b}	0.66 ± 0.16^{ab}	1.00 ± 0.36^{c}	0.78 ± 0.08^{a}	0.3 mg/L
(Fe)	(0.24 – 1.15)	(0.46-0.85)	(0.56 – 2.06)	(0.88 – 1.98)	(0.38 – 1.12)	(0.71 – 1.34)	(0.48 – 1.64)	
Nickel	0.05 ± 0.00^{a}	0.04 ± 0.01^{a}	0.03 ± 0.01^{b}	0.04 ± 0.01^{a}	0.04 ± 0.01^{a}	0.03 ± 0.02^{b}	0.04 ± 0.01^{a}	0.02 mg/L
(Ni)	(0.01- 0.08)	(0.01 - 0.09)	(0.01 – 0.08)	(0.008 – 0.06)	(0.01 – 0.08)	(0.007 – 0.05)	(0.01 – 0.09)	
Cadmium	0.01 ± 0.02^{a}	0.003 ± 0.00^{b}	0.005 ± 0.02^{b}	0.03 ± 0.01^{c}	0.003 ± 0.00^{b}	$0.001\pm0.00b^{c}$	0.004 ± 0.03^{b}	0.003 mg/L
(Cd)	(0.001 – 0.06)	(0.003 - 0.06)	(0.001 – 0.09)	(0.002 – 0.05)	(0.001 – 0.06)	(0.001 – 0.005)	(0.002 –0.009)	
Chromium	0.04 ± 0.01^{a}	0.001 ± 0.00^{b}	0.003 ± 0.02^{ab}	0.06 ± 0.04^{c}	0.02 ± 0.02^{a}	0.06 ± 0.02^{c}	0.003 ± 0.00^{ab}	0.05 mg/L
(Cr)	(0.001 – 0.08)	(0.001 – 0.02)	(0.003 – 0.08)	(0.01 – 0.09)	(0.01 – 0.04)	(0.01 – 0.08)	(0.001 – 0.04)	
Copper	0.73 ± 0.03^{a}	1.83 ± 0.05^{b}	0.63 ± 0.03^{a}	1.35 ± 0.23^{c}	0.53 ± 0.43^{a}	0.88 ± 0.30^{a}	0.75 ± 0.21^{a}	1.0 mg/L
(Cu)	(0.52 – 0.81)	(0.84- 2.36)	(0.21 – 0.88)	(0.42 – 2.63)	(0.30 – 0.94)	(0.24 – 1.18)	(0.13 – 0.78)	
HPI	**288.2**	**92.3**	**166.8**	**743.5**	**92.4**	**61.4**	**113.3**	
Cd	**6.43**	**1.85**	**4.12**	**16.3**	**3.04**	**2.12**	**0.94**	
CPI	**2.07**	**1.32**	**1.67**	**3.72**	**1.05**	**1.36**	**1.16**	

Notes: ±= standard error; means values with different superscript in the same row are significantly different ($p<0.05$)

Biswal (2016). The value recorded in station IV (743.5) is similar with the value reported by Anyanwu et al. (2022) in Ikwu River, Nigeria. According Prasad & Bose (2001), the acceptable limit for HPI is 100 for drinking water. The value recorded in stations I, III, IV and VII were greater than 100 being the acceptable limit, suggests to accumulation of metallic pollutants in the water, owing to high levels of anthropogenic activities such as indiscriminate used of heavy metal containing fertilizer and pesticides in agricultural activities at the banks of these stations (Nouri et al., 2008). The obtained value in stations II, V and VI indicate that the water are slightly polluted with respect to trace metals attributed to mining activities. The values of contamination index (Cd) ranged from 0.94 to 16.3, with the highest value recorded in station IV (16.3), while the lowest was in station VII (0.94). The value recorded across the stations indicates that the water bodies are contaminated with metallic pollutants. The value recorded in station IV (16.3) is greater than the values (1.69 to 9.85) reported by Anyanwu & Umeham (2020b) from Eme River, Nigeria, attributed it to impacts of human activities such as domestic wastes discharge, sand mining and surface runoffs from the farm around the station. The CPI recorded ranged from 1.05 to 3.72, the highest value (3.72) was recorded in station IV) and the lowest was recorded in station V (1.05). The value recorded in stations I and IV indicate high level of metallic pollution, while station II, III, V, VI and VII showed that the water bodies are moderately polluted with trace metals owing to combined effects of human activities. The elevated HPI, C_d and CPI value in station IV attributed high content of Pb, Fe, Cd, Cu and Cr due to agricultural activities, weathering of rocks and predisposed of the station to municipal runoffs.

