Research Journal of Pure Science and Technology E-ISSN 2579-0536 P-ISSN 2695-2696
Vol 6. No. 1 2023 www.iiardjournals.org

Levels of Heavy Metals in Surface Water of Oge-Etche River, Etche, Rivers State, Nigeria

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DOI: 10.56201/rjpst.v6.no1.2023.pg53.65

ABSTRACT

The levels of heavy metals in surface water of Oge-Etche River, Etche, Rivers State, Nigeria was assessed. Analysis of the heavy metals was performed after due laboratory procedures with a thermo Atomic Elemental Absorption Spectrophotometer (model SE-71906). The average levels of the investigated heavy metals in the surface water of the river within the stations in the months of investigations were in the range as follows; Fe; 1.6585±0.069-3.8758±0.123mg/L, Pb; 1.7164±0.078-2.2913±0.101mg/L, Cu; 1.4271±0.068-3.7419±0.188mg/L, Cr; 4.6070±0.284-6.2551±0.241mg/L, Cd; 0.0246±0.018-1.5386±0.051mg/L, Ni; 3.0057±0.040-4.4311±0.135mg/L, and As; 0.0473±0.056-1.3072±0.063mg/L. The average occurrence of heavy metals in the stations of the river during the period of investigation were in the order Cr > Ni > Fe > Cu > Pb > Cd > As. The pollution assessment indices adopted in the evaluation of the influence of anthropogenic input on the level of heavy metals in the river using WHO maximum acceptable limit as basis were, contamination factor, pollution load index, contamination degree, and modified contamination degree. These indices indicated that the heavy metals examined have contaminated the river to a high degree and the river may not be suitable for domestic use.

Keywords: *Contamination, contamination factor, heavy metals, Oge-Etche River, pollution*

INTRODUCTION

Heavy metals stand for metallic element that has a relatively high density. Some heavy metals are toxic, poisonous or hazardous even at very low concentrations. Heavy metals are dangerous due to their propensity to bio-accumulate in tissues and organs of living creatures. The source of heavy or trace metals in the aquatic environment could be either through natural or anthropogenic impact (Aghoghovwia et al., 2015). Natural means by which heavy metals could enter the aquatic environment comprise volcanic eruption, weathering of rocks and through forest fires, while human/anthropogenic habits comprise industrial/municipal effluent release, urban storm water drift, drainages, water runoffs, leaching from waste dumpsites and refuse and inputs from countryside regions.

In Nigeria, there is the practice of direct release or discharge of sewages and other forms of wastewater into the aquatic ecosystem. This particular life pattern exhibited by the inhabitants that dwell or live along the coastline (littoral communities) has considerably affected the ecology of the shoreline, communities and organisms that make use of the affected ecosystems and has resulted in varied pollution difficulties and challenges which has brought about many environmental interventions in the country. Human activities and impact can naturally generally lead to an increase in heavy metals sources of input in the waterway systems (Sánchez-Chardi *et al*., 2007; Edori *et al*., 2019).

Leachates and discharges of agricultural substances like as fertilizers, pesticides and composts which contain heavy metals which originates from farmhouses or farmlands most frequently end up in aquatic bodies. During the process of transportation of heavy metals in the aquatic system, they can go through frequent variations or fluctuations in levels within the water environment as a result of suspension, precipitation, solubility and adsorption processes (Adebanjo and Adedeji, 2019).

In an investigation undertaken by Izonfuo and Bariweni (2001), certain anthropological activities have been acknowledged to produce water pollution. Such activities include industrialization, agriculture, mining, irrigation, and urbanization. Despite the fact that several studies on Nigerian surface waters have been embark on (Kan et al., 2007; Adeyemo et al., 2008) recently, the understanding of the biogeochemistry of heavy metals in water bodies has changed significantly in the last two decades (Martinez et al., 2006). An extra detailed comprehension of heavy metal cycle in the environment might perhaps, need information on the biochemical speciation of metals in solution, which is, the detailed physicochemical nature that are part and parcel of the whole nature or level of metal in solution.

Trace amounts of heavy metals usually exist in fresh waters originating from terrigenous foundations such as rocks' weathering which bring about the geochemical recycling developments of heavy metals within an ecological systems (Sekabira et al, 2010; Jire & Imeokparia, 2018). The effect on the environment of elements through sea sprays and haze, often transported some kilometres in land is widely documented. Mn and Cu emanating from aquatic sources have been observed in rain water sources to terrestrial settings. Also heavy metals may come into the water environments through human bases such as fossil fuel combustion, industrial and municipal discharges of wastewater and sewage, and atmospheric deposition (Idress, 2009; Jire & Imeokparia, 2018). Contamination or pollution of the water surface and subsurface through the presence of heavy metals has required the necessity to appreciate metal interfaces in the aquatic or marine environment.

