International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Estimating the Pollution Status and Toxicity of Heavy Metals in Water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

Okwet Joseph Yawo [a], Simeon Reuben Ubulom[b], Ita Okon Akpan [c], Anthony Enemaku Amodu [d], Usenobong Benjamin Akpan [a], Emaediong Anthony Ubak [a]

[a] *Department of Physics, Akwa Ibom State University, Ikot Akpaden, Nigeria*

[b] *Department of Fishery and Aquatic Environmental Management, University of Uyo, Uyo, Akwa Ibom State, Nigeria*

[c] *Department of Physics, Faculty of Physical Sciences, University of Calabar, P.M.B, Calabar, Nigeria*

[d] *Department of Physics with Electronics, Federal Polytechnic, Idah, Kogi State*

Email: okwetyawo33@gmail.com

ABSTRACT

The pollution status and toxicity of heavy metals in water of Ukwuyok drinking stream of Okorombokho, Eastern Obolo was estimated. Three (3) water samples were obtained from different site of the stream and were conveyed to Centre for Energy and Energy Development (CERD), Obafemi Awolowo University (OAU) in Ile Ife and were subjected to Atomic Absorption spectrometric (AAS) technique. Eleven (11) heavy metals such as chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) were detected. From the results, the mean concentrations values of the heavy metals in the study area follows the ascending trend as; (0.04 ppm)<Pb(0.10ppm)<As(0.12ppm)=Cd(0.12)<Ni (0.27 ppm)<Cr (0.34 ppm)<Co (0.40 ppm)<Zn (0.78 ppm)<Cu(0.96 ppm)<Mn (1.09 ppm)<Fe (1.36 ppm). The concentration of iron (Fe) was the highest at the respective three sampled sites. Pollution indices such as enrichment factor (EF), geo-accumulation index (Igeo), contamination factor (CF), pollution load index (PLI). The mean values of MI for respective heavy metals detected follow the ascending order as Zn<Co<Cu<Pb<As<Fe<Cr<Ni<Mn<Cd<Hg and the heavy metals with MI greater one follows the increasing sequence as Pb (2.07)<As(2.33)<Fe (4.54)<Cr(6.73)<Ni(10.67)<Mn(21.80)<Cd(23.33)<Hg(86.67). This shows that that water is severely polluted with heavy metals from Pb in an increasing order to Hg. These toxicity threats could be due to runoff agricultural wastes, patches of crude oil from oil spillage, gas flare that resulted in acid rain which eventually drained into the stream and other anthropogenic processes in the study area. Appropriate authority should be monitoring the influx of wastes into this drinking stream to save the life of living organism that depends on that stream as the source of drinking water.

Keywords: Heavy metals, drinking stream, AAS, Enrichment factor (EF), geo-accumulation index (Igeo), Contamination factor (CF), metals index (MI**).**

Introduction

Water bodies in the Okoromboko community, a riverine community, are subject to a variety of environmental disturbances, ranging from anthropogenic activities like farming, poor waste management, and unhygienic practices, to natural disturbances like Nypa palm invasion and salt stress from the Atlantic Ocean. Water has been considered, the most suitable medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns, etc.). These activities have undesirable, effects on the natural environment. Also, uncontrolled land use, urbanization, deforestation, accidental (or unauthorized) release of chemical substances and discharge of untreated wastes or leaching of noxious liquids from solid waste deposits have impacted negatively on the quality of water resources (UNESCO, 2003). Continuous introduction of wastes materials into coastal bodies from agricultural produce, industrial activities such as oil spill and other anthropogenic activities constantly disrupt sediments settling and increased the concentration of heavy metals in sediments (Yawo et al., 2022). Potentially harmful heavy metals are effectively accumulated in the sediments and in certain conditions they can be readily released into water in an unpredictable way (Yawo et al., 2022; Ubulom et al., 2023).

Rivers is one of the most important freshwater resources, and most developmental activities are dependent upon them (Al Obaidy *et al.* 2015). Surface waters like lakes, rivers and streams and groundwater like springs and well waters usually serve as sources of drinking water. Rivers in a watershed play a major role in assimilating or carrying of municipal and industrial wastewater and run of from agricultural land (Wang *et al.* 2007). Industrialization is considered a necessity for the development of a country's economy, through the establishment of plants and factories (Ho *et al.* 2012). However, the waste or by-products discharged from them are destructive to the environment; contaminating the surface water, ground water and soil (Adakole 2011). The wastewaters are not safely treated because of the lack of highly efficient and economic treatment technology (Ho *et al.* 2012) and failure in institutional monitoring and control. Knowing the sources of inputs of certain heavy metals to a particular aquatic system through which their levels of concentrations rises to toxicity level is vital in addressing the extents of their contamination (Yawo et al., 2023). Pollution of natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms when permissible concentration levels are exceeded (Yawo et al., 2023; Abata et al., 2016; Ghrefat and Yusuf, 2006).

The term ‘‘heavy metals’’ refers to any metallic element that has relatively high density and applies to the group of metals and metalloids with atomic density greater than $5gcm^{-3}$ (Oves et al. 2012). Some of them are essential elements without which the biochemical processes in living organisms would not be possible; however, when they exceed normal concentrations, they become harmful to organisms (Goorzadi et al. 2009; Bytyçi et al. 2018). The entry of these contaminants such as heavy metals into the environment can be due to human and natural activities which is the most serious issues facing most communities currently (Ubulom et al., 2022). Due to the industrial and economic growth and the production of a variety of compounds and chemicals by increased consumption, man makes some unwanted pollutants in the ecosystem which causes serious hazards to both the environment and livelihood (Eaton and Franson, 2015; Ubulom et al., 2023).

Heavy metal pollution of soil and water has become one of the main concerns of human beings recently (Namaghi et al. 2011) and is often associated with variables of concealment, persistency and irreversibility (Zhu et al. 2012). Heavy metals occur naturally in rocks, but most of the heavy metals occurrences originate from anthropogenic sources (Obaroh et al. 2012). Heavy metals may contaminate the surface water, springs and groundwater resulting in deterioration of drinking water quality. Heavy metal pollution in water can be assessed by measuring their concentrations (Senarathne and Pathiratne, 2007). About 884 million people in the world, mostly in developing countries do not have access to drinking water sources that conform to the permissible limit specification of WHO (WHO/UNICEF, 2010). The principal sources of surface and groundwater pollution by heavy metals are natural processes and anthropogenic activities like mining, disposal of effluents (Amman et al., 2002) from industries, and indiscriminate use of fertilizers and pesticides in agriculture. According to Demirbas *et al., (*2005), heavy metals are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Yawo and Akpan, 2021).

The rise in concentration of heavy metal in water of any source poses a serious health threats to human and aquatic ecosystems. Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn) are the most familiar heavy metals of health concern to human (WHO, 2008). When the concentrations of heavy metal in water surpass the environmental acceptable border, the use of such water for agricultural purposes might be detrimental to the aquatic ecosystem and human through the food chain (Wright and Welbourn, 2002). For instance, several kinds of diseases besides organ dysfunction had correlation with raised levels of heavy metal concentrations in drinking water sources above the permissible limit specified by regulatory bodies (Lenntech, 2013). Additionally, heavy metal contamination of drinking water sources has been linked with deficiencies of some essential nutrients, which culminates in compromised immunological defenses, disabilities associated with malnutrition, intrauterine growth retardation, impaired psychosocial faculties, and increased prevalence of upper gastrointestinal cancers (Arora *et al*., 2008). Although few of these heavy metals like Cu, Iron (Fe), Ni and Zn are essential nutrients required in trace amount for animals and plants; they are harmful at high levels. However, some heavy metals like Cd, Cr, Pb and cobalt (Co) have no known physiological functions and are deleterious at certain levels (Aktar et al., 2010; Kar et al., 2008). Despite the substantial contribution of small-scale mining to the economy of Akwa Ibom State and Nigeria at large since the discovery of Pb-Zn deposit in Okorombokho and its environs in the early 1900s, it has impacted negatively on the environment and health of the residents (Nnabo, 2015).

Heavy metals can be toxic in very little concentrations and usually accrue in the surrounding and later become a health risk to people. Increasing metal pollution has severely disturbed the natural ecosystem and harmed human health through food chain (Cai *et al*, 2009, Liu *et al*, 2016; Dominic et al., 2022). The entry of these contaminants such as heavy metals into the environment can be due to human and natural activities which is the most serious issues facing most communities currently **(Ubulom et al., 2023).** The concentrations of heavy metals in a particular coastal sediments sample varies irrespective of the season and time thus there is that need for regular analysis of those sediments sample so as to ascertain the rise or fall in concentrations of the heavy metals which are considered toxic substances present in them (**Ubulom et al., 2023).**

Studies have revealed the hazardous impacts of some heavy metals in the ecosystem when the intakes of such metals are high in the body of either human of aquatics being. Arsenic poisoning from naturally occurring arsenic compounds in drinking water remains a problem in many parts of the world. Residents who consumed water that had arsenic level greater than 5μg/L for ten years or longer were more likely to report a diagnosis of skin cancer, adult onset diabetes, and cardiovascular disease than age matched residents who drank water that contained no detectable arsenic (Knobeloch, 2002). It also seems to have a negative impact on reproductive processes (infant mortality and weight of newborn babies) (Hopenhayn, 2006).The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies. Arsenic is not absorbed very well through the skin. Therefore, exposure from skin contact alone, such as bathing in arsenic-contaminated water, is unlikely to cause health problems (Fact sheet, 2003). Lead is a highly toxic metal whose wide spread use has caused extensive environmental contamination and health problems in many parts of the world (Rahman, 2012). Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Not only does lead poisoning stunt a child’s growth, damage the nervous system, and cause learning disabilities, but also it is now linked to crime and anti-social behavior in children. These diseases were apparently related to contaminant drinking water with heavy metals such as Pb, Cd, Cu, Mo, Ni, and Cr (Rahman 2012).

Okorombokho is like other communities in Eastern Obolo surrounded with Rivers of different tributaries that the water is salty. This salt water is intruded to even borehole which has made most of the people residing within this locality to fully rely on a stream as their source of drinking water. This community like other communities in Eastern Obolo is endowed naturally with crude oil which eventually caused waters obtained from borehole to be unhygienic due to the float of parches of crude oil on water obtained from borehole. Other anthropogenic processes within this community among which are industrial operations, agricultural activities and incessant disposal of wastes into bushes through which pollutants can get drained into this drinking streams is so alarming. Therefore, monitoring these metals is important for safety assessment of the environment and human health which could be directly affected by intake of polluted water from stream. Thus this work is with the aim of estimating the state of pollution and toxicity of heavy metals in water of Ukwuyok drinking stream of Okorombokho with the specific objectives which are to determine concentration of heavy metals in Ukwuyok drinking stream of Okorombokho; ascertain its water quality; determine the pollution indices in that drinking stream; determine the metal index and ecological risk assessment of the above contaminants and to also ascertain the respective sources through which those heavy metals got into that stream.