The chronic daily intake (CDI) of the metals and oral toxicity reference dose (RfD) values are presented in Table 4, while Hazard quotient (HQ) and Hazard index (HI) values are presented in Table 5. The CDI values of Pb and Ni did not exceeded the oral reference dose (RFD) for both children and adults in all the stations, while Fe exceeded the oral reference dose (RFD) for both children and adults in all the stations. The CDI values of Pb for children ranged between 0.0002 and 0.0013 mg/kg/day, while for the adults extend from 0.0001 to 0.0008 mg/kg/day. The highest value for children (0.0013 mg/kg/day) was recorded in stations I and III, while the lowest (0.0002 mg/kg/day) was recorded in stations V and VII respectively. For the adults, highest value was in station IV (0.0008 mg/kg/day), while the lowest (0.00005 mg/kg/day) was found in stations V and VII. The CDI values of Fe for children ranged between 0.044 and 0.095 mg/kg/day. The highest value was in station IV (0.095 mg/kg/day), followed by station III (0.086 mg/kg/day). In adults, the range values were between 0.018 and 0.040 mg/kg/day, the highest was recorded in station IV, while the lowest was recorded in station V. The values recorded for both adults and children exceeded the oral reference dose (RfD) in all the stations. Similar findings were reported by Maigari et al. (2016) from Dadinkowa Dam and River Gombe Abba, Gombe state and Anyanwu et al. (2020) from Iyiakwu River, Abia state. High intake of Fe associated with genetic disorder in human (Edokpayi et al., 2016). The high values of CDI recorded in Fe attributed to high contents of Fe in the water bodies emanated from domestic waste discharge rich in Fe and runoff from the underlying soil rich in Fe oxide. Some Fe compounds could have their source in fertilizers, herbicide and pesticides use in farming within the stations. Surface runoff could transport these compounds into the water body. The Ni CDI values ranged between 0.0008 and 0.0014 mg/kg/day for adults, the lowest value was recorded in stations III and VI, while the highest was in station I. For children, the highest value of 0.0033 mg/kg/day was recorded in station I, and the lowest (0.002 mg/kg/day) was in station III and VI. Cadmium had it highest CDI value for adults in station IV (0.0008 mg/kg/day) and the lowest in station VI (0.00002 mg/kg/day), while the highest value for children was in station IV (0.002 mg/kg/day) and the lowest value (0.00006 mg/kg/day) was recorded in station VI. The values in station IV for both adult the oral toxicity reference dose RfD values of 0.0005 mg/kg/day. Cadmium pose health threat to both adult and children exposed to drinking water in station IV, while station I is for children. The higher

Table 4. Chronic Daily Intake (CDI) and Oral Toxicity Reference Dose (RfD) for Adult and Children of Water from Akwa Ibom North-West Zone

