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Physicochemical Parameters and Heavy Metals Assessment of Surface Water and Sediment from Issiet Ekim Stream in Uruan Local Government Area, Akwa Ibom State, Nigeria

Calvin Onyedika Nwokem*, Idongesit Bassey Anweting, Idongesit Edem Okon, and Nathaniel Oladunni

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Abstract: This work examined the physicochemical parameters and heavy metal of surface water and sediment of Issiet Ekim stream in Uruan Local Government Area, Akwa Ibom State, Nigeria. Physicochemical parameters examined were temperature, pH, turbidity, electrical conductivity, dissolved oxygen, total dissolved solids (TDS), total suspended solids (TSS), salinity as chlorine, total alkalinity and bi-carbonate. All the physicochemical parameters were within the standard limits except for pH (6.98) which is above the WHO limit (6.5-8.5). Heavy metals examined include Pb, Hg, Co, As, Fe, Cu, Cd, Cr, Mn, Ni and Zn. Absorption Spectrophotometer (AAS) (XplorAA GBS Model) was used for heavy metal analysis. The heavy metals concentration in the water descends with the following order: Zn > Fe > Mn > Cu > Cd > Ni > Pb> Cr > Co > Hg = As, similarly that of sediments flow in the order: Zn > Fe > Cu > Pb > Cd > Cr > Mn > Ni > Co, Hg = As. Most of the metals exhibited higher concentrations in sediment than in the surface water. The water quality index (WQI) concerning physicochemical properties was 17.5421 suggesting that the stream was safe for drinking and domestic usage as 17.5421 falls within the range of 0 - 25 classification, which signifies excellent water quality.

Keywords: *Physicochemical parameters, Heavy Metal, Water Quality Index, Standard Limits, correlation*

Calvin Onyedika Nwokem*
Department of Pure and Applied Chemistry, Kaduna State University, Kaduna, Nigeria
Email: onyenwokem@gmail.com
Orcid id: 0009-0001-0220-0714

Idongesit Bassey Anweting
Chemistry Department, University of Uyo, Uyo, Akwa Ibom State, Nigeria.
Email: idongesitanweting@uniuyo.edu.ng
Orcid id: 0000-0002-9251-3991

Idongesit Edem Okon
Department of Chemistry, Ahmadu Bello University, Zaria, Kaduna, Nigeria; Transport Technology Centre, Nigerian Institute of Transport Technology, Zaria, Nigeria.
Email: idokon22@yahoo.com
Orcid id: 0000-0002-8801-1913

Nathaniel Oladunni
Department of Science Laboratory Technology, Nigerian Institute of Leather and Science Technology (NILEST), Zaria, Nigeria.
Email: nathola2010@gmail.com

1. 0 Introduction

Physicochemical analysis is based on actual measurement of physical parameters such as pH, temperature, colour etc., and chemical parameters such as metal copper, lead, and iron among others. Physicochemical monitoring provides quantitative information about the presence of pollutants in natural streams (Faiza *et al.*, 2012), and changes in the physicochemical properties of water can affect water quality (Faiza *et al.*, 2012; Okon *et al.*, 2023a). Physicochemical parameters play an important role in determining the water quality. The distribution processes of the metals entering natural waters are controlled by a dynamic set of physicochemical interactions and their solubility is principally controlled by hydrogen ion concentration (pH), metal concentration, type of metal species, oxidation state and the redox environment of the aquatic system (Koffi *et al.*, 2014).

Heavy metals pollution represents a serious problem for human health and for life in general. Heavy metals such as zinc, lead, cadmium, chromium, mercury and copper can cause serious health problems. Virtually all metals, including essential micronutrients, are toxic to aquatic ecosystem. Although some metals including manganese (Mn), iron (Fe), copper (Cu) and zinc (Zn) are essential micro-nutrients, many others such as mercury, cadmium and lead are not required even in small amounts by organisms as they can cause serious health problem to both plants and animals in the ecosystem. Okon *et al.* 2023b observed a negative impact of lead and chromium on the growth rate of young plants when the effect of soil heavy metal concentrations on the early growth performance of cowpea (*vigna unguiculata*) and groundnut (*arachis hypogea*) seeds was investigated. Metals can never be eliminated once they enter a water body. They remain persistent in sediment and slowly get released causing serious hazards to aquatic life forms as they further move up in the food chain (Oyeyiola *et al.*, 2020).