Heavy metals possesses the ability to persist in the environment and remain unaffected for many years and subsequently becomes harmful and toxic to human and other living organisms (Ama *et al*., 2017). The degree of occurrence of heavy metals in any given environment are commonly affected separately by anthropological influence, inputs and precipitation. (Shomar *et al*., 2005). Heavy metals are readily linked with particulates and combine easily in the environment immediately they are released into the aquatic and littoral environments (Iwegbue *et al*., 2012). Heavy metals are poisonous to the body and can also accumulate easily in the tissues of humans mainly when they are not broken down and absorbed by the organs of the body (Nwajei and Iwegbue, 2007). The presence of heavy metals like lead, cadmium, mercury, nickel and arsenic in the human system could readily result in health difficulties and challenges in human. These metals may likely accumulate in the body organs such as the kidneys, brain and in the human immune system where they will be able to severely interrupt normal body metabolism and functioning (Dibofori-Orji & Edori, 2013; Ama et al., 2017).

MATERIALS AND METHODS

Water Sampling for Heavy Metals

Pre-rinsed plastic bottles with acid were used in the collection of water samples. The pre-rinsed acid bottles were first washed thoroughly with detergent and was rinsed with de-ionized water and was kept to dry. After which the dried plastic bottles were again rinsed with dilute nitric acid and was allowed to dry before they were used for water sampling. The pre-rinsed plastic bottles were lowered into the water at a depth range of 30-40cm and were covered beneath the water surface to prevent air from interfering with the sampled water. Nitric acid was added into the already collected water samples for the determination and analysis of heavy metals and was immediately moved to vessels packed with ice and then sent to the laboratory for pretreatment, determination and analysis.

Heavy Metals Analysis and Determination

The analysis and determination of heavy metals was performed for the samples using thermo Atomic Elemental Absorption Spectrophotometer (model SE-71906). A number of wavelengths were used for the analysis/determination of different metals which basically depends on the hollow cathode lamp type that is appropriate for that particular heavy metal to be examined or analyzed. The digested samples were aspirated directly into air–acetylene flame for each of the heavy metals to be examined or analyzed. The instrument was initially calibrated using known concentrations of heavy metals for determination (Sehgal *et al*., 2012).

Blank sample re-run was carried out after every 10 samples has been analyzed, in order that error will be reduced to a minimum level during the process of the determination and analysis of the heavy metals. This procedure is useful in checkmating the performance and effectiveness of the instrument. Each heavy metal was analyzed thrice for a specific sample and the results were indicated as mean ± standard deviation (Sehgal *et al*., 2012).

Contamination factor/pollution index

Contamination factor and Pollution index are instruments used in effectively explaining the pollution/ contamination outline of heavy metals in the environment undergoing examination. Contamination factor is a single factor index used in investigating specific heavy metals, while pollution index is an integrated evaluation index used in establishing the degree of contamination/pollution of all the heavy metals investigated.

The contamination factor method was first initiated for determining the level of heavy metals contamination of the environment by Lacatusu (2000); and it is mathematical stated thus;

Contamination Factor (CF) = Cm/Cb

The mathematical formula for pollution index (PI) is given as:

Pollution Index (PI) = n√(CF1 X CF2 X CF3 X… X CFn)

Where, CF = contamination factor, n = the number of heavy metals investigated, Cm = the level of heavy metals in the environment under consideration and Cb = the background value of the studied heavy metals or the maximum value of the heavy metal allowed within the ecosystem under investigation. In this research work WHO (2012) tolerable maximum levels of heavy metals in surface water was adopted.

The classification intervals for contamination factor and pollution index used in the interpretation of contamination factor and pollution index as used by Lacatusu (2000) is < 0.1; very slightly contaminated, 0.10-0.25; slightly contaminated, 0.26-0.5 moderately contaminated, 0.51-0.75; severely contaminated, 0.76-1.00; very severely contaminated, 1.1-2.0; slightly polluted, 2.1-4.0; moderately polluted and 4.1-8.0; severely polluted.