Metals	Rfd* (mg/kg/day)	Station I		Station II		Station III		Station 1V		Station V		Station VI		Station VII	
		AD	CH	AD	CH	AD	CH	AD	CH	AD	CH	AD	CH	AD	CH
Pb	0.0035	0.0005	0.0013	0.0001	0.0003	0.0005	0.0013	0.0008	0.002	0.00005	0.0002	0.0002	0.0006	0.00005	0.0002
Fe	0.007	0.026	0.062	0.022	0.050	0.037	0.086	0.040	0.095	0.018	0.044	0.028	0.066	0.022	0.052
Ni	0.2	0.0014	0.0033	0.001	0.005	0.0008	0.002	0.0011	0.003	0.0011	0.003	0.0008	0.002	0.0011	0.003
Cd	0.0005	0.0002	0.0006	0.00008	0.0002	0.0001	0.0003	0.0008	0.002	0.00008	0.0002	0.00002	0.00006	0.0001	0.0003
Cr	0.003	0.0011	0.0026	0.00002	0.00001	0.00008	0.0002	0.0017	0.004	0.0005	0.002	0.0017	0.004	0.00008	0.0002
Cu	0.037	0.020	0.048	0.052	0.002	0.018	0.042	0.038	0.09	0.015	0.035	0.025	0.058	0.021	0.05

*USEPA IRIS (2011), AD = Adult (70 years), CH =Children (6 years)

Table 5. Hazard Quotient(HQ) and Hazard Index (HI) for Adult and Children of Water from Akwa Ibom North-West Zone

Metals	Station I		Station II		Station III		Station IV		Station V		Station VI		Station VII	
	AD	**CH**	**AD**	**CH**	**AD**	**CH**	**AD**	**CH**	**AD**	**CH**	**AD**	**CH**	**AD**	**CH**
Pb	0.14	0.37	0.028	0.085	0.14	0.37	0.022	0.57	0.014	0.057	0.057	0.17	0.014	0.057
Fe	3.71	8.85	3.14	7.14	5.28	12.3	5.72	13.6	2.57	6.28	4.0	9.42	3.14	7.43
Ni	0.0007	0.016	0.005	0.025	0.004	0.01	0.005	0.015	0.005	0.015	0.004	0.01	0.005	0.015
Cd	0.4	1.2	0.16	0.4	0.2	0.6	0.6	4.0	0.16	0.4	0.04	0.12	0.2	0.6
Cr	0.36	0.86	0.006	0.0003	0.026	0.066	0.056	1.33	0.16	0.66	0.56	1.33	0.026	0.066
Cu	0.54	1.29	1.40	0.05	0.48	1.13	1.02	2.43	0.40	0.94	0.67	1.56	0.56	1.35
HI=ΣHQ	**5.15**	**12.6**	**4.74**	**7.70**	**6.13**	**14.5**	**7.43**	**21.9**	**3.30**	**8.35**	**5.33**	**12.6**	**3.95**	**9.52**

HI = Hazard index, AD = Adult (70 years), CH = Children (6 years)

CDI value of cadmium in these stations could be as a result of intense farming activities with constant used of pesticide and other related agrochemical which suddenly get into the water body by runoff process. Cadmium is toxic trace element (Mondour, 2012). Cadmium toxicity is through ingestion and chronic exposures in humans affect the kidney (Johri et al., 2010 & Unisa et al., 2011). Higher CDI value for cadmium was reported by Anyanwu et al. (2020) owing to sand mining in Iyiaku River. The CDI values of chromium for adult ranged between 0.00002 and 0.0017 mg/kg/day, while for the children were between 0.00001 and 0.0026 mg/kg/day. The highest value for adult (0.0017 mg/kg/day) was recorded in stations IV and VI, while the lowest (0.00002 mg/kg/day) was recorded in station II. For the children, the highest CDI was in station I (0.0026 mg/kg/day) and the lowest (0.00001 mg/kg/day) was recorded in station II. The values recorded for both adult and children in stations I, IV and VI and adult in station V exceeded the RfD value (0.003 mg/kg/day). The high CDI value of Cr may have linked to domestic wastes discharge and leaching from wastes on the hinterlands during raining season. Strachan (2010) reported that kidney, liver and tissue dysfunctions in human being are associated with long-term exposure of chromium. Fatemeh et al. (2016) added that high concentration of chromium when consumed leads to destruction of stomach and intestines. Chromium is considered carcinogenic and genotoxic at high concentrations (Paustenbach et al., 2003; Moffat et al., 2018 & Anyanwu et al., 2022). Cupper had it CDI values for adult ranged between 0.015 and 0.052 mg/kg/day, while children had it values between 0.002 and 0.058 mg/kg/day. The highest value for adult was recorded in station II, while the lowest was in station V. For the children, the highest value was in station IV, while the lowest was recorded in station II. The values in station I, III and VI for children and in station II and IV for adult exceeded the oral toxicity reference dose (RfD) mg/kg/day, which pose health risk to children and the adult.