The accumulation of metals from the overlying water to the sediment is dependent on several external environmental factors such as pH, dissolved oxygen, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution (Davies *et al.*, 2006; Davies and Ekperusi, 2021; Ebong *et al.*, 2022). However, metals cannot always be fixed in sediments permanently. Some of the sediment-bound metals may remobilize and be released back to waters via the variation of environmental conditions such as acidification, and redox potential conditions, and impose adverse effects on living organisms (Liu *et al.*, 2009). Despite the release, the concentration of heavy metals available in the sediment is higher when compared to water (Uba *et al*., 2020). Surface water is a natural water source which collects from water running across the surface of the ground (Barry, 2019). As this water runs across the ground surface, it picks up microorganisms, organic matter and minerals. Sediment is matter (sand, dirt, gravel) that settles to the bottom of the water (Barry, 2019). Surface waters serve various purposes ranging from drinking, sources of fish, irrigation to recreation but frequently these waters are polluted. Water pollution is one of the most important environmental problems faced by third-world countries (Barry, 2019). The key to effective environmental quality management is the ability to continuously monitor the concentration of various pollutants of interest in the sample. The significance of various substances in water is obvious and it is their level that gives a measure of the quality of the water. As a result of industrialization, most of the substances discharged into the water display an attraction towards the particulate matter. Consequently, the chemical makeup of sediment at the bottom reflects the influx of discharged materials into the marine ecosystem (Chukwura, 2021).

Pollution from heavy metals is inflicting water bodies worldwide, especially in developing countries (Wang *et al*., 2019). As an important component in riverine ecosystems, sediment serves as both a sink and a source of heavy metals (Pejman *et al.*, 2015; Okon *et al.*, 2022). Most heavy metals quickly deposit into the sediment after entering streams, and are much more concentrated in the sediment than in the water body of riverine systems. Conversely, when the physicochemical or hydrological conditions change, the heavy metals in the sediment may desorb or re-suspend to cause secondary pollution in the water body (Kouidri *et al.*, 2016; Liang *et al.*, 2015). The accumulation of heavy metals in the sediment directly affects benthic organisms and also influences many other organisms through the food web, and endangers the wellbeing of the aquatic ecosystem. There are many reasons for heavy metal pollution, it is mainly caused by natural factors such as floods, weathering, riverbed erosion and human activities such as mining, mechanical and electronic industry, urban construction, urban transportation, and agriculture (Ke *et al.*, 2015; Hu *et al.*, 2020; Mu *et al.*, 2020). Therefore, there is a need for an assessment and a comprehensive analysis of the status, potential risks and sources of heavy metals in surface water and sediments to aid in environmental control and management.

In recent times, pollution of the aquatic environment by heavy metals has become a problem worldwide because they cannot be destroyed. Most of them are toxic and have adverse effects on the aquatic environment (Ozturk *et al.*, 2009). The toxicity effects of these heavy metals on aquatic organisms and its environment can be direct or indirect. Both changes in physicochemical characteristics and concentrations of heavy metals in water are as a result of human activities, and these metals are adsorbed by aquatic vegetation and are consequently introduced into the food web (Şener *et al.*, 2017). Activities such as mining and construction alter physicochemical properties in the water sources, they change the pH of water, increase water turbidity, and also raise the total content of total dissolved solids and heavy metals. Given the dangers of heavy metal pollution, a comprehensive assessment of their presence and potential risks in the Issiet Ekim stream is necessary. This study aims to analyze the physicochemical parameters and heavy metal concentrations in both the water and sediment of this stream to aid in environmental control and management strategies.