Degree of contamination (CD)

The degree of contamination is also a multiple evaluation index method that was proposed to describe the rundown or summation of all the contamination factors of the heavy metals investigated within an ecosystem. The idea of this model was first initiated and articulated by Hakanson (1980) to authenticate and evaluate the combined effect of contamination of the investigated environment by the number of heavy metals studied. The contamination degree is mathematically expressed as:

$$\mathrm{CD} = \sum_{i=1}^{n} C\,F$$

Where

CD = degree of contamination

CF = the contamination factor of a particular heavy metal and n = the number of heavy metals used in the research

The category interpretation adopted in validating the degree of contamination in the studied environment is CD < 8; low degree of contamination, 8 ≤ CD < 16; moderate degree of contamination, 16 ≤ CD < 32; considerable degree of contamination and CD > 32; very high degree of contamination.

Modified degree of contamination (mCD)

The modified degree of contamination index is used in evaluating the total sum of all the degree of contamination of the heavy metals examined in any given environment under investigation. It was originally stated by Hakanson (1980). The mathematical equation for calculating mCD is given as:

$$\mathrm{mCD} = \frac{1}{N}\sum_{i=1}^{N} CFI$$

Where, N = the number of heavy metals studied, i = i^{th} heavy metal (or contaminant) and
CF = the contamination factor.
The mathematical relation for modified degree of contamination (mCD) is the totaling of all the contamination factors (CF) of the different heavy metals divided by the number of heavy metals examined.
The categories for the interpretation of mCd is mCd < 1.5; nil to very low contamination degree, 1.5 ≤ mCd < 2; low contamination degree, 2 ≤ mCd < 4; moderate contamination degree, 4 ≤ mCd

<8; high contamination degree, 8 ≤ mCd < 16; very high contamination degree, 16 ≤ mCd < 32; extremely high contamination degree and mCd ≤ 32; ultra-high contamination degree.

RESULTS AND DISCUSSION

Heavy Metals Levels in Surface Water of Oge-Etche River

The levels of the different heavy metals studied in the surface water of the Oge-Etche River in the months of April, June and August are shown in Tables 1-3 and the mean monthly levels for each of the heavy metals are provided in Figure 1, while the average levels of the investigated heavy metals in the various stations of the river used in the study during the months of examination is provided in Table 4.

Table 1: Concentrations of Heavy Metals in Ego-Etche River in April

Heavy Metals (mg/L)	Stations		
	1	2	3
Fe	2.9438	3.7147	1.6343
Pb	1.6341	2.3145	2.0167
Cu	2.6742	1.3967	3.6542
Cr	5.6321	6.5389	4.432
Cd	1.6321	ND	1.5065
Ni	3.7164	4.6134	2.9569
As	0.614	1.3376	ND

Table 2: Concentrations of Heavy Metals in Ego-Etche River in June

Heavy Metals (mg/L)	Stations		
	1	2	3
Fe	2.7892	3.9006	1.5886
Pb	1.8210	2.1579	2.4113
Cu	2.7109	1.3634	4.0028
Cr	6.1028	5.9492	5.0073
Cd	1.3469	0.0321	1.6102
Ni	4.1013	4.2899	3.0051
As	0.5932	1.2191	0.0162

Table 3: Concentrations of Heavy Metals in Ego-Etche River in August

Heavy Metals (mg/L)	Stations		
	1	2	3
Fe	2.8994	4.0121	1.7525
Pb	1.6940	2.4014	2.3115
Cu	2.4686	1.5211	3.5688
Cr	6.2293	6.2773	4.3816
Cd	1.4451	0.0418	1.4992
Ni	3.6925	4.3899	3.0551