The HQ values of Pb for adult ranged between 0.014 and 0.14, with higher values (0.14) in stations I, III and VII. In children, the values ranged between 0.057 and 0.57. Higher value was recorded in station IV. The HQ value greater than 1 is an indication of adverse non-carcinogenic effects, while value less than 1 is acceptable level with no effect. The Pb HQ values for both adult and children did not exceed 1. The HQ values for Fe in both adult and children exceed the threshold limit value (1). The highest value for adult and children was recorded in station IV, followed by station III, while the lowest was recorded in station V. The values recorded attributed to high concentration of Fe in the water. This could pose hazardous threat to both adult and children expose to water for drinking purpose. The HQ values of Ni for both adult and children did not exceed the threshold value (1) in all the stations. Nickel poses no health effect on the consumer of the water for drinking. The HQ value for Cd in children for stations I and IV exceed the threshold value of 1.00. The value recorded in these stations is influenced by CDI value linked to anthropogenic activities. Similar observation was reported by Anyanwu et al., (2020).

The HQ value for Cr in children in stations IV and VI exceed the threshold value of 1. The values recorded were influenced by CDI value linked to human activities and impact of precipitation in these stations. Cupper had it higher HQ values for children in stations I, III, VI and VII, while for adult include stations II and IV. The value in these stations exceeded 1, indicating adverse health effect on both children and adult exposed to drinking water from these stations.

The Hazard Index (HI) values recorded for both adult and children was higher than the threshold limit (1). Similar findings were reported by Ayantobo et al. (2014), Anyanwu et al. (2020) and Rahman et al. (2020). In this study, it generally observed that higher values of HQ and HI were recorded for children across the stations, thereby making the children more susceptible to water bone diseases. These affirm the report of Onyele & Anyanwu (2018) and Anyanwu et al., (2020).

CONCLUSION

The health risk assessment (CDI, HQ and HI) showed that the water bodies are not really good for consumption. The CDI and HQ values indicates that Fe, Cd, Cr and Cu exceeded the oral toxicity reference dosage of the contaminant and stipulated threshold (1) for HI in some stations for both children and adult, which pose serious health risk to people especially the children. The observed levels of contaminations could be influenced by human activities and seasonal influential factors. Based on the findings, the water is not recommended for human consumption. With this, awareness on the impacts of metal pollution in aquatic ecosystem, strict enforcement and monitoring of human activities within the watershed is highly recommended, Also, care should be taken to ensure strict adherent in quality monitoring to ensure that activities detrimental to water quality are restricted from taken place near water bodies; all these will help to minimize the level of metallic pollution and the adverse impacts impose on the water bodies.

ACKNOWLEDGMENTS

The authors acknowledge the contribution of the Commissioner of Science and Technology, Akwa Ibom State and Mr Utibe Michael Usanga of Department of Geography, University of Uyo, Uyo, Nigeria.

GRANT SUPPORTED DETAILS

The present research did not receive any financial support.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCE

Agneta, F. F., Annika, H., katarina, V., Margareta, W. and Wallen, M. (2006). Assessment factors-applications in health risk assessment of chemicals. Environmental Research, 104; 108-127.

Ahmed, M. K., Islam, S., Rahman, S., Haque, M. R., Islam, M. M. (2010). Heavy metals in water, sediment and some fishes of Buriganga River, Bangladesh. Int. J. Environ. Res., 4(2); 321-332.

Ali, H., Khan, E. and Ilahi, I. (2019). Review: Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity and Bioaccumulation. https://doi.org/10.1155/2019/6730305.