2. 0 Materials and Method

2.1 Study Area

The stream, which served as a study point was the Issiet Ekim stream in Uruan Local Government Area of Akwa Ibom State, Nigeria (Fig. 1). Uruan Local Government is located at Latitude 5^0 02' 0'' North; Longitude 8^0 03' 0'' East; it covered an area about 449km^2, and population of 164,000 (National Population Census, 2016). It is made up of clans, the clans include Akwa Uruan, Etongko Mkpe Uruan, Mutaka Uruan, Ekondo Uruan, Mosongko Uruan, Ibonda Uruan, and Akpe Iboku Uruan. Uruan people developed the Uruan language which they derived from the proto-language. It is a variant of the Ibibio language. Uruan language is what has for historical reasons been referred to as Efik language, and Uruan and Efik are all Iboku people. The area lies in the rainforest belt with extensive arable land and the region abounds with wildlife, raffia palm, timber and crude oil. The rich coastal plains support the cultivation of crops such as cassava and maize.

2.2 Materials

Materials for laboratory work were beakers, a conical flask, an oven, a petro-dish, a spatula, a measuring cylinder, analytical weighing balance, volumetric flask, a burette, a retort stand, a white tile, a funnel, a heating mantle, pipette, cuvettes, methyl orange and Atomic Absorption Spectrophotometer (AAS) (XplorAA GBS Model). All reagents used were of analytical grade and they were freshly prepared. All sampling containers and glass wares were washed with 0.05M HNO_3 solution and rinsed with deionized water.

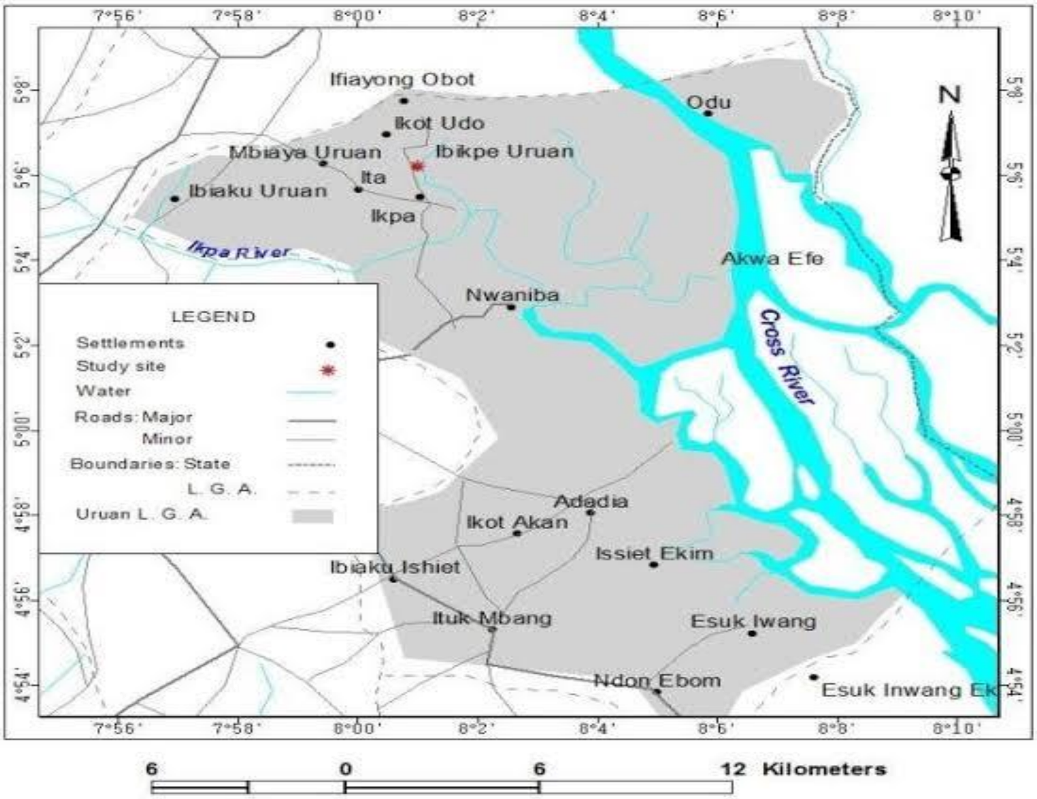

Fig. 1: Map of Study Area

2.3 Sample collection

Water Samples were collected at the sampling station (Issiet Ekim stream). The collection was done using airtight 1-litre polyethylene plastic bottles at a depth of 50 cm. Sample bottles were washed thoroughly with a solution of detergent and rinsed with deionized water. The sampling bottles were treated with 10% HNO_3 and rinsed with deionized water to remove trace elements contamination according to Abah, *et al*. (2016). Before collection of the water sample, the sample bottles were rinsed with the stream water, samples were filtered at the point of collection, acidified with 1.5 mL concentrated HNO_3 for preservation, and then moved to the laboratory, at the laboratory; the samples were stored in the refrigerator before analyses. The