2.0 MATERIALS AND METHODS

2.1 STUDY AREA

The Ukwuyok drinking stream of Okorombokho in Eastern Obolo , Southern part of Akwa Ibom State, Nigeria, has been the source of drinking water for the populace of that community and its environs for many hundreds of years now. Its water flows during raining season and remain stagnant during dry season. Water flows from other sources to the stream during raining season due to the sloppy topography of the stream and eventually flows down to Utibete Rivers. Its coordinates are n Latitude 08°47.344' N, and Longitude 007°44.063' E. The Map of the study is shown in Figure 1.

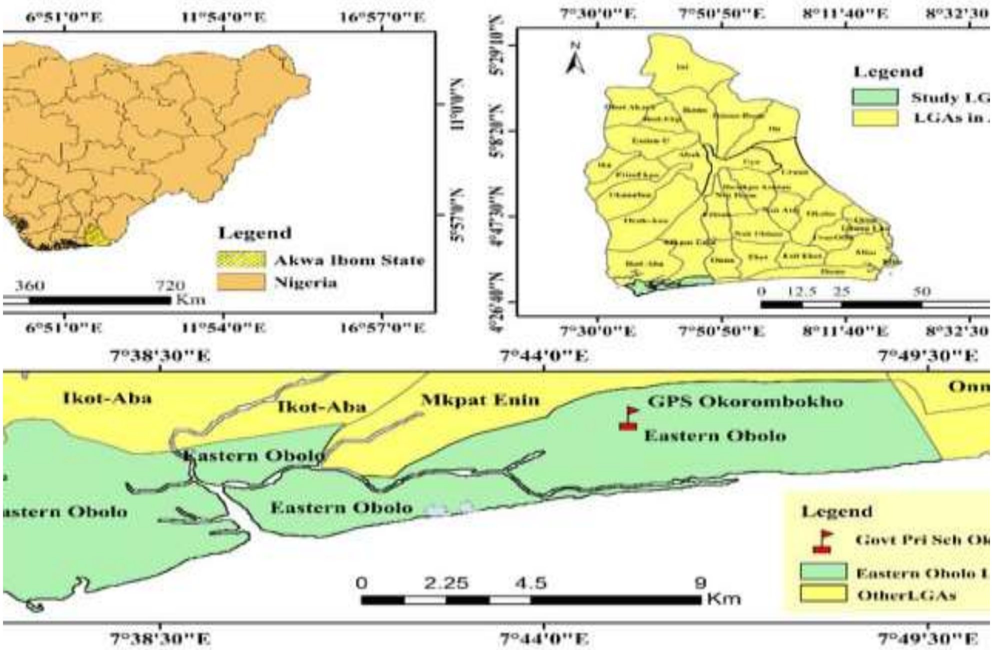

Figure.1: Map showing the sampling location

2.2 Samples Collection

Water samples were collected from the sampling sites using HDPE (high density polyethylene or polyester) bottles. The samples were collected from four (4) different points of the stream namely; upstream, midstream, downstream and the side stream within the study area. All sampling points were however geo-referenced. At every sampling point, the sampling containers were thoroughly washed with the water sample before final collection. Coordinates of the sampling location were recorded using global positioning system (GPS). The samples were put in a portable carton correctly labeled which was then conveyed to the Centre for Energy and Research Development (CERD) in Obafemi Awolowo University (OAU), Ile-Ife

2.3 Data Analysis

At the Centre for Energy Research and Development (CERD) in Obafemi Awolowo University (OAU), Ile-Ife, those samples were subjected to Atomic Absorption Spectrometric (AAS) analysis to establish the concentration of heavy metals present in them. The principle behind it is that the sample solution is evaporated and then metal ions contained are converted to free atoms (Beaty and Kerber, 1993). The atoms then absorb the emitted radiation from the lamp cathode which is the source of light and contains the elements to be determined. Atoms of various elements absorb the characteristics wavelength of lights (The Perkin-Elmer Corporation, 1996).

The intensity of light absorbed is proportional to the number of atoms in the sample. Atomic Absorption Spectrophotometer (AAS) has three basic components; light source, atomizer, and detector (The Perkin Elmer Corporation, 1996). The Hollow cathode lamp (HCL) has a tungsten anode and a cylindrical hollow cathode made with the element under study. They are enclosed in an inert medium with a glass tube. When a potential is exerted between the anode and cathode some gaseous atoms are ionized and the ions bombard the cathode hence producing some metal atoms. Some of the scattered atoms becomes excited state and emit characteristic radiation of the metal which is then concentrated into a beam of light and passed through a quartz window. The atomization of the sample occurs when the sample is aspirated into an acetylene flame. Here the sample is transformed into atoms at ground state in the vapor phase. The vaporized sample absorbs the radiation from Hollow cathode lamp (HCL). A monochromator selects the absorbed characteristic light and directs it to a detector (made of a photomultiplier tube) that emits an electric signal proportional to the intensity of light. The concentrations of those heavy metals detected were recorded and subjected to pollution models so as to determine the contamination status of those heavy metals detected.

The levels of contamination of heavy metals detected from the water of Ukwuyok drinking stream of Okorombokho were assessed by employing some pollution models such as the enrichment factor (EF), geo-accumulation index (Igeo), contamination factor (CF), metal index(MI), modified degree of contamination (mCd), Pollution load index ({PLI), potential ecological risk factor (PERF), and potential ecological risk index (PERI).

2.3.1 Enrichment factor (EF)

According to Huu et al.2010, Abata et al., 2016 and Yawo et al., 2023, "a common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the enrichment factor (EF) for metal concentration above un-contaminated background levels". "The EF normalizes the measured heavy metals content with respect to a sample reference such as Fe, Al or Zn" (Mediolla et al., 2008). Deely and Fergusson, (1994) proposed "Fe as an acceptable normalization element to be used in the calculation of the enrichment factor since they considered the Fe distribution was not related to other heavy metals (Abrahim and Parker, 2008). "Fe usually has a relatively high natural concentration, and is therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments (Niencheski et al., 1994). "A wide range of studies have used Fe and Al normalisation as an alternative to grain size normalisation (Bruland et al., 1974, Breslin et al., 1999,Yawo et al., 2023). Sharma et al. (1999) used "both Al and Fe to distinguish natural and anthropogenic sources in recent sediments from Texas estuaries (Abrahim and Parker, 2008,Yawo et al., 2023). "Iron (Fe) was employed in this study as the normalizing metal or reference element. The assumption was made so that the association or influence of anthropogenic sources to the atmosphere is insignificant or unimportant (Modh et al., 2015). The EF for each heavy metals was calculated to evaluate anthropogenic influences of heavy metals in water using the following formula

$$EF = \frac{\{Cm/CFe\}sample}{\{Cm/CFe\}backgrund} \qquad 1$$

Where $\{Cm/CFe\}sample$ is the ratio of concentration of heavy metals (Cm) to that of Iron (CFe) in the water sample, and $\{Cm/CFe\}background$ is the same reference ratio in the background sample. Generally, EF value of about 1 suggests that a given metal may be entirely from crustal materials or natural weathering process"(Zhang and Liu, 2002; Yawo et al., 2023) EF values in the ranges 0.5 to 1.5 suggested that the trace metals sources might be entirely from crustal materials or natural weathering process, while, EF values > 1.5 suggested that a significant portion of trace metal was delivered from non crustal materials or non natural weathering processes (Ekaete et al., 2015) and EF of 1.5 -3; 3- 5; 5 -10 and > 10 are considered the evidence of minor, moderate, severe, and very severe modification as presented by (Birch, 2003' Abata et al., 2016; Yawo et al., 2023). The values of the enrichment factor for the heavy metals in water of Ukwuyok drinking stream of Okorombokho are shown in Table 5.

2.3.2. Geo-accumulation Index (Igeo)

According to Yawo et al., (2023) a common approach to estimating the enrichment of metal concentrations above background or baseline concentrations is to calculate the geo-accumulation index (Igeo) as proposed by Müller, (1969) . "In order to assess the contamination of the examined sediment or water with organic and inorganic substances, the geo-accumulation index is utilized by comparing the control level with the current concentration of the metals (Abraham and Parker, 2008; Modh et al., 2015). "The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index" (Modh et al., 2015, Ubulom et., 2023, Yawo et al., 2023).

The geo-accumulation index (Igeo) is calculated by using the model equation:

$$I_{geo} = Log_2\{C_m/1.5B_m\} \qquad 2$$

where C_m is the concentration of the element in the enriched samples, and the B_m is the background or pristine value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Stoffers et al., 1986; Abrahim and Parker, 2008).

The Igeo descriptive classes as proposed by Muller, (1969) is shown in Table 1.

The Igeo interpretation as applied in this study is presented in Table1 and the Igeo values for the heavy metals in water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is shown in Table 6.

2.3.3 **Contamination Factor (CF)**

This reflects the enrichment of heavy metal in sediments or water. It is the ratio of the concentration of heavy metals in sediments or water to the concentration of that heavy metal in the background source. CF is expressed as given below as proposed by Hakanson, 1980.

$$CF = C_{metal}/C_{background} \qquad 3.$$

Where C_{metal} is the concentration of metal in sediments or water, $C_{background}$ is the background value for the metal. The description of CF is presented in Table 2. The values of CF for the detected heavy metals in this study are shown in Table 7.

2.3.4. Metal Index (MI)

Metal indices provide details on the relative levels of pollution that each metal in a water sample contributes Akpoveta et al (2011). The technique used to compute MI is as follows:

$$MI = \frac{Mc}{Mpc} \quad 4$$

Where Mc denotes the metal content in the test sample and Mpc is the maximum permitted concentration of metal in drinking water, as set out by WHO. MI values > 1 demonstrate severe contamination, whereas MI values < 1 show no contamination (Akpoveta et al, 2011). The maximum permitted concentrations (Mpc) of some heavy metals in drinking water by WHO are as follows; Cr = 0.05, Mn =0.05, Fe = 0.3, Co = 0.9, Ni = 0.02, Cu =1.5, Zn = 5.0, As = 0.05, Cd = 0.005, Hg = 0.001, and Pb = 0.05. The values of MI for the detected heavy metals in this study are shown in Table 5.