Akan, J. C., Abdulrahman, F. I., Ogugbuaja, V. O. and Reuben, K. D. (2009). Physico-chemical pollutants in Kano Industrial Area, Kano State, Nigeria. Journal of Applied Sciences and Environmental Sanitation, 4 (2); 89-102.

Akoto, O., Bruce, T. N., Darko. G. (2008). Heavy metals pollution profiles in streams serving the Owabi reservoir. African J. Environ. Sci. Tech., 2(11); 354-359.

Anyantobo, O. O., Awomeso, J. A., Oluwasanya, G. O., Bada, B. S. and Taiwo, A. M. (2014). Non-cancer human health risk assessment from exposure to heavy metals in surface and groundwater in IgunIjesha, Southwest Nigeria. American J. Environ. Sci., 10 (3); 301-311.

Anyanwu, E. D. and Umeham, S. N. (2020a). An index approach to heavy metal pollution assessment of Eme River, Umuahia, Nigeria. Sustainability, Agriculture, Food and Environmental Research, 8 (x).

Anyanwu, E. D. and Umeham, S. N. (2020b). Identification of water body status in Nigeria using predictive index assessment tools: a case study of Eme River, Umuuahia, Nigeria. International. Journal Energy and water resources, 4(3); 271-279.

Anyanwu, E. D., Adetunji, O. G. and Nwachukwu, E. D. (2020). Application of pollution indices and health risk assessment in the heavy metal content of a south-eastern Nigeria river. Pollution, 6 (4);