pretreated water samples were digested according to a standard method as described by the American Public Health Association (APHA, 1999). Sediment samples were collected at the same locations where water samples were obtained; the sediment samples were collected from top layer 3 – 10 cm of the waterbed and stored in clean airtight polythene bags. The sediment samples were treated with nitric acid to prevent the growth of microbes. The sediment samples were air-dried at room temperature and ground with clean ceramic mortar, sieved, and reserved for wet digestion. The ground sediment samples were digested according to the standard method as described by the American Public Health Association (APHA, 1999).

2.4 Analysis of heavy metal ions and physicochemical parameters

All analyses were carried out at the Ministry of Science and Technology Laboratory, Uyo, Akwa Ibom, Nigeria. Analysis of Physicochemical parameters was carried out using standard methods as described by the American Public Health Association (APHA, 2018). The various physicochemical parameters examined in the water sample were temperature, pH, turbidity, electrical conductivity, dissolved oxygen, total dissolved solids (TDS), total suspended solids (TSS), salinity as chlorine, total alkalinity and bicarbonate. The APHA, 2018 standard methods were used in the determination of heavy metal in the sample. An Atomic Absorption Spectrophotometer (AAS) (XplorAA GBS Model) was used as the instrument for the determination. The heavy metals determined were Lead (Pb), Mercury (Hg), Cobalt (Co), Arsenic (As), Iron (Fe), Copper (Cu), Cadmium (Cd), Chromium (Cr), Manganese (Mn), Nickel (Ni) and Zinc (Zn).

2.5 Water quality assessment

The assessment of the water quality of the studied stream was done using the Water Quality Index (WQI). The WQI was calculated using standards of drinking water quality recommended by the World Health Organization (WHO 2019; 2022). The Weighted Arithmetic Index method (Brown *et al*., 2018) was used for the calculation of WQI in this study. Three steps were followed for computing WQI.

Each of the ten (10) parameters was assigned a weight, wi according to its relative importance in the overall quality of water for drinking purposes.

The relative weight, Wr was computed using the Equation 1 below:

$$W_r = \frac{W_i}{\sum W_i} \quad (1)$$

where, Wr = relative weight, Wi = weight of each parameter and ΣWi = sum of parameters.

A quality rating scale, qi for each parameter was assigned by dividing its concentration in each water sample by its respective standard according to the guidelines laid down by Nigeria Standard for Drinking Water (NSDW) (2007), WHO (2019) and WHO (2022) and the result multiplied by 100.

$$qi = \frac{Ci}{Si} \quad (2)$$

where, qi = quality rating, Ci = concentration of each chemical parameter in each water sample in mg/l and Si = NSDW/WHO drinking water standards for each parameter. To compute the WQI, SI was first computed for each of the chemical parameters, which was then used to determine the WQI using the following equations:

$$SI = Wi \times qi \quad (3)$$

Therefore WQI (Water Quality Index) = $\sum SI$

where, SI = the index of each parameter and qi = rating based on the concentration of each parameter. Table 1 shows the rating for the drinking water quality values:

Table 1: Drinking Water Quality Classification based on WQI Values (Brown *et al*., 2018)

Water Quality Index Level	Water Quality Status
0-25	Excellent water quality
25-50	Good water quality
51-75	Poor water quality
76-100	Very poor water quality
>100	Unsuitable for drinking

3.0 Results and Discussion

3.1. Physicochemical parameters

In computing the results for this research, the standard limits for physicochemical determinants approved by the World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) were adopted as standard in determining the quality index of the sample.

The results obtained from analyzing the concentration of ten (10) evaluated physicochemical parameters (temperature, pH, turbidity, electrical conductivity, dissolved oxygen, total dissolved solids (TDS), total suspended solids (TSS), salinity as chlorine, total alkalinity and bi-carbonate) are presented in Table 2. Water quality assessment was calculated from the results of the parameters and was compared in line with the recommended standard limits as set out by WHO as presented in Table 3.