2.3.5. Modified degree of contamination (mCd)

Modified degree of contamination is based on the calculation for each pollutant of a contamination factor (CF). According to Uwah et al., (2013), the numeric sum of the *K* specifies contamination factors which express the overall degree (Hakanson, 1980; Yawo et al., 2023) of sediment contamination using the following formula;

$$Cd = \sum_{i=1}^{k} CF_i \quad 5$$

"The is aimed at providing a measure of the degree of overall contamination in surface layers of the sediment. Furthermore, all n species must be analyzed in order to calculate the correct for the range of classes defined by Hakanson, (1980)". "The modified formula is generalized by defining the degree of contamination as the sum of all the contamination factors *C*F for a given set of estuarine pollutants divided by the number of analyzed pollutants (Uwah et al., 2013). Since it is not always feasible to analyze all of the components used for this index, a variation of this method was proposed by Abrahim and Parker (2008) providing the modified degree of contamination (mCd) using the following equation:

$$mCd = \frac{\sum_{i=1}^{k} CF_i}{n} \quad 6$$

where n is the number of analyzed elements and (i) is *ith* element (or pollutant) and *C*F is the contamination factor applied to calculate *mCd*. It allows the incorporation of as many metals as the study may analyze with no upper limit (Abrahim and Parker, 2008). The classification of the heavy metals of the sediments of the study area according to the modified degree of contamination is shown in Table 3 and the values of modified degree of contamination of heavy metals in water for a respective station of Ukwuyok drinking stream of Okorombokho in Eastern Obolo, Southeastern Nigeria is shown in Table 7.

2.3.6. **Pollution load index (PLI)**

The pollution load index (PLI) provides a simple, comparative means for assessing the level of heavy metal pollution (Tomlinson et al., 1980; Harikrishnan et al., 2015; Ubulom et al., 2023; Yawo et al., 2023). To assess the sediment quality, an integrated approach of pollution load index (PLI) of the nth metals was calculated according to Suresh et al. (2011). The PLI is the nth root of multiplication of contamination factor of metals (CF) expressed as;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots . CF_n)^{1/n} \quad 7$$

Where CF is the contamination factor, n is the number of metals.

The PLI value >1 implies the present of pollution where as PLI value < 1 indicates no pollution.

The PLI values for the heavy metals in water of Ukwuyok drinking stream in Okorombokho are shown in Table 7.

2.3.7. Potential Ecological Risk Factor (PERF)

This is a ecological risk model employ to ascertain the level of toxicity of heavy metals on ecosystem. The ecological risk index has been calculated through the equations as follows;

$$C_f^i = \frac{C_D^i}{C_k^i} \quad 8$$

$$E_f^i = T_f^i \times C_f^i \quad 9$$

C_f^i is the pollution coefficient of single metal; C_D^i is the measured concentration of sample; C_k^i is the background concentration of sediments; E_f^i is the potential ecological risk factor of single metal; T_f^i is the biological toxicity factor of different metals. Biological Toxicity factor for each heavy metals is; Cu = 5, Mn = 5, Pb = 5, Co = 5, Zn = 1, Fe = 1, Cd =30, Cr = 2, Ni = 5, As = 10, Hg = 30 (Balakrishnan et al., 2015; Abata et.al.,2016). The interpretation of the potential ecological risk factor (PERF) is shown in Table 2 according to **Hakanson, (1980), Yawo et al., (2023).** The values of PERF for heavy metals in water of Ukwuyok drinking stream of Okorombokho in Eastern Obolo, Southeastern Nigeria is shown in Table 8.

2.3.8. Potential Ecological Risk Index (PERI)

Potential ecological risk index (PERI) was introduced to assess the degree of heavy metal pollution in sediments according to the toxicity of the heavy metals and the response of the environment (Hakanson, 1980). "Hakanson's method has been used often in ecological risk assessment as a diagnostic tool to potential ecological risk (Stoffers et al., 1986). RI (PERI) is calculated as the sum of all risk factors for heavy metals in sediments across the stations. The degree of ecological risk caused by heavy metal in sediment is calculated as stated in equation 10 below.

$$PERI = \sum_{i=1}^{m} E_f^i. \qquad 10$$

Where RI (PERI) is the potential ecological risk index of many metals, E_f^i is the potential ecological risk factor of single metal. The description of the interpretation of the potential ecological risk index is presented in Table 2. The values of PERI for all the respective heavy metals in water of Ukwuyok drinking stream of Okorombokho is shown in Table 8.

2.3.9. Multivariate statistical analysis

The relationships and origin of occurrences of heavy metals present in sediments sample were analyzed using the multivariate statistical analysis such as the Pearson's correlation coefficient and cluster analysis.

2.3.9.1 Pearson's correlation coefficient (PCC)

Pearson Correlation coefficient is a statistical measure of the strength of a linear relationship between paired data. This is applied to establish the sources through which the heavy metals are introduced into the coastal bodies and relationships among the detected heavy metals. The strong positive correlation indicates similar sources while strong negative correlation implies different sources of the affected heavy metals (Yawo et al., 2023). Statistical Package for the Social Sciences (SPSS) version 22 software was applied to obtain the PCC of the detected heavy metals. Statistics were judged to be significant at $P< 0.05$ for interpretation of the result levels. Bivariate correlation coefficient using Pearson correlation coefficient, R, a dimension index has value in the range $-1.0\leq R\leq 1.0$. In a sample it is denoted by R, such that positive values denote positive linear correlations, negative values denote negative linear correlation, and a value of 0 denotes no liner correlation. The closer the value is to 1 or -1, the stronger the linear correlation (Yawo and Akpan, 2021). A Pearson correlation matrix was calculated for heavy metals in water of the study area and its shown in Table 10.

2.3.9.2 Cluster Analysis (CA)

This is another method of establishing the sources and relationships of the heavy metals detected. This is always employed to affirm the results established using the PCC especially the Hierarchical dendrogram with Pearson's correlation interval results. This was obtained using the Statistical Packages for the Social Sciences (SPSS) version 22. The most used of the cluster analysis is classification. That is subjects are separated into groups such that each subject is more similar to other subjects in its group than to subjects outside the group. That is cluster analysis (CA) classifies the studies of heavy metals in terms of their similarity and difference. Cluster analysis was performed on the data set using average linkage between groups (rescaled distance cluster) to visualize elemental groupings in the studied samples. The results are illustrated in the dendrogram on Hierarchical cluster analysis. Element belonging to the same cluster are likely to have originated from a common source (Denutsui et al., 2011).

3. Results and Discussion

3.1 Concentration of Heavy Metals in Water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo,

The range and mean concentration of heavy metals in water of Ukwuyok drinking stream of Okorombokho is shown in Table 4. The range values of the concentration of the heavy metals in water of Ukwuyok drinking stream of Okorombokho is as follows; $0.24 - 0.55\, ppm\ for\ Cr$, $0.82 - 2.05\, ppm\ for\ Mn$, $1.11 - 2.08\, ppm\ for\ Fe$, $0.38 - 0.93\, ppm\ for\ Co$, $0.20 - 0.38\, ppm\ for\ Ni$, $0.71 - 1.61\, ppm\ for\ Cu$, $0.51 - 2.30\, ppm\ for\ Zn$, $0.06 - 0.22\, ppm\ for\ As$, $0.10 - 0.21\, ppm\ for\ Cd$, $0.03 - 0.05\, ppm\ for\ Hg$, $0.08 - 0.20\, ppm\ for\ Pb$. The mean concentrations values of the heavy metals in water of the study follow the ascending trend as follows; $(0.04\, ppm) < Pb(0.10ppm) < As\ (0.12ppm) = Cd(0.12) < Ni\ (0.27\, ppm) < Cr\ (0.34\, ppm) < Co\ (0.40\, ppm) < Zn\ (0.78\, ppm) < Cu(0.96\, ppm) < Mn\ (1.09\, ppm) < Fe\ (1.36\, ppm)$. Fe has been reported to occur at high concentrations in Nigeria soil/sediments (Godwin *et al*., 2015; Yawo and Akpan, 2021) and its possible for it to be high in water especially in drinking stream.

3.2 Assessment of Pollution Levels of Heavy Metals in Water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo

The mean concentration values of heavy metals reveal the ascending sequential trends as $Hg < Pb < As = Cd < Ni < Cr < Co < Zn < Cu < Mn < Fe$ as shown in Table 4. The concentrations of Cr, Co, Zn, Cu, and Mn which are higher than that of other heavy metals incurred in the study area could be due to anthropogenic influences among which are industrial processes, agricultural activities, incessant dumping of untreated wastes materials in regions liable to drain pollutants uncontrollably, etc. The spatial variations of the value of concentration of heavy metals in water of Ukwuyok drinking stream of Okorombokho, Eastern Obolo is shown in Figure 1.

The enrichment factor (EF) values of the heavy metals present in water of Ukwuyok drinking stream of Okorombokho are shown in Table 5. At Ukwuyok drinking stream of Okorombokho I (UDSO I), the EF values follow the ascending sequential trends as $Ni < Zn < As < Pb = Mn < Co < Cu < Cr < Cd < Fe < Hg$. At UDSO II, the EF values follow the ascending sequential trends as $Zn = As < Co < Mn = Cr < Cd < Pb < Cu < Fe < Ni < Hg$. At UDSO III, the EF values follow the ascending sequential trends as $Zn < Co < Pb < Cd < Mn < Cu < Fe = Hg < Cr < As < Ni$. The mean values of the EF at UDSO follow the ascending trend as $Zn < Co < As < Pb < Mn < Cd < Ni < Cu < Cr < Fe < Hg$. The values of EF at every point including the mean values as shown in Table 6 are less than 1.5 for the respective heavy metals. According to Ekaete et al., (2015), EF values in the ranges 0.5 to 1.5 suggested that the trace metals sources might be entirely from crustal materials or natural weathering process, while, EF values > 1.5 suggested that a significant portion of trace metal was delivered from non crustal materials or non natural weathering processes. The spatial variations of the values of enrichment factor for heavy metals in water of Ukwuyok drinking stream of Okorombokho, Eastern Obolo is shown in Figure 2.

The values of the geo-accumulation index of heavy metals in water of Ukwuyok drinking stream (Table 6) is as follow; at site 1 (UDSO 1), the trend is $Zn < As < Mn = Pb < Co < Cu < Cr < Cd < Fe < Ni < Hg$ with which their values ranges from -0.53 to -0.10. The water at this point is unpolluted with the detected heavy metals. At site 2 (UDSO 2), the sequential trend is $Zn < AS < Co < Cr < Mn < Cd < Pb < Cu < Fe < Ni < Hg$. Their values ranged from -1.32 to -0.03. This part of the water is unpolluted with the heavy metals detected though the pollution of some heavy metals such as Ni and Hg are higher than that at site 1. At site 3 (UDSO 3), the sequential trend as $Zn < Co < Pb < Cd < Mn < Fe = Hg < Cr < As < Cu < Ni$ and their values ranged from -0.24 to 0.17. Thus this part of the water is not contaminated with the heavy metals detected. The mean values of the geo-accumulation index of heavy metals detected in water is of the sequential trend as $Zn < As < Pb < Mn < Cd < Cr < Cu < Fe = Co < Hg < Ni$ with the range values from -0.34 to 0.00. Thus the water at that point in time was not polluted with the heavy metals detected.