As	0.6885	1.3649	0.1256

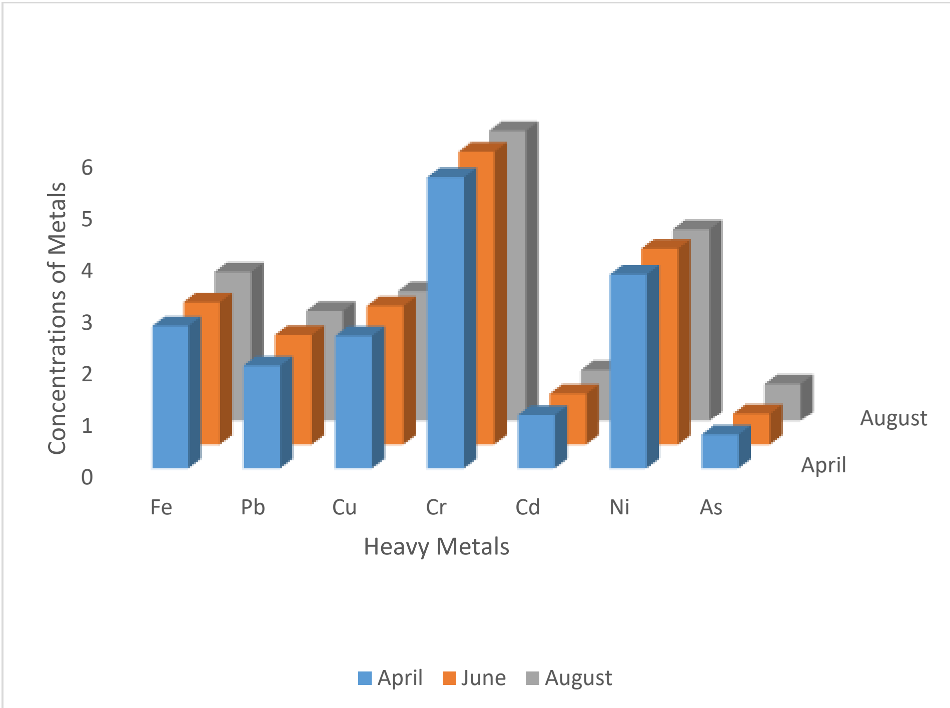

Figure 1: Mean Variations of Heavy Metals' Concentrations in Ego-Etche River within the Months under Investigation

Table 4: Mean Concentrations of Heavy Metals in Ego-Etche River in the Months

Heavy Metals (mg/L)	Stations			WHO Limit (mg/L) (2012)
	1	2	3	
Fe	2.8775±0.065	3.8758±0.123	1.6585±0.069	0.3
Pb	1.7164±0.078	2.2913±0.101	2.2465±0.168	0.025
Cu	2.6179±0.107	1.4271±0.068	3.7419±0.188	2.0
Cr	5.9881±0.257	6.2551±0.241	4.6070±0.284	0.05
Cd	1.4747±0.118	0.0246±0.018	1.5386±0.051	0.005
Ni	3.8367±0.187	4.4311±0.135	3.0057±0.040	0.02
As	0.6319±0.041	1.3072±0.063	0.0473±0.056	0.01

Iron (Fe)

The mean level of iron (Fe) recorded in the surface water of the river within the stations in this research ranged from 1.6585±0.069 to 3.8758±0.123mg/L. The mean level of iron (Fe) recorded for the various stations of the river during the time of the investigation was far above the acceptable limit of 0.3mg/L by WHO (2012) for potable water. The results obtained for Fe in this investigation were higher than that which was recorded in the work of Ekeanyanwu et al. (2010) in the surface water of Okumeshi River, Delta State, Nigeria. Fe is an important constituent of the blood, and it is a major factor responsible for the colour of blood (Edori & Kpee 2018). At levels above 0.03mg/L, it produces taste and colour in water (Iyama *et al*., 2014).

Lead (Pb)

The mean level of lead (Pb) obtained in the surface water from the various stations of the river in this investigation ranged from 1.7164±0.078 to 2.2913±0.101mg/L. The mean levels of lead (Pb) recorded for the various stations of the river at the time of this investigation was far higher than the tolerable limit of 0.025mg/L by WHO (2012), for potable water. The degree of occurrence of Pb obtained in this study was higher than that which was obtained in the work of Iwegbue et al. (2012) in the Orogodo River during the dry and wet seasons and that which was obtained in effluents discharged into Ekerekana River by the petrochemical industry (Marcus and Edori, 2017). Lead (Pb) is a metal that is hazardous to both plants and animals at any given level. It is a well-known poisonous substance or toxicant even at very low levels or concentrations (Edori & Edori, 2012).

Copper (Cu)

The mean levels of copper (Cu) observed in the investigated stations of the Oge-Etche River in this research ranged from 1.4271±0.068 to 3.7419±0.188mg/L. The mean levels of copper (Cu) recorded for the various stations of the river during the period this research was conducted was either higher or below the limit of 2.0mg/L which is acceptable by WHO (2012) for potable water and other domestic usage. The levels of Cu obtained in this research were higher than those reported in the work of Nwoke and Edori (2020) in boreholes within five communities in Ikono, Akwa Ibom State, Nigeria and that of Faanu et al. (2011) in water near gold mining areas in Ghana. Copper is known to vital in foetus formation, human immune system building, brain development, message transmission by neurons and antioxidative properties (Edori & Kpee, 2016).