909-923.
Anyanwu, E. D., Adetunji, O. G., Nwoke, O. B. (2022). Heavy metal content of water in Ikwu River (Umuahia, Nigeria): Pollution indices and health risk assessment approach. Acta Aquatica Turcica, 18 (0); 000-000. DOI:10.22392/actaquatr.1060806.
Asaolu, S.S. and Olaofe, O. (2004). Biomagnification factors of some heavy and essential metals in sediments, fish and crayfish from Ondo state Coastal Region. Bio. Sci. Res. Commu. 16;33-39.
Backman, B., Bodis, D., Lahermo, P. and Rapant, S. (1997). Application of groundwater contamination index in Finland and Slovakia. Environmental Geology, 36 (1-2); 55-64.
Baghvand, A., Nasrabadi, T., Nabi Bidhendi, G. R., Vosoogh, A., Karbassi, A. R., Mehrdadi, N. (2010). Groundwater quality degradation of an aquifer in Iran central desert. Desalination, 260 (1-3); 264-275.
Balakrishnan, A. and Ramu, A. (2016). Evaluation of heavy metal pollution index of groundwater in and aro+und the coastal area of Guilf of Mannar Biosphere and Palk strait. Journal Advance Chemical Sciences, 2(3); 331-333.
Bolger, M., Carrington, C. Larsen, J. C. and Petersen, B. (2000). Safety evaluation of certain food additives and contaminations. Lead. WHO Food Additive Series, 44; 212-273.
Brraich, O. S. and Jangu, S. (2015). Evaluation of water quality pollution indices for heavy metal contamination in the water of Harike Wetland (Ramsar Site), India. Inter. Journal of Scientific and Research Publications, 5 (2);1-6.
Calylak, K. (2012). Health Risk Assessment for Trace Metals, Polycyclic Aromatic Hydrocarbons and Trihalomethanes in Drinking Water of Cankiri, Turkey. E-Journal of Chemistry, 9 (4); 1976-1991.
Dibofori-Orji, A. N., Ihunwo, O. C., Udo, K.S., Shahabinia, A. R., Onyema, M. O., Mmom, P.C. (2019). Spatial and temporal distribution and contamination assessment of heavy metal in Woji Creak. Environ. Res. Commun., 1:1-11.
Edokpanyi, J. N., Odiyo, J.O., Popoola, O. E. and Msagati, T. A. M. (2016). Assessment of trace metals contamination of surface water and sediment: Sustainability, 8 (135); 1-13.
Effendi, H. (2016). River water quality preliminary rapid assessment using pollution index. Procedia Environmental Sciences, 33; 562-567.
Ekere, N. R., Ihedioha, J. F., Eze, I. S., Agbazue, V. E. (2014). Health risk assessment in relation to heavy metals in water sources in rural regions of south east Nigeria. International Journal of Physical Sciences, 9 (6); 109-116.
Fatemeh, F., Amir, H. M., Yadollah, J.(2016). Carcinogenic and non-carcinogenic risk assessment of chromium in drinking water source: Birjand, Iran. Research Journal of Environmental Toxicology, 10; 166-171.
George, U.U and Edak, E. (2018). Physical and chemical variations in water quality of Imo River owing to human perturbation in the system, Researcher, 10(6);47-54.
Hashem, M. A., Nur-A-Tomal, M.S., Mondal, N. R. and Rahman, M. A. (2017). Hair burning and liming to tanneries is a source of pollution by As, Pb, Zn, Mn and Fe. Environmental Chemistry Letters, 15(3); 501-506.
Howlader, M. F., Hossain, M. N., Anjuk, K. A. and Das, D. (2021). Ecological and health risk assessment of trace metals in water collected from Haripur gas blowout area of Bangladesh. Scientific Reports, 11; 15573.
Hortion, R. K. (1965). An index system for rating water quality. Journal of the Water Pollution Control Federation, 27 (3); 300-315.
Imneisi, I. and Aydin. M. (2018). Water quality assessment for Elmali stream and Karacomak stream using the comprehensive pollution index in kastomonu, Turkey. Fresenius Environmental Bulletin, 27 (10);7031-7038.
Ileperuma, O.A. (2000). Environmental pollution in Sri Lanka: A review. Journal of the National Science Foundation of Sri Laknka, 28 (4);301-325. .
Johri, N., Jacquillet, G. and Unwin, R. (2010). Heavy metal poisoning the effects of cadmium on the kidney. Biometals, 23 (5);783-792.
Jonah, A. E., Solomon, M. M. and Ano, A.O. (2015). Assessment of the physico-chemical properties and heavy metal status of water samples from Ohii Miri River in Aia state, Nigeria. Merit Research Journal of Environmental Science and Toxicology, 3(1); 1-11
Karbassi, A. R., Nouri, J., Ayaz, G. O. (2007). Flocculation of trace metals during mixing of Talar river water with Caspian seawater. Int. J. Environ. Res., 1 (1); 66-73.

Liu, N., Zhu, Q., Qian, X., Yang, L., Dai, M., Jiang, X., Li, N., Sun, L., Liu, Z. and Lu, G. (2012). Non-carcinogenic risks induced by heavy metals in water from Chines River. Polish Journal of Environmental Studies, 21 (4); 967-972.

Maigari, A. U., Ekanem, E. O., Garba, I. H., Harami, A., Akan, J. C. (2016). Health risk assessment for exposure to some selected heavy metals via drinking water from Dadinkowa Dam and River Gombe Abba in Gombe State, Northeast Nigeria. World Journal of Analytical Chem., 4 (1); 1-5.

Majhi, A. and Biswal, S. K. (2016). Application of HPI (Heavy metal pollution index) and correlation coefficient for the assessment of ground water quality near Ash ponds of thermal power plants. Int. J. Eng. Adv. Tech., 4(8); 395 - 405.

Mandour, R. A. (2012). Human health impacts of drinking water (surface and ground) pollution Dakahlyia Governorate, Egypt. Applied Water Science, 2; 157-163.

Matta, G., Naik, P. K., Machell, J. Kumer, A. (2018). Comparative study on seasonal variation in hydro-chemical parameters of Ganga River water using comprehensive pollution index at Rishikesh, India. Desalination and Water Treatment, 118;87-95.

Moffat, I., Martinova, N., Seidel, C. and Thomson, C. M. (2018). Hexavalent Chromium in Drinking water. Journal AWWA, 110 (5); E22- E35.