On the basis of the values of CF (Table 7), the water of Ukwuyok drinking stream of Okorombokho at site 1 (UDSO1) is enriched with the heavy metals in the sequential orders as $Zn < As < Mn = Pb < Co < Cu < Cr < Cd < Fe < Ni < Hg$ with the values that ranged from 0.22 to 0.60. The water of Ukwuyok drinking stream of Okorombokho at this site at that is not polluted by the heavy metals detected base on the evaluation of pollution indices in Table 2 by Hakanson, (1980) and Yawo et al., (2023). The sequential trend on the pollution of the heavy metals in water of Ukwuyok dreaming stream at site 2 (UDSO2) is as follows; $Zn = As < Co < Cr = Mn < Cd < Pb < Cu < Fe < Ni < Hg$ with the range values of 0.36 to 0.80. The contamination trends of the heavy metals detected at site 3 (UDSO3) in water follows the ascending order as $Zn < Co < Pb < Cd < Mn < Cu < Fe = Hg < Cr < As < Ni$. The range value is from 0.44 to 0.79. The mean values of CF of the heavy metals in water of Ukwuyok drinking stream follow the sequential trends as $Zn < Co < Pb < Mn = As < Cd < Cu < Cr < Fe < Hg < Ni$ and the range values of 0.34 to 0.79. This indicates that the pollution status of the heavy metals detected in water of Ukwuyok drinking stream is low as presented by the pollution indices in Table 2 (Hakanson, 1980; Yawo et al., 2023). The spatial variation of contamination factors (CF) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is in Figure 4.

The values of the metal index (MI) model of pollution evaluation of heavy metals detected in water of Ukwuyok drinking streams (Table 8) reveals the sequential trends of the heavy metals at site 1 (UDSO1) as $Zn < Co < Cu < As < Pb < Fe < Cr < Ni < Mn < Cd < Hg$. The values ranged from 0.2 to 30. According to Akpoveta et al, (2011), MI values > 1 demonstrate severe contamination, whereas MI values < 1 show no contamination. This implies that $As\ (1.20) < Pb(1.60) < Fe(3.70) < Cr(5.00) < Ni(10.00) < Mn(16.40) < Cd(20.00) < Hg\ (30.00)$ with their values greater than one (1) severely polluted that part of the water in an increasing order from As to Hg. At site 2 (UDSO2), the sequential order of MI is as follows;

$Zn < Co < Cu < As < Pb < Fe < Cr < Ni < Mn < Cd < Hg$. The values ranged from 0.17 to 110. Obtaining $As(1.60) < Pb(2.20) < Fe(4.40) < Cr(4.80) < Ni(11.00) < Mn(18.00) < Cd(20.00) < Hg(110.00)$ with which their respective values are greater than one (1) signifies severe pollution of that site of the water by those heavy metals detected from As to Hg. At site 3 (UDSO 3), the sequential trend is as follows; $Zn < Co < Cu < Pb < As < Fe < Cr < Ni < Cd < Mn < Hg$. The range of the values is from 0.20 to 120. With $Pb\ (2.40) < As(4.20) < Fe(5.53) < Cr(10.40) < Ni(11.00) < Cd(30.00) < Mn(31.00) < Hg(120)$ of values greater than one (1), this site of the water was severely polluted with the detected heavy metals in an ascending order from As to Hg. The mean values of MI for respective heavy metals detected follow the ascending order as $Zn < Co < Cu < Pb < As < Fe < Cr < Ni < Mn < Cd < Hg$. The range value is from 0.16 to 86.67. The pollution status of the detected heavy metals follows the increasing sequence as $Pb\ (2.07) < As(2.33) < Fe\ (4.54) < Cr(6.73) < Ni(10.67) < Mn(21.80) < Cd(23.33) < Hg(86.67)$. This shows that that water is severely polluted with heavy metals from Pb in an increasing order to Hg . The spatial variation of Metal index values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is shown in Figure 5.

The values of modified degree of contamination (mCd) of the heavy metals detected for each of the site is shown in Table 7. The values at each of the site are of an increasing order as $UDSO1 < UDSO2 < UDSO3$ with the range values of 0.44 to 074 and the mean value of 0.60. According to Abrahim and Parker, (2008) and Uwah et al.,(2013**)** description of the modified degree of contamination (mCd), $mCd < 1.5$ indicates nil to low degree of contamination. The spatial variation of the mCd is shown in Figure 6.

The values of the pollution load index (PLI) for heavy metals detected in water of Ukwuyok drinking stream is shown in Table 7. The PLI values for respective stations follows the sequential trends as $UDSO\ 2 < UDSO\ 1 < UDSO\ 3$ with the range values of 0.50 to 0.74 and the mean values of 0.65. According to Tomlinson et al., (1980), Harikrishnan et al., (2015), Ubulom et al., (2023) and Yawo et al., (2023) the PLI value >1 implies the present of pollution where as PLI value < 1 indicates no pollution. The spatial variation of Pollution Load Index (PLI) values of heavy metals in water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is shown in Figure 7.

The values of the potential ecological risk factor of heavy metals in water of Ukwuyok drinking stream, Okorombokho, Eastern Obolo, Southeastern Nigeria is presented in Table 9. The PERF values for the respective heavy metals detected at site 1 (UDSO 1) is of the sequential trend as $Zn < Fe < Cr < Mn = Pb < Co < Cu < As < Ni < Cd < Hg$ with the range values. of 0.22 to 18.00. At station 2 (UDSO 2) the PERF values of heavy metals follows the order as $Zn < Fe < Cr < Co < Mn < Pb < Cu < Ni < As < Cd < Hg$. Their values ranged from 0.36 to 24.00. At station 3 (UDSO 3), the sequential trend of the heavy metals are as follows $Zn < Fe < Cr < Co < Pb < Mn < Cu < Ni < As < Hg < Cd$. The range values are from 0.44 to 30.71. The mean values of PERF for heavy metals in water of Ukwuyok drinking stream of Okorombokho follow the ascending order as $Zn < Fe < Cr < Co < Pb < Mn < Cu < Ni < As < Cd < Hg$. The mean values ranged from 0.34 to 22.00. According to Hakanson, (1980) and Yawo et al., (2023), $PERF < 40$ indicates low contamination of the ecosystem by the heavy metals, all the values of PERF are below 40 which implies low pollution status but with increasing order from As to Hg. The spatial variation of Potential Ecological Risk Factor (PERF) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is shown in Figure 8.

The values of potential ecological risk index (PERI) of heavy metals in water of Ukwuyok drinking stream of Okorombokho follow the ascending sequential trend as $Zn < Fe < Cr < Co < Pb < Mn < Cu < Ni < As < Cd < Hg$. The range of values are from 1.02 to 66.00. This implies that the ecological risk factor of those heavy metals on the ecosystem is low according to Hakanson, (1980). The spatial variation of Potential Ecological Risk Index (PERI) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria is shown in Figure 9.

The relationships and sources through which the heavy metals present in the investigated water of Ukwuyok drinking stream of Okorombokho were considered using Pearson's correlation coefficient (PCC) and cluster analysis (CA). The Pearson's correlation coefficient shows only positive significant correlations. The positive significant correlations between heavy metals in water of Ukwuyok drinking stream are as follows; Cr and Cd ($r = 1.000$), Mn and Co ($r = 0.999$), Mn and Ni ($r = 1.000$), Mn and As (1.000), Fe and Pb($r = 0.999$), Co and Ni ($r = 0.999$), Co and As ($r = 0.999$), Ni and As ($r = 1.000$). These indicate the same sources of inputs of those heavy metals. Other heavy metals not in the matrix indicate separate different sources for those heavy metals (Yawo and Akpan, 2021).

Hierarchical clustering results from heavy metals concentrations in water of Ukwuyok drinking stream of Okorombokho, Eastern Obolo, (Fig. 10) reveals two main clusters namely clusters 1 and 2. Cluster 1 is divided into 3 sub clusters. Sub clusters (1) Cd-Pb-As-Hg (2)As-Ni (3) Cr-Ni-Co. Cluster 2 is divided into two (2) sub clusters. Sub clusters (1). Mn-Cu (2) Mn-Zn (3) Fe in terms of their similarities. This indicates that Cd, Pb, As, and Hg are from same sources. Also As and Ni are from similar source and Cr, Ni and Co are from same sources. For sub cluster 2, Mn and Cu are from similar source. Mn and Zn are also same source while Fe is from a different source.

Conclusion

In Nigeria, most domestic sewage and industrial effluents from both rural and urban areas are released into the environment without proper treatment. Such practice is so pronounce among rural dwellers due to nonchalant attitudes among them and lack of inadequate sensitizations from appropriate authority. The incessant releases of pollutants into the ecosystem through gas flare and other unhygienic activities of the industrial processes within Eastern Obolo can likely increase the level of the concentrations of heavy metals in both water and sediments thereby affecting the livelihood of people and other part of the ecosystem in that region. Thus, information in water quality condition is essential for evaluating the overall status of aquatic ecosystems.

The mean concentrations of Fe in all the sampling sites are the highest indicating feldspar water base of Ukwuyok drinking stream of Okorombokho. This is also affirmed from the dendrogram results in which Fe is in one sub cluster alone.

Among the pollutions equation models employed to ascertain the toxicity status of water of Ukwuyok drinking stream, Metal index (MI) pollutions model revealed the extend of which the detected heavy metals could pose serious environmental imbalance due to the hazardous ability of the respective heavy metals. According to Akpoveta et al, (2011), MI values > 1 demonstrate severe contamination, whereas MI values < 1 show no contamination. The mean values of MI for respective heavy metals detected follow the ascending order as $Zn < Co < Cu < Pb < As < Fe < Cr < Ni < Mn < Cd < Hg$ and the heavy metals with MI greater one are follows the increasing sequence as $Pb\ (2.07) < As(2.33) < Fe\ (4.54) < Cr(6.73) < Ni(10.67) < Mn(21.80) < Cd(23.33) < Hg(86.67)$. This shows that that water is severely polluted with heavy metals from Pb in an increasing order to Hg. These toxicity threats could be due to runoff agricultural wastes, patches of crude oil from oil spillage, and other anthropogenic processes in the study area.

Acknowledgement

We sincerely express our indebtedness to the director, technologists and staff of the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU), Ile Ife for ensuring that the sediments were properly handled and the analysis was correctly done.