Chromium (Cr)

The mean results obtained for the levels of chromium (Cr) in the surface water of the various stations of the river ranged from 4.6070±0.284 to 6.2551±0.241mg/L during the period of this research. The average levels of chromium (Cr) obtained for the various stations of the river in this research was far above the WHO (2012) required tolerable limit of 0.05mg/L in water for both potable and other domestic uses. The levels of chromium observed in this work were above that reported by Nwineewii and Edem (2014) in water of Niger Delta rivers which ranged from of 0.0010 to 0.4310.0mg/L within the dry and wet seasons. Research have shown that intake of about 1-5g of “chromate” could bring about severe and acute disorders like gastrointestinal effects, convulsions, diathesis and haemorrhagic (Nwineewii & Edem, 2014).

Cadmium (Cd)

The mean levels of cadmium (Cd) recorded in the surface water in the various stations of the river in this research ranged from 0.0246±0.018 to 1.5386±0.051mg/L. The mean levels of cadmium (Cd) obtained for the various stations in the river at the time of this study was far higher than the limit of 0.005mg/L required by WHO (2012), for potable water and water for other domestic usage. The values obtained in this research was above that obtained in the work of Ama et al. (2017) and that which was recorded by Nwineewii and Edem (2014). Cadmium is poisonous even at very low concentrations**.** Cd has established carcinogenic properties and is known as one of the most dangerous elements in nature with widespread effects in humans. Cd is broadly spread in the aquatic setting and has the capability to bio-accumulate at the different trophic levels and its accumulation in the kidneys and livers of fishes is a normal occurrence (Sindayaigaya, *et al*., 1994). At high concentrations Cd attacks human organs such as the kidney and liver, but at lower concentrations, it attacks the pancreas and spleen. Cadmium is a vital element in coastal/marine monitoring investigations, this is due to its toxic effects to water inhabiting organisms.

Nickel (Ni)

The mean level of nickel (Ni) recorded in the surface water in the various stations of the river in this study ranged from 3.0057±0.040 to 4.4311±0.135mg/L. The mean level of nickel (Ni) obtained at the time of this research were far above the allowable level of nickel which is 0.02mg/L required by WHO (2012), for potable water and other household usages. The levels of Ni reported in this investigation was higher than that obtained from the Elelenwo River (Edori *et al*., 2019) and that reported by Okegye and Gajere, (2015) in river water from Udege, North Central Nigeria and also that which was recorded by Aghoghovwia et al. (2018) in River Nun, Bayelsa State, Nigeria. In natural marine ecosystem, Ni normally occur as Ni $(H2O)_6^{2+}$ complex (WHO, 2007). Nickel (Ni) frequently undergo translocation from one part of the river to the other and attach on to particles that are linked with organic substances and has the ability to bio-accumulate in living creatures suach as phytoplankton (Edori *et al*., 2019).

Arsenic (As)

The mean level of arsenic (As) recorded in the surface water in the various stations of the river ranged from 0.0473±0.056 to 1.3072±0.063mg/L. The mean value of arsenic (As) obtained during the time this research was undertaken were far above higher the recommended appropriate limit of arsenic which is 0.01mg/L acceptable by WHO (2012), in potable water and also for other household usages. The values obtained in this work were higher than that which was reported by Nwoke and Edori (2020) in boreholes from five communities in Ikono Local Government Area, Akwa Ibom State, Nigeria. Arsenic is an environmental pollutant which has high toxicity. It usually occur in the +5 and +3 oxidation states and is could be easily absorbed into the gastrointestinal walls tracts (Smith and Steinmaus, 2007). Peripheral neuropathy, peripheral vascular disease, hypo and hyper pigmentation are notable signs of arsenic toxicity that affects children and adults and could also retard intellectual development in children. The effects of arsenic poisoning could bring about skin lesion and stigmatization which can potentially ruin the life of an individual at the developmental periods which could also eventually upset the life and wellbeing of a whole family (UNICEF, 2013).

Pollution Indices of Heavy Metals Pollution in Oge-Etche River

Contamination factor

The contamination factor of the studied heavy metals in the surface water of Oge-Etche River is shown in Table 5.