Table 2: Physicochemical parameters of surface water (SW)

S/N	Parameters	WHO Limit	Measured Value in SW (mg/L)
1	Temp (^{0}C)	30 - 32	27.5
2	pH	6.5-8.5	6.98
3	Turbidity (NTU)	5	5.14
4	Electrical Conductivity (µs/cm)	1000	25.7
5	Dissolved Oxygen (mg/L)	5.00	4.6
6	Total Dissolved Solid (mg/ L)	250	18.3
7	Total Suspended Solid (mg/L)	1500	0.008
8	Salinity as Cl^- (mg/L)	250	17.55
9	Total Alkalinity (mg/L)	200	15
10	Bi-Carbonate (mg/L)	30 - 400	18.3

Table 3: Quality index of surface water

Parameters	**WHO Limit**	**Values (Ci)**	**Assigned Weight (Wi)**	**Relative Weight (Wr)**	**Quantity (qi)**	**Sub-Index (SI)**
Temp (^{0}C)	30 - 32	27.5	4	0.1250	0.8871	3.5484
pH	6.5-8.5	6.98	4	0.1250	0.9971	3.9886
Turbidity (NTU)	5	5.14	3	0.0938	0.0343	0.1028
Electrical Conductivity (µs/cm)	1000	25.7	3	0.0938	0.0257	0.0771
Dissolved Oxygen (mg/L)	5.00	4.6	4	0.1250	0.9200	3.6800
Total Dissolved Solid (mg/ L)	250	18.3	3	0.0938	0.0732	0.2196
Total Suspended Solid (mg/L)	1500	0.008	2	0.0625	0.0000	0.0000
Salinity as Cl^- (mg/L)	250	17.55	3	0.0938	0.0702	0.2106
Total Alkalinity (mg/L)	200	15	3	0.0938	0.0750	0.2250
Bi-Carbonate (mg/L)	30-400	18.3	3	0.0938	1.8300	5.4900
Summation (∑)			32			17.5421

Source: ***Researcher's Computation, 2023***

3.1.2. Heavy metal parameters

The results obtained from analyzing the concentrations of eleven heavy metals (Pb, Hg, Co, Ar, Fe, Cu, Cd, Cr, Mn, Ni and Zn) are presented in Fig.s 2 and 3. Tables 2 and 3 show results for the physicochemical analysis of the water samples and their quality assessment. The temperature of the sample is within the recommended range by WHO (30 – 32 ^{0}C) as it was 27.5 ^{o}C. The pH was 6.98, this is slightly acidic and it is a little higher than the WHO range of 6.5 – 6.85. pH level of water is an important index in determining the acidity and alkalinity of water. It provides an important piece of information in many various geological equilibriums or solubility calculations (Edward, 2016). Through the pH was slightly above the range recommended by WHO, but it aligns with the assumption of APHA (2018) that natural water has pH values in the range of 4 to 9 and most are slightly basic due to the presence of bicarbonate and carbonates of alkali and alkaline earth metals.