Table 1**. Geo-accumulation Index (Igeo) and pollution grade {Muller 1969; Ngeve et al., 2015; Yawo et al., 2023}**

Igeo class	**Igeo value**	**Sediment quality**
0	Igeo ≤0	Unpolluted
1	0<Igeo ≤1	Unpolluted to moderately polluted
2	1<Igeo ≤2	Moderately polluted
3	2<Igeo ≤3	Moderately to strongly polluted
4	3<Igeo ≤4	Strongly polluted
5	4<Igeo ≤5	strongly to extremely polluted
6	Igeo ≥5	Extremely polluted

Table 2. **Corresponding relationships between evaluation degree of pollution indices and potential ecological risks (Hakanson, 1980; Yawo et al., 2023)**

CF	**Monomial Contamination factor**	**Eir**	**Monomial potential ecological risk factor**	**RI**	**Sum of all risks factors**
< 1	Low	< 40	Low	< 150	Low
1-3	Moderate	40-80	Moderate	150-300	Moderate
3-6	High	80-160	Moderate to high	300-600	High
≥ 6	Very high	160-320	High	≥ 600	Very high
≥ 320			Very High		

Table 3. **Hakanson, (1980)** classification of the modified degree of contamination **(Abrahim and Parker, 2008; Uwah et al., 2013)**

mCd values	**Sediment quality**
mCd<1.5	Nil to low degree of contamination
1.5≤mCd<2	Low degree of contamination
2≤mCd<4	Moderate degree of contamination
4≤mCd<8	High degree of contamination
8≤mCd<16	Very high degree of contamination
16≤mCd<32	Extremely high degree of contamination
mCd>32	Ultra high degree of contamination

Table 4: Concentration (ppm) of Heavy Metals in Water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy Metals	UDSO 1 (ppm)	UDSO 2 (ppm)	UDSO3 (ppm)	Background value (ppm)	Mean (ppm)
Cr	0.25 ± 0.005	0.24 ± 0.008	0.52 ± 0.01	0.55 ± 0.011	0.34
Mn	0.82 ± 0.01	0.90 ± 0.011	1.55 ± 0.014	2.05 ± 0.018	1.09
Fe	1.11 ± 0.008	1.32 ± 0.012	1.66 ± 0.013	2.08 ± 0.018	1.36
Co	0.38 ± 0.005	0.39 ± 0.007	0.44 ± 0.01	0.93 ± 0.016	0.40
Ni	0.20 ± 0.004	0.22 ± 0.004	0.38 ± 0.006	0.34 ± 0.007	0.27
Cu	0.71 ± 0.007	0.92 ± 0.01	1.26 ± 0.011	1.61 ± 0.013	0.96
Zn	0.51 ± 0.007	0.83 ± 0.011	1.00 ± 0.016	2.3 ± 0.022	0.78
As	0.06 ± 0.003	0.08 ± 0.004	0.21 ± 0.006	0.22 ± 0.01	0.12

Cd	0.10 ± 0.004	0.10 ± 0.003	0.15 ± 0.005	0.21 ± 0.005	0.12
Hg	0.03 ± 0.001	0.04 ± 0.002	0.04 ± 0.002	0.05 ± 0.004	0.04
Pb	0.08 ± 0.002	0.11 ± 0.003	0.12 ± 0.004	0.20 ± 0.005	0.10

UDSO implies Ukwuyok drinking stream of Okorombokho

Table 5: Enrichment Factor of Heavy metals in water of Ukwuyok Drinking Stream, Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy Metals	UDSO 1	UDSO 2	UDSO 3	Mean
Cr	0.85	0.69	1.18	0.91
Mn	0.75	0.69	0.95	0.80
Fe	1.00	1.00	1.00	1.00
Co	0.77	0.66	0.59	0.67
Ni	0.23	1.02	1.40	0.88
Cu	0.83	0.90	0.98	0.90
Zn	0.42	0.57	0.54	0.51
As	0.51	0.57	1.20	0.76
Cd	0.89	0.75	0.90	0.85
Hg	1.12	1.26	1.00	1.13
Pb	0.75	0.87	0.75	0.79

Table 6. Geo-accumulation Index of Heavy Metals in Water of Ukwuyok Drinking Stream, Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy Metals	UDSO 1	UDSO 2	UDSO 3	Mean
Cr	-0.22	-0.24	0.10	-0.12
Mn	-0.27	-0.23	0.01	-0.16
Fe	-0.15	-0.07	0.03	-0.06
Co	-0.26	-0.25	-0.20	-0.06
Ni	-0.11	-0.06	0.17	0.00
Cu	-0.23	-0.12	0.12	-0.08
Zn	-0.53	-1.32	-0.24	-0.34
As	-0.44	-0.31	0.11	-0.21
Cd	-0.20	-0.20	-0.02	-0.14
Hg	-0.10	0.03	0.03	-0.01
Pb	-0.27	-0.13	-0.10	-0.17

Table 7. Contamination factor (CF), modified degree of contamination (mCd), and PLI of Heavy metals in water of Ukwuyok Drinking Stream, Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy metals	UDSO 1	UDSO 2	UDSO 3	Mean
Cr	0.45	0.44	0.95	0.61
Mn	0.40	0.44	0.76	0.53
Fe	0.53	0.64	0.80	0.66
Co	0.41	0.42	0.47	0.43
Ni	0.59	0.65	1.12	0.79
Cu	0.44	0.57	0.78	0.60
Zn	0.22	0.36	0.44	0.34
As	0.27	0.36	0.96	0.53
Cd	0.48	0.48	0.71	0.56
Hg	0.60	0.80	0.80	0.73
Pb	0.40	0.55	0.60	0.52
Sum CF	4.79	6.78	8.39	
mCd	0.44	0.62	0.74	0.60
PLI	0.42	0.50	0.74	0.65

Table 8. Metal index (MI) of Heavy Metals in Water of Ukwuyok Drinking Stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy metal	UDSO 1	UDSO 2	UDSO 3	Mean
Cr	5.00	4.80	10.40	6.73
Mn	16.40	18.00	31.00	21.80
Fe	3.70	4.40	5.53	4.54
Co	0.42	0.43	0.49	0.45
Ni	10.00	11.00	11.00	10.67
Cu	0.47	0.61	0.84	0.64
Zn	0.10	0.17	0.20	0.16
As	1.20	1.60	4.20	2.33
Cd	20.00	20.00	30.00	23.33
Hg	30.00	110.00	120.00	86.67
Pb	1.60	2.20	2.40	2.07

Table 9. Potential Ecological Risk Factor (PERF) and Potential Ecological Risk Index (PERI) of Heavy Metals in Water of Ukwuyok Drinking Stream, Okorombokho, Eastern Obolo, Southeastern Nigeria

Heavy metals	UDSO 1	UDSO 2	UDSO 3	Mean	PERI
Cr	0.90	0.88	1.90	1.23	3.68
Mn	2.00	2.20	3.80	2.67	8.00

Fe	0.53	0.64	0.80	0.66	1.97
Co	2.05	2.10	2.35	2.17	6.50
Ni	2.95	3.25	5.60	3.73	11.2
Cu	2.20	2.85	3.90	2.98	8.95
Zn	0.22	0.36	0.44	0.34	1.02
As	2.70	3.60	9.60	5.30	15.90
Cd	14.40	14.40	30.71	19.84	59.51
Hg	18.00	24.00	24.00	22.00	66.00
Pb	2.00	2.75	3.00	2.58	7.75

Table 10. Pearson's Correlations Matrix for Heavy Metals in Water of Ukwuyok Drinking Stream, Okorombokho, Eastern Obolo, Southeastern Nigeria

	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Cr	1	.990	.646	.982	.991	.913	.745	.988	1.000*	.472	.670
Mn	.990	1	.746	.999*	1.000**	.961	.831	1.000**	.994	.590	.767
Fe	.646	.746	1	.777	.742	.901	.990	.756	.670	.978	.999*
Co	.982	.999*	.777	1	.999*	.973	.856	.999*	.988	.629	.797
Ni	.991	1.000**	.742	.999*	1	.959	.827	1.000*	.995	.585	.763
Cu	.913	.961	.901	.973	.959	1	.952	.965	.926	.790	.914
Zn	.745	.831	.990	.856	.827	.952	1	.839	.766	.940	.994
As	.988	1.000**	.756	.999*	1.000*	.965	.839	1	.992	.603	.777
Cd	1.000*	.994	.670	.988	.995	.926	.766	.992	1	.500	.693
Hg	.472	.590	.978	.629	.585	.790	.940	.603	.500	1	.971
Pb	.670	.767	.999*	.797	.763	.914	.994	.777	.693	.971	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

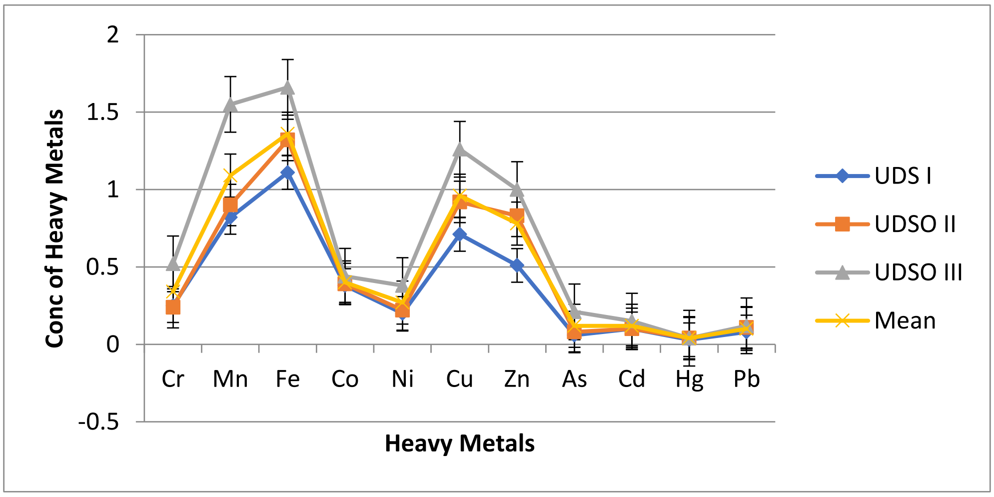

Fig. 1. Spatial variation of values of concentrations (ppm) of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