Mohan, S. V., Nithila, P. and Reddy, S. J. (1996). Estimation of heavy metals in drinking water and development of heavy metal pollution index. Journal of Environmental Science and health, Part A: Toxic / Hazardous Substances and Environmental Engineering, 32 (2); 283-289.

Morillo, J., Usero, J. and Gracia, I. (2002). Partitioning of metals in sediments from the Odiel River (Spain).Environment International, 28;263-271.

Moses, E. A. and Etuk, B. A. (2015). Human health risk assessment of trace metals in water from Qua IboeRiver Estuary, Ibeno, Nigeria. J. Environ. and Occupational Science, 3 (4); 150-157.

Muhammad, S., Shah, M. T. and Khan, S. (2011). Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, Northern Pakistan. Microchemical Journal, 98; 334-343.

Nasrabadi, T. (2015). An index approach to metallic pollution in river waters. Int. J. Environ. Res., 9 (1); 385-394.

Nasrabadi, T., Ruegner, H., Sirdari, Z. Z; Schwientek, M., Grathwohi, P. (2016). Using Total Suspended Solids (TSS) and Turbidity as proxies for evaluation of metal transport in river water. Applied Geochemistry, 6; 1-9.

Naveedullah, N. Z., Chunna, Y., Hui, S. I., Dechao, D., Chaofeng, S., Liping, L. and Yinexu, C. (2014). Concentration and human health risk assessment of selected heavy metals in surface water of the Siling reservoir watershed in Zhejing Province, China. Polish Journal of Environmental Studies, 23(3); 801-811.

NPCN (2016). Bureau of Statistic. Data from Nigerian Population Commission of Nigeria, 2016.

Nouri, J., Mahvi, A. H., Jahed, G. R., Babaei, A. A. (2008). Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environ. Geo., 55(6);1337-1343.

Obaroh, I.O., Elinge, M. and Nwankwo, C. (2012). Assessment of some heavy metals and physico-chemical parameters of Jega River North Western Nigeria. International Journal Natural Science, 8;78-81.

Okoro, E.E., Okolie, A. G., Sanni, S.E. and Omeje, M. (2020). Toxicology of heavy metals to Subsurface Lithofacies and drillers during drilling of hydrocarbon wells. Scientific Reports, 10 (1); 6152.

Okon, S.U., Atakpa, E. O. and Ewa-Oboho, I. (2019). Spatial and seasonal characteristics of heavy metals in Ikpa River, Niger Delta, Nigeria. International Journal of Fisheries and Aquatic Studies, 7(2); 193-199.

Onyele, O. G. and Anyanwu, E. D. (2018). Human health risk assessment of some heavy metals in a rural spring, Southeastern Nigeria. African Journal of Environment and Natural Science Research, 1 (1); 15-25.

Paustenbach, D. J., Finley, B.L., Mowat, F. S. and Kerger, B. (2003). Human health risk and exposure assessment of chromium (VI) in tap water. J. Toxic. Environ. Health. Part A, 66 (14); 1295-1339.

Prasad, B. and Bose, J. M. (2001). Evaluation of heavy metals pollution index for surface and spring water near a limestone mining area of the lower Himalayas. Environmental Geology, 41; 183- 188.

Prasad, B. and Mondal, K. K. (2008). The impact of filling an abandoned opencast mine with fly ash on groundwater quality: A case study. Mine Water Environ. , 27 (1); 40-45.