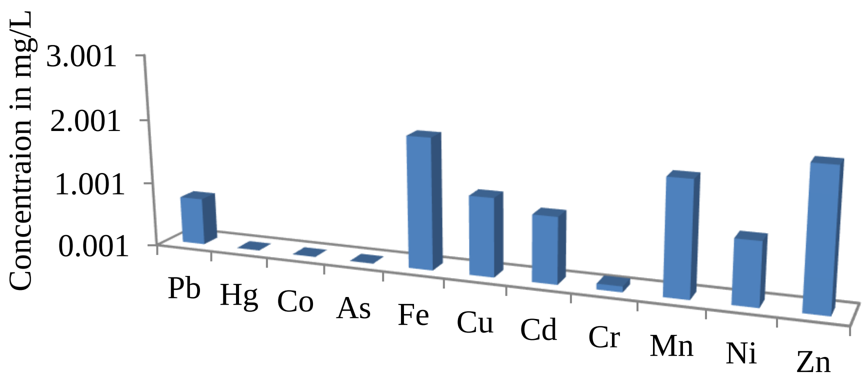

Fig. 2: Heavy Metal Constituents in Surface Water

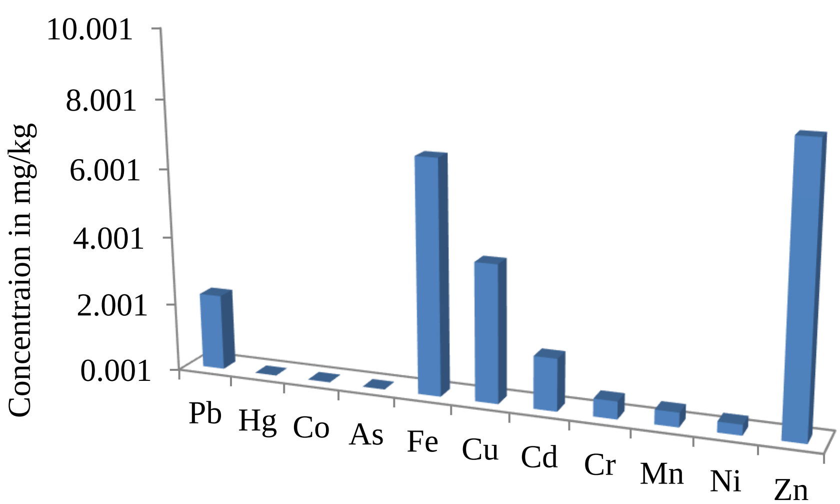

Fig. 3: Heavy Metal Constituents in Sediment

The result obtained from the analysis indicated that the sample had a turbidity of 5.14 NTU which is out of range concerning the standard limit (5 NTU) set by WHO (2019) for drinking water.

Electrical Conductivity (EC) is a direct function of its total dissolved salts. In this study, the value of EC (25 µs/cm) was within the accepted value set by WHO as shown in the results in Tables 2 and 3. Water with high conductivity may cause corrosion of the metal surface of equipment such as a boiler; the effect is also applicable to home appliances such as water heater systems and faucets. Dissolved Oxygen is a very important water quality parameter and also an index of physical and biological processes going on in water. The result was 4.6 mg/L, which is lower than the WHO limit of 5 m /L. Water low in dissolved oxygen has an unpleasant smell while waters high in dissolved oxygen are good for drinking purposes (Iqbal *et al*. 2019). Total Dissolved Solid (TDS) present in the water sample was 18.3 mg/L as shown in Tables 2 and 3. The value is within the 250 mg/L recommended by WHO. Water with a high dissolved solid is generally of lower palatability and may induce an unfavourable physiological reaction in the consumer, high concentration of dissolved solid in water is also responsible for hardness, turbidity, odour, taste, colour and alkalinity (Golterman, 2018).

Results from the analysis revealed that the sample has a Total Suspended Solid (TSS) value of 0.008 mg/L as shown in Tables 2 and 3. This is negligible compared to the WHO standard limit of 1500 mg/L. This result portrays that the water of Issiet Ekim stream is safe for consumption in terms of TSS and helps in checking pollution as high TSS increases the extent of pollution and also accounts for odour and colour (Golterman, 2018).

Salinity as Chloride (Cl^-) ion is present in appreciable amounts in all natural waters, the water sample contained chloride ions at a concentration of 17.55 mg/L, which is within the WHO recommended value of 250 mg/L. The 17.55 mg/L portrays that the water is not polluted from salinity as Chloride (Cl^-) ion. Ademorati (2019) postulated that excess chlorides in water can cause pollution and is usually taken as an index of pollution and natural levels in rivers and other fresh waters are usually in the range of 15-35 mg/L.

The result from the water samples revealed that it has a total alkalinity of 15 mg/L as shown in Tables 2 and 3. The result is lower than the 200 mg/L set as standard by WHO. It is close to the result of bi-carbonate, which was 18.3 mg/L, and the closeness corresponds with the postulation of Verma *et al*. (2019) which state that the change in alkalinity depends on carbonates and bicarbonates, which in turn depend upon release of CO_2 within the water environment.

It was observed that the amount of bi-carbonate (18.3 mg/L) was below the standard limit of 30 – 400 mg/L as given by WHO, this means that the water of Issiet Ekim stream was not polluted by bi-carbonate. This could emanate from the fact that the area is not rich in limestone. The presence of bi-carbonate at acceptable level is beneficial as it increase capacity of water to neutralize or buffer acids.