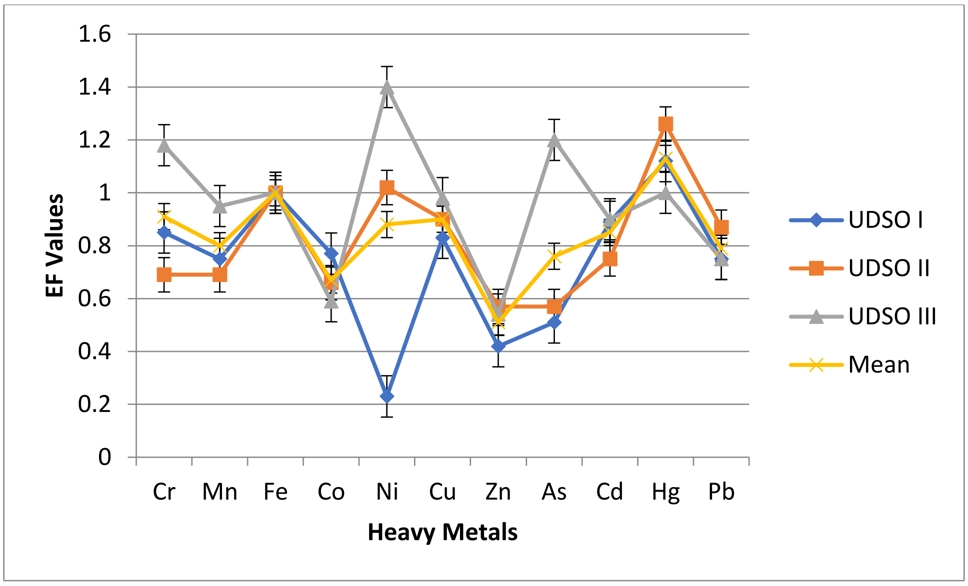

Fig. 2. Spatial variation of Enrichment Factor (EF) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

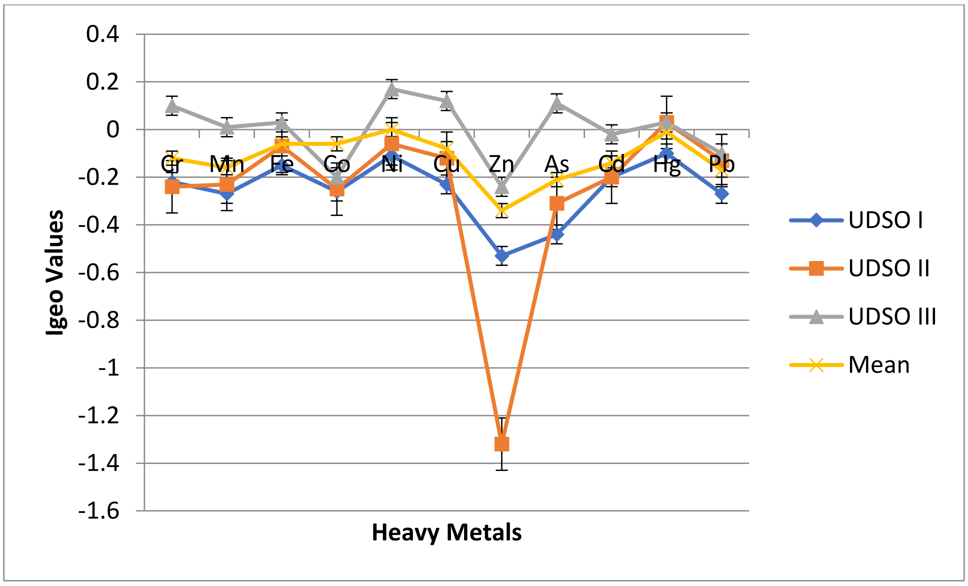

Fig. 3. Spatial variation of geo-accumulation index (Igeo) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

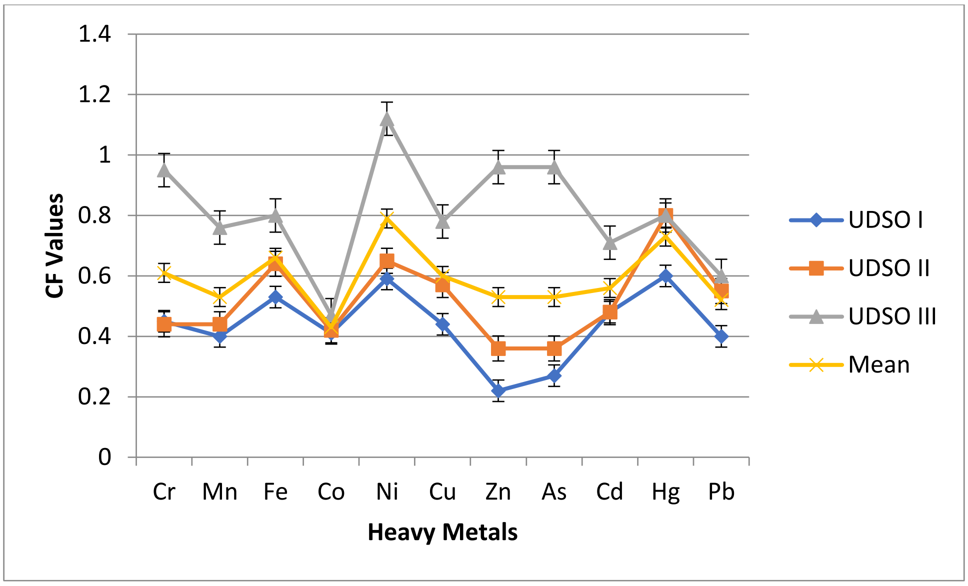

Fig. 4. Spatial variation of contamination factors (CF) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

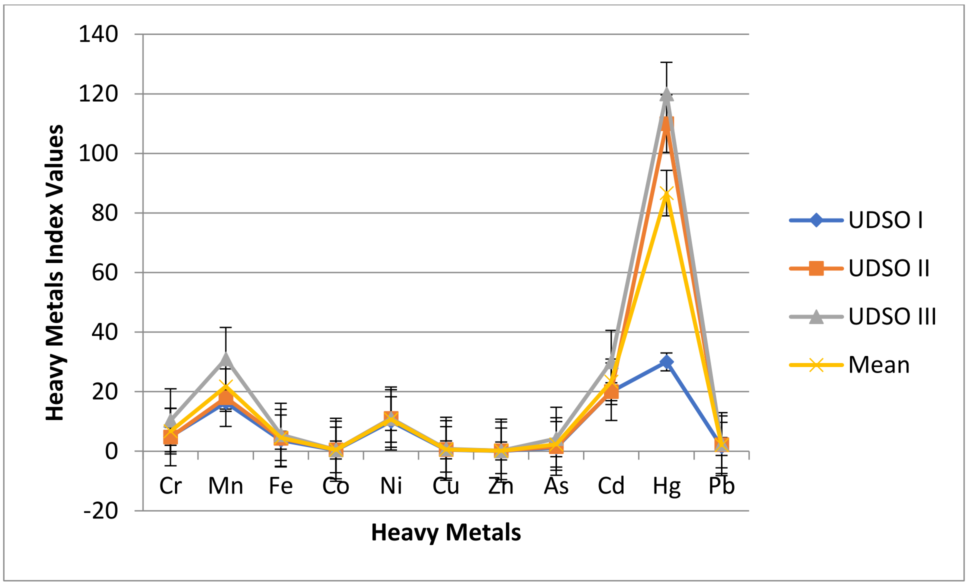

Fig. 5. Spatial variation of Metal index values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

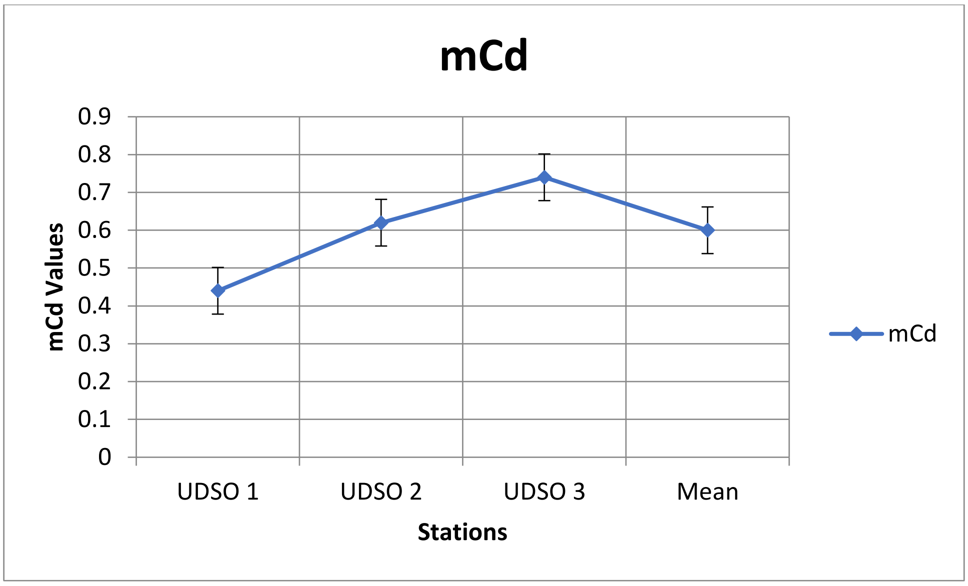

Fig. 6. Spatial variation of modified degree of contamination (mCd) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

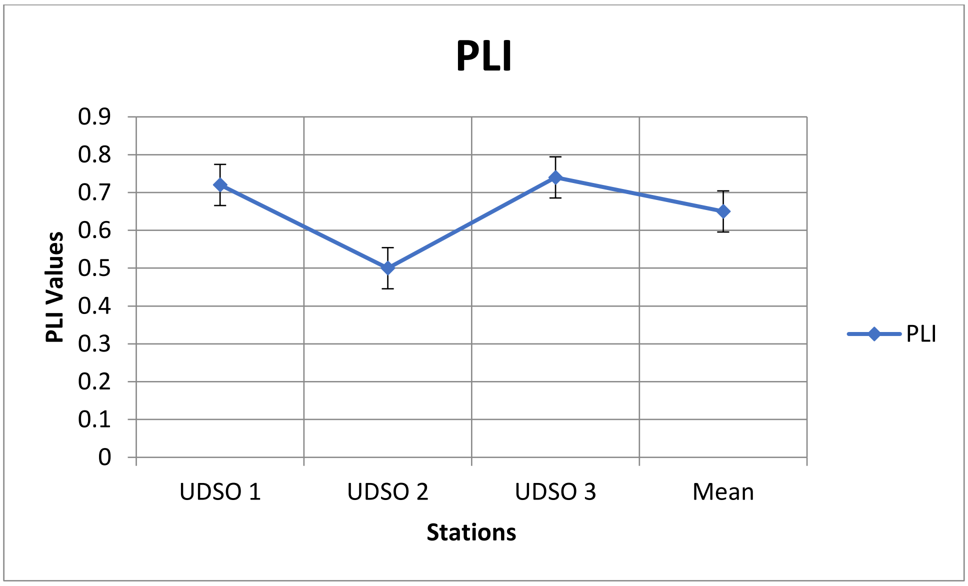

Fig. 7. Spatial variation of Pollution Load Index (PLI) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