Table 5: Contamination Factor (CF) Analysis of Heavy Metals in Water Samples of the Oge-Etche River

Heavy metals	Sample Locations		
	1	2	3
Fe	9.5917	12.9193	5.5283
Pb	68.6600	91.6520	89.8600
Cu	1.3090	0.7136	1.8710
Cr	119.7620	125.1020	92.1400
Cd	294.9400	4.9200	307.7200
Ni	191.8350	221.5550	150.2850
As	63.1900	130.7200	4.7300

Table 5 provides the contamination factors of the heavy metals investigated in the surface water of Oge-Etche River**.** The results recorded indicated that contamination factors in stations ranged between Fe; 5.5283-12.9193, Pb; 68.6600-91.6520, Cu; 0.7136-1.8710, Cr; 92.1400-125.1020, Cd; 4.9200-307.7200, Ni; 150.2850-221.5550 and As; 4.7300-130.7200. Application of the category of classification originated by Hakanson (1980) revealed that the surface water of Oge-Etche River has been polluted severely by all the investigated heavy metals in all the stations of the river. The degree of contamination and pollution by the investigated heavy metals in the various stations of the river could be as a result of human activities such as sand mining in farmland close to the river which is widespread within the Etche axis of Rivers State and has been possibly washed into the river. There is also the possibility that the geologic composition of the studied heavy metals is high in the adjoining farmlands and are constantly being drained to the river through runoffs due to exposure to the soil surface.

Pollution Load Index, Contamination Degree and Modified Contamination Degree

The pollution load index, contamination degree and the modified contamination degree of the examined heavy metals in the surface water of Oge-Etche River are provided in Tables 3.

Table 6: Pollution Index (PLI), Contamination Degree (CD) and Modified Contamination Degree (mCD) Water Samples from the Oge-Etche River

Assessment Index	Sample Locations		
	1	2	3
PLI	72154.4788	23353.7966	24092.9214
CD	743.2877	587.5819	652.1343
mCD	107.0411	83.9403	93.1620

Pollution Load Index (PLI)

The results obtained for pollution load index in the surface water of various stations of the Oge-Etche River were in the order 1 > 3 > 2. The pollution load index were, 72154.4788, 23353.7966 and 24092.9214, for Stations 1, 2 and 3 respectively. Application of classification interval for pollution load index showed that the surface water of the river at the time of study was at a very severe pollution level by the heavy metals used in the study. The recorded values for the surface water in the river were far above the interval, 4.1-8.0 which stand for severe pollution. The values recorded for PLI for the river indicated that the level of pollution caused by the heavy metals investigated have come to a stage that was alarming and therefore necessary measures should be taken to mitigate any possible future effect**.**

Contamination Degree (CD)

The results recorded for the contamination degree for the surface water in the different stations of the Oge-Etche River were in the order 1 > 3 > 2. The contamination degree were, 746.2871, 587.5819 and 652.1343, for Stations 1, 2 and 3 respectively. Application of classification interval for contamination degree showed that the surface water of the river is at the level of very high contamination degree by the heavy metals used in the study. The values recorded in the river were far above the interval, CD > 32 which stand for very high contamination level by studied heavy metals.

Modified Contamination Degree (mCD)

The results obtained for the modified contamination degree in the surface water of the Oge-Etche River within the stations used for the study were in the order 1 > 3 > 2. The recorded results were 107.0411, 83.9403 and 93.1620 for Stations 1, 2 and 3 respectively. The application of classification interval for the interpretation of modified contamination degree in the river indicated that the river was at the level of Ultra-high degree of contamination by the studied heavy metals. The results recorded in all the stations of the river used in the investigation were far above than the level of classification of mCd ≤ 32 which stands for Ultra-high contamination level or degree.

CONCLUSION

The levels of the studied heavy metals (Fe, Pb, Cu, Cr, Cd, Ni and As) in the Oge-Etche River, Etche, Rivers State Nigeria indicated high degree of contamination. The results obtained for heavy metals in water samples of the river used for the study in this research indicated that all the studied heavy metals in the river were far higher than the value acceptable by WHO for portable water and that for domestic purposes. Analysis of contamination indices indicated that the surface water of the river has been utterly contaminated by the various heavy metals used in the study. Government agencies and other relevant bodies should henceforth introduce measures or laws that will control certain anthropogenic activities like sand mining in the agricultural farmlands and oil exploration/exploitation close to the river in Etche communities. This will likely reduce the level of heavy metals observed in the river, for if the above condition is permitted to continue, it may give rise to ill health among the dwellers along the coast and make use of the river and also affect plant and animals that inhabit the river.

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