Prasad, B. and Kumari, S. (2008). Heavy metal pollution index of groundwater of an abandoned open

cast mine filled with fly ash: A case study. Mine Water Environ. , 27 (4); 265-267.
Rahman, M. M., Bodrud-Doza, M., Muhib, M. I., Hossain, K.F.B., Sikder, M. T., Shammi, M., Akter, R., Uddin, M. K. (2020). Human health risk assessment of nitrate and trace metals v i a groundwater in central Bangladesh. Pollution, 6 (2);253-266.
Rattan, R. K., Datta, S. P., Chhonkar, P. K., Suribabu, K. and Singh, A. K. (2005). Long-term impact of irrigation with wastewater effluents on heavy metals content in soils, crops and groundwater - a case study. Agriculture, Ecosystems and Environment, 109; 310-322.
Rajaei, G., Mansouri, B., Jahantigh, H. and Hamidian, A. H. (2012). Metal concentrations in the water of ChahNimeh Reservoirs in Zabol, Iron. Bulletin of Environmental Contamination and Toxicology, 89 (3); 495-500.
Raza, R. and Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. Int. J. Environ. Sci. Tech., 7 (4); 785-792.
Reilly, C. (1991). Metal Contamination of Food. 2nd Edition. Elsevier Applied Sciences, London
Salem, H. M., Eweida, E. A., Farag, A. (2000). Heavy metals in drinking water and their environmental impact on human health. ICEHM, 542-556
Sanchez-castillo, C. P., Dewey, P. J. S., Aguirre. A. I., Lara, J. S., Vaca, R. and De Las Barra, P.L. (1998). The mineral content of mescican fruits and vegetables. Journal of Food Composition and Analysis, 11;340-356.
Sengupta, D. and Agrahari, S. (2017). Heavy metal and Radionuclide contaminant migration in the vicinity of thermal power plants: monitoring, remediation and utilization.
Singh,M.R.(2007).Impurities Heavy Metals: IR Perspective. Available from http:/www.usp.org/pdf/EN/meetings/asMeeting India/20085ession4track1.pdf.
Strachan, S. (2010). Heavy metal. Current Anaesthesia and Critical Care, 21; 44- 48.l
Steenland, K. and Boffeta, P. (2000). Lead and Cancer in Humans: Where Are We Now? American Journal of Industrial Medicine, 28; 295-299.
Slaveykova, V. I. and Cheloni, G. (2018)." preface". special issue on environmental toxicology of trace metals. Environments, 5(12); 138.
SON (2015). Nigerian Standard for Drinking Water Quality. Nigerian Industrial Standard (NIS 554-2015). Standards Organization of Nigeria (SON) Abuja, Nigeria.
Talalaj, I. (2014). Assessment of groundwater quality near the Landfill site using the modified water quality index. Environmental Monitoring Assessment. 186; 3673-3683.
Tamasz, K. and Dominika, D. (2021). The use of the contamination index and the LWPI index to assess the quality of groundwater in the area of a municipal waste landfill. Taxics, 9 (3);66
USEPA IRIS (2011). US Environmental Protection Agency's Integrated Risk Information System; Environmental Protection Agency Region 1. United States Environmental Protection Agency. Washington dc, USA.
USEPA (2006). Guidelines for carcinogenic risk assessment. EPA/630/P-03/00IF, Risk Assessment Forum. United State Environmental Protection Agency. Washington DC, USA.
Unisa, S., Jagannath, P., Dhir, V., Khandelwal, C., Sarang, L. and Roy, T. K. (2011). Population based study to estimate prevalence and determine risk factors of gallbladder diseases in the rural Gangetic basin of North India. HPB (Oxford), 13;117-125.
Wieczorek-Dabrowska, M., Tomza-Marciniak, A., Pilarczyk, B. and Balicka-Ramisz, A. (2013). ROE and Red Deer as Bioindicators of heavy metals contamination in North-Western , Chemistry and Ecology, 29 (2);100-110.
WHO (2015). World Health Organization. Water related disease; lead poisoning. Available online:**Error! Hyperlink reference not valid.**. Access on 1 May, 2021.
WHO (2017). Guidelines for drinking water quality. World Health Organization, Geneva, Switzerland. 4th Edition. 631pp.
Zheng, W., Aschner, M. and Ghers- Egea, J. F. (2003). Brain barrier system: a new frontier in metal Neurotoxicological Research. Toxicol. Appl. Pharmacol., 192 (1); 1-11.