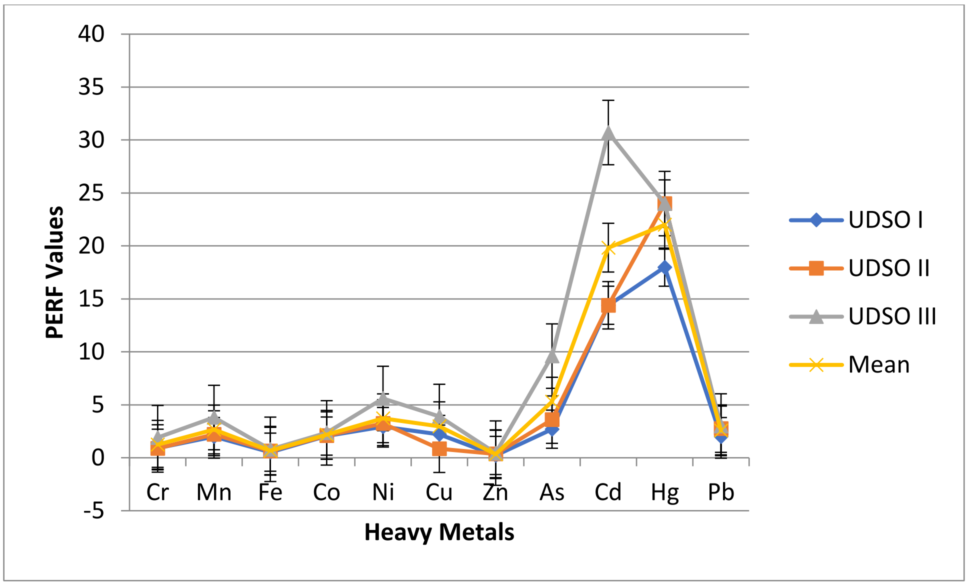

Fig. 8. Spatial variation of Potential Ecological Risk Factor (PERF) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

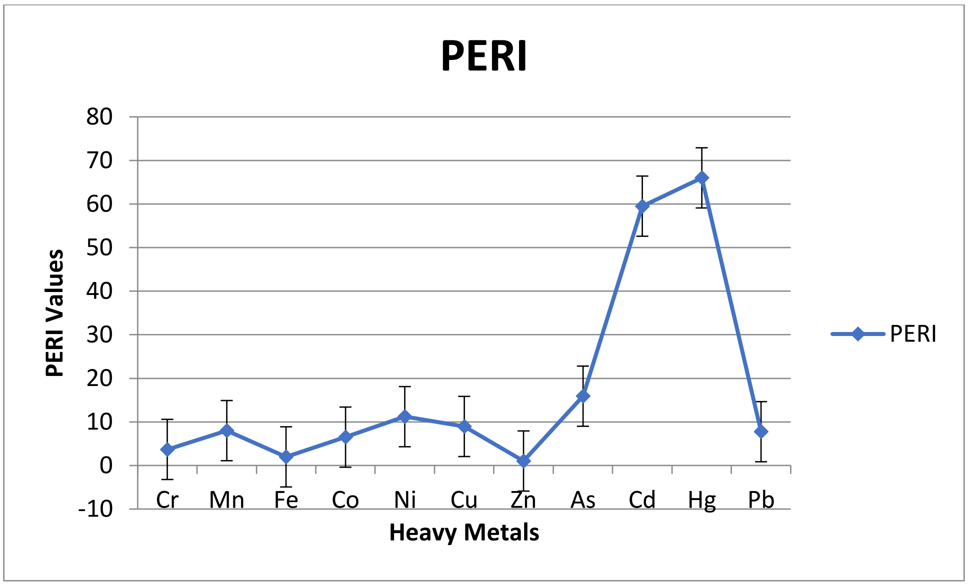

Fig. 9. Spatial variation of Potential Ecological Risk Index (PERI) values of heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

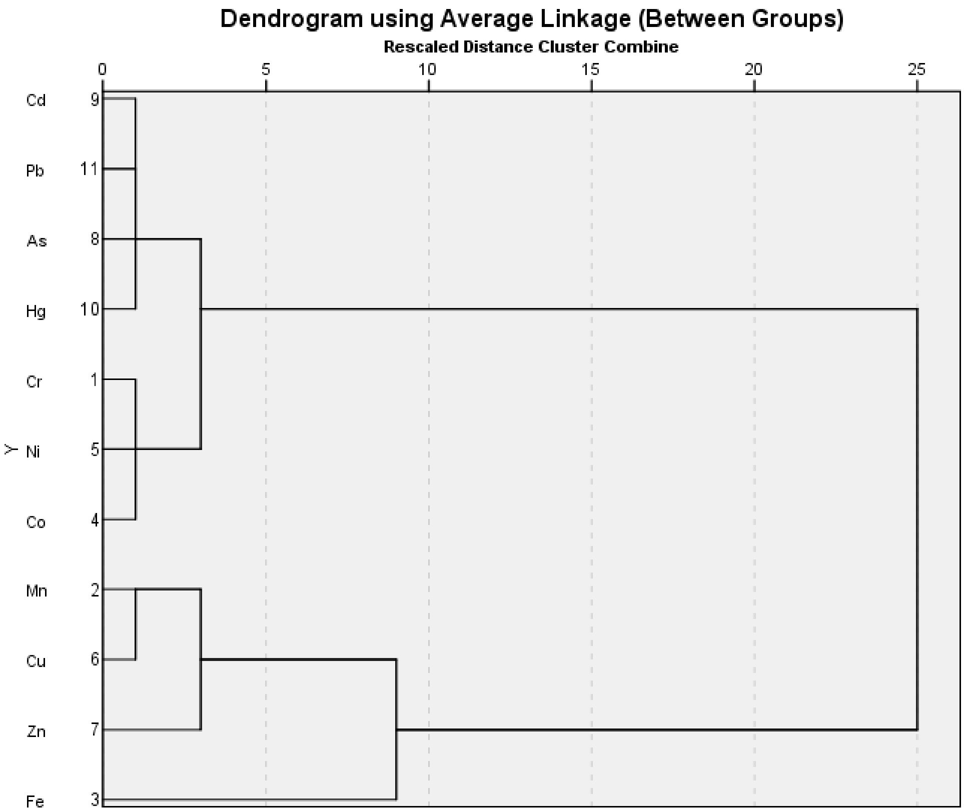

Fig. 10. Hierarchical dendrogram cluster analysis for heavy metals in water of Ukwuyok Drinking stream of Okorombokho, Eastern Obolo, Southeastern Nigeria

References

Abata, E.O., Aiyesanmi, A.F., Adebayo, A.O., Ajayi, O.O., Kazuhiko, T., & Hiroshi, S. 2016.

Contamination and ecological risk assessment of heavy metal in the sediment of Ala River, South-West: an Index –Analysis Approach. Int J Sci Engr Res.7:1.

Abrahim, G.M.S., & Parker, R.J. 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ Monit Assess. 136(1-3):227-38.

Adakole, J.A., 2011. Toxicological assessment using clarias gariepinus and Characterization of an edible oil mill wastewater Brazil Journal Aquatic Science Technology 15(2), 63–67.

Akpoveta , O.V., Okoh, B.E., & Osakwe, S.A. 2011. Quality assessment of borehole water used in the vicinities of Benin, Edo State and Agbor, Delta State of Nigeria. Current Research in Chemistry 3, 62-69.

Aktar, M. W., Paramasivam, M., Ganguly, M., Purkait S. & Sengupta, D., (2010). River

Assessment and occurrence of various heavy metals in surface water of Ganga around Kolkata: a study for toxicity and ecological impact. Environment Monitoring Assessment. 160, 207-213.

Al Obaidy, A.M. J, Talib, A.H. & Zaki, S.R., 2015. Application of water pollution index for assessment of Tigris River Ecosystem. International Journal Advance Research. 3(2), 219–223.

Amman, A. A., Michalke, B. & Schramel, P., (2002). Speciation of heavy metals in environmental water by ion chromatography coupled to ICP-MS. Analytical Biochemistry,372, 448-452.

Arora, M., Kiran B., Rani S., Rani A., Kaur B. & Mittal N., (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. Food Chemistry 111, 811-815.

Balakrishnan, T., Sundaramanickam, A. & Shekhar S. 2015. Distribution and seasonal variation of heavy metals in sediments of Muthupet Lagoon, Southeast Coast of India. J. Ecological. Eng. 16 (3) 49-60.

Beaty, D. R., & Kerber, D. J., 1993. Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry.

Birch, G. A. 2003. scheme for assessing human impacts on coasta aquatic environments using sediments. In: Woodcoffe CD, Furness RA, editors; 2003 (Ed, Coastal GIS. Wollongong

university papers in centre for maritime policy. Available: http://www.ozestuaries. Org/indicators. Vol. 14. Austria; 2003/ DEF sediment scheme. Html.).

Breslin, V.T., Sañudo-Wilhelmy, S.A., & Sanudo-Wilhelmy, S.A. 1999.High spatial resolution sampling of metals in the sediment and water column in port Jefferson Harbour, New York. Estuaries. 1999;22(3):669-80.

Bruland, K.W., Bertine, K,, Koide, M., & Goldberg, E.D.1974. History of metal pollution in southern California coastal zone. Environ Sci Technol. 8(5):425-32.

Bytyçi, P., Fetoshi O., Durmishi, B.H., Etemi, F.Z, Çadraku H., Ismaili, M. & Abazi, A.S.,

2018. Status Assessment of Heavy Metals in Water of the Lepenci River Basin, Kosova Journal Ecol Engr 19(5):19–32. https ://doi.org/10.12911/22998993/91273.

Cai ,D., Zhang, H., Shen, D., Zhao, X., & Li, C. 2009. Environmental changes record derived from sediment cores in Huixian Karst wetlands, Guilin, China. J. Guangxi Norm. Univ. Nat. Sci. Ed, 27, 94–100.

Deely, J.M., & Fergusson, J.E. 1994. Heavy metal and organic matter concentration and distributions in dated sediments of a small estuary adjacent to a small urban area. Sci Total Environ. 1994;153(1-2):97-111.

Demirbas, A., Pehlivan, E., Gode, F., Altun, T. & Arslan, G., 2005.Adsorption of Cu (II), Zn(II),

Ni (II), Pb(II), and Cd (II) from aqueous solution on amberlite IR-120 Synthesis Resin. J. Colloid and Interface. Sci. 282: 20-25.

Denutsui, D., Akiti, T., Osae, S., Dampare, S. B., Tutu, A. O., Blankson-Arthur, S., Ayivor, J. E.

& Adomako, D., 2011. Assessment of pollution into the Densu Delta Wetland using instrumental neutron activation analysis. Research Journal Environmental Earth Sciences. 3(6), 772-781.

Dominic, A.P.,Akpan, I.O., & Yawo, O. J.2022. Assessment of Heavy Metals Concentration in

Soil of Champion Breweries Plc, Aka Offot, Uyo, Southern Nigeria Using X-Ray Fluorescence Technique. Researchers Journal of Science and Technology. 2(1):64 – 76

Eaton, A.D. & Franson, A. H., 2015. *Standard Methods for the Examination of Water and Waste Water,* American Public Health Association

Ekaete, A.J., Ibironke, O.K., Olatunde P.S., & Olaoye O.P. 2015. Heavy metals pollutions and its associated Ecological Risks in Lagos Lagoon Sediments, South-Western Nigeria. ACSJ. 9(3):1-13

Fact Sheet, 2003. Arsenic in the environment, Washington State Department of Health: http://www.doh.wa.gov/ehp/factsheets.htm. (Assessed, 2011 March 11).

Ghrefat, H., & Yusuf, N. 2006. Assessing Mn, Fe, Cu, Zn and Cd Pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. Chemosphere. 65(11):2114-21.

Godwin, A., Oghenekohwiroro, E., Funso, A., & Olaniyi, O. 2015. Using EF, PLI and Igeo For the Assessment of Heavy metal pollution and sediment quality of Asejire Reservoir, Southwest Nigeria. *Int. J. Environ. Pollut. Res*. 3(4): 77-90.

Goorzadi, M., Vahabzadeh, G., Ghanbarpour, M.R. & Karbassi, A.R., 2009. Assessment of heavy metal pollution in Tilehbon river sediments, Iran. Journal Applied Sciences 9, 1190–1193.

Hakanson, L. 1980. Ecological risk index for aquatic pollution control, a sedimentological approach. Water Res.14(8):975-1001.

Harikrishnan, N., Suresh Grandhi, M., Chandrassekaran, A., & Ravisankar, R. 2015. Assessment of heavy metal pollution and potential ecological risk of sediments of East Coast of Tamil Nadu by energy dispersive X-ray fluorescence spectroscopy (EDXRF) and Sediment Toxic Dis.1:1-3.

Ho, Y.C., Show K.Y., Guo X.X., Norli I., Abbas F.M.A.,& Morad N., 2012. Industrial discharge and their effect to the environment. In: Show KY, Guo XX (eds) Industrial waste. Intech Open. https://doi. org/10.5772/38830.

Hopenhayn, C., (2006). Mineralogical Society of America, Arsenic in Drinking Water: Impact on Human Health, International Journal Environmental Research Public Health 3 (4), 316–22.

Huu, H.H., Rudy, S., & Damme, A, V. 2010. Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong harbor, Ha Long Bay, Vietnam. Geol Belg. 13(1-2):37-47.

Knobeloch, L. 2002. Health Effects of Arsenic Contaminated Drinking Water Association of arsenic-contaminated drinking-water with prevalence of skin cancer in Wisconsin's Fox River Valley Journal Health Population Nutrition 24 (2), 206–13. PMID 17195561.

Lenntech, B.V., 2013. Acids and Alkalis in Fresh water in water treatment solutions. Http://www.Lenntech.com/aquatic/acidsalkalis.htm Accessed on 27th June, 2017.

Liu D., Li Y., Ma J., Li C., Chen X., 2016. Heavy metal pollution in urban soil from 1994 to 2012 in Kaifeng City, China. Water Air Soil Pollut, 227, 154.

Mediolla, L.L.M., Domingues, M.C.D.D., & Sandoval, M.R.G.S. 2008. Environmental assessment of and active tailings pile in the state of Mexico (Central Mexico). Res J Environ Sci. 2(3):197-208.

Modh, Z. A., Nur, R. A., M., Ahmad, S., Zaini, H., & Mohd, T. A. 2015. Evaluation of heavy metal contamination levels of Balok River sediments in Pahang, Malaysia based on geoaccumulation index and supported with enrichment factor. Malays J Anal Sci.19(4):707-14.

Muller, G. 1969. Index of geo-accumulation in sediments of the Rhine River. Geol J. 2(3):108-18.

Namaghi, H.H., Karami, G.H. & Saadat S.A., 2011. Study on chemical properties of groundwater and soil in ophiolitic rocks in Firuzabad, east of Shahrod, Iran: with emphasis to heavy metal contamination. Environ Monit Assess 174, 573–583.

Ngeve, M.N., Leermakers, M., Elskens, M., & Kochzius, M. 2015. Assessment of trace metal pollution in sediments and intertidal fauna at the coast of Cameroon. Environ Monit Assess. 187(6):337.

Niencheski, L.F., Windom, H.L, & Smith R. 1994. Distribution of particulate trace metal in Patos Lagoon Estuary (Brazil). Mar Pollut Bull. 28(2):96-102.

Nnabo, P.N., (2015). Assessment of Heavy metal contamination of water sources from Enyigba Pb-Zn District, South Eastern Nigeria. International Journal of Scientific and Technology Research 4(09), 2277-6616.

Obaroh, I.O, Elinge, M., & Nwankwo, C., 2012. Assessment of some heavy metals and Physico-chemical parameters of Jega River, North Western Nigeria. International Journal Natural Applied Sciences 8, 78–81.

Oves, M., Khan, M. S., Zaidi, A. & Ahmad, E., 2012. Soil contamination, nutritive value,

and human health risk assessment of heavy metals: an overview. In: Zaidi A, Wani PA, Khan MS (eds) Toxicity of heavy metals to legumes and bioremediation. Springer, Vienna, pp 1–27.

Rahman, M.S., 2012. Study of heavy metals levels and the risk assessment in some edible fish from Bangsho River, Sava, Dhaka Bangledesh. Food Chemistry, 13(4), 1847 – 1854.

Selvaraj, K., Ram, M. V., & Szefer, P. 2004. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical 49(3):174-85.

Senarathne, P. & Pathiratne, K.A.S., 2007. Accumulation of heavy metals in a food fish, Mystus gulio in habiting Bolgoda Lake, Sri Lanka. Sri Lanka Journal Aquatic Sciences 12, 61–75.

Sharma, V.K., Rhudy, K.B., Koenig, R., Baggett, A.T., Hollyfield S, & Vazquez, F.G. 1999. Metals in sediments of Texas estuaries, USA. J Environ Sci Health.34(10):2061-73.

Stoffers, P., Glasby, G.P., Wilson, C.J., Davis, K.R., & Walter, P. (1986). Heavy metal pollution in Wellington Harbour. N Z J Mar Freshw Res. 20(3):495-512.

Tomlinson, D.L, Wilson, J.G., Harris, C.R., & Jef-frey, D.W. 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Hel-gol. J Mar Res. 575:33-566.

The Perkin-Elmer Corporation, 1996. Analytical Methods for Atomic Absorption Spectroscopy, USA. Pp56-179.

Ubulom, S. R., Akpan, U. E., Yawo, O. J., Essien, I, C., Edemumo, F. O., 2023. Evaluation of

the Effects of Heavy Metals on Sediments and Rainwater Samples Due to Gas Flaring in the South Eastern Nigeria, , J. Glob. Ecol. Environ. 18(3): 1-16

Ubulom, S. R., Ekanem, M. P., Etim, I. N., Yawo, O.J., & Ewa-Oboho, I. (2022). Assessment of Contamination Status of Heavy Metals in Sediment due to Gas Flaring at Esit Eket, South

Eastern Nigeria, Researchers Journal of Science and Technology, 2(1): 50 -63

Ubulom, S. R., Yawo, O. J., Akpan, U. E, 2023. Evaluating the Distributions and Impacts of Macroplastic Pollutants in Agansa Coastal Community, South Eastern Nigeria , J. Glob. Ecol. Environ. 18(2): 32-45

UNESCO, 2003. Water for people, water for life: UN world water development report, executive summary. Paris: United Nations Educational, Scientific and Cultural Organization.

Uwah, I.E., Dan, S.F., Etiuma, R.A., & Umoh, U.E. 2013. Evaluation of status of heavy metals pollution of sediments in Qua-Iboe River estuary and associated creeks, South Eastern Nigeria. Environ Pollut. 2(4):4.

Wang, X., Lu Y, Han J, He G, & Wang, T., 2007. Identification of anthropogenic influences on water quality of rivers in Taihu watershed. Journal Environmental Sciences 19, 475–481.

WHO, 2008.World Health Organization. Guidelines for drinking water quality,Geneva 1(3), 306-492.

WHO, 2008. Guidelines for Drinking Water Quality, 3rd ed. Vol 1. Incorporating the first and Second Addenda, WHO, Geneva (2008). ISBN 978 92 4 154761 1.

WHO/UNICEF 2010. Progress on sanitation and drinking water, World Health Organization. Geneva, Switzerland. pp.7. Http://www.unwater.org/downloads/JMP-report-2010 pdf. Accessed on 25th June, 2017.

Wright, D.A. & Welbourn P. 2002. Environmental toxicology Cambridge University Press, Cambridge, UK.

Yawo, O. J., Akpan, I. O., 2021. Assessment of heavy metals concentration in sediments of Utibete River, Eastern Obolo, Southeastern Nigeria using particle induced X-ray emission (PIXE) technique. Res. J. Sci. Tech. 1:17-36.

Yawo, O.J,, Inyang, E.P,, Akpan, I.O., 2022. Application of pollution indices in estimating the toxicity of heavy metals in sediments of Okoro river in Eastern Obolo, Southeastern Nigeria. Res. Sci Technol.;2:1-17.

Yawo, O. J., Ubulom, S. R., Akpan, I. O., Nathaniel, E. U., Amodu, A. E., Azogor, W. E., 2023.

Evaluating the Pollution Levels and Ecological Risks of Heavy Metals in Sediments of Apapa Port in Lagos, South-western Nigeria, J. Glob. Ecol. Environ. 19(2); 15-33

Zhang, J., & Liu, C.L. 2002. Riverine composition and estuarine geochemistry of particulate metals in China- weathering features, anthropogenic impact and chemical fluxes. Estuarine Coastal and Shelf Science. 54(6):1051-70.

Zhu, X., Ji, H., Chen Y., Qiao M. & Tang, L. 2012. Assessment and sources of heavy metals in surface sediments of Miyun Reservoir, Beijing Environment Monitoring Assessment 185, 6049–6062.