3.2.2 Water Quality of the Issiet Ekim Stream

The overall water quality index (WQI) value of 17.5421 as shown in Table 3 is an indication that the quality of the stream was safe for drinking concerning the physicochemical parameters studied as the value (17.5421) fall within the range of 0 - 25 classification, which signifies excellent water quality as shown in Table 1.

3.2.3 Heavy Metal Analysis

The results obtained from determining the concentrations of the eleven heavy metals (Pb, Hg, Co, Ar, Fe, Cu, Cd, Cr, Mn, Ni and Zn) are presented in Fig. 2 and Fig. 3. From the results, the following concentrations in mg/L were obtained from the water sample (Pb = 0.729, Hg = 0.001, Co = 0.003, As = 0.001, Fe =

2.016, Cu = 1.203, Cd = 1.016, Cr = 0.089, Mn = 1.745, Ni = 0.962 and Zn = 2.108) as presented in Fig. 2. From the sediment result, the concentrations (mg/kg) of the metals were Pb = 2.218, Hg = 0.001, Co = 0.008, As = 0.001, Fe = 6.824, Cu = 4.012, Cd = 1.525, Cr = 0.517, Mn = 0.423, Ni = 0.310 and Zn = 8.114 as presented in Fig. 3. From the result, Hg and As exhibited the same concentrations of 0.001 mg/L and 0.001 mg/kg respectively for both water and sediment. The concentrations of metals in the sediment were higher ($p \leq 0.05$) than in the water with the exemption of Mn and Ni where the concentration of 0.423 mg/kg (Mn) and 0.310 mg/kg (Ni) in the sediment were lower than the 1.745 mg/L and 0.962 mg/L respectively in the water. Higher concentration of metals in sediment compared to water was also observed and reported by Adakole and Abolude (2012), when heavy metal status of River kubanni Dam in sediment and water columns was studied. It also aligns with the postulation by Butu and Ati (2013) that sediments in aquatic environment serve as pool that can retain and release metals to the water column. The high levels of some of these heavy metals in the sample especially in the sediment could result from accumulated effect of continuous release and deposition of wastes materials containing these metals through run-off from land and direct dumping of wastes. This is in line with the conclusion of Nwajei *et al.*(2007). It could also emanate from oil spillage as the area is close to an oil well in the nearby community.

In the water, the concentrations (mg/L) 0.729, 2.016, 1.016, 0.089, 1.745 and 0.962 for Pb, Fe, Cd, Cr, Mn and Ni as presented in Fig. 2 are higher than the WHO limits of 0.01, 0.3, 0.003, 0.05 0.5 and 0.02 respectively. The higher concentration of these metals in the water compared to the WHO standard limit is an indication that these metals have polluted the water. The higher concentration of metals in the water compared to the WHO standard is consistent with the result obtained by Adakole and Abolude (2012) and Garba, *et al*. (2014), where the range of concentrations measured exceeded the standard limit.

In the sediment, the concentrations (mg/kg) for As (0.001), Cr (0.517), Cu (4.012), Pb (2.218), Hg (0.001), Ni (0.310), Zn (8.114) and Mn (0.423) as presented in Fig. 3 are within the Threshold Effect Level (TEL**)** (mg/kg) of 5.9, 37.3, 35.7, 35, 0.174. 18, 123 and 460 respectively as given by the United State Environmental Agency (USEPA), 1997; MacDonald *et al*. (2000) and Peiyue *et al*. (2014).

The predominance in concentration (mg/L) of the metals in water descends with the following order: Zn (2.108) > Fe (2.016) > Mn (1.745) > Cu (1.203) > Cd (1.016), Ni (0.962), Pb (0.729), Cr (0.089), Co (0.003), Hg (0.001) = As (0.001) as presented in Fig. 2. In sediment, the concentration (mg/kg) was observed to flow in the order: Zn (8.114) > Fe (6.824) > Cu (4.012) > Pb (2.218), > Cd (1.525) > Cr (0.517) > Mn (0.423) > Ni (0.310) > Co (0.008), Hg (0.001) = As (0.001) as presented in Fig. 3. Zn exhibited highest concentration in both water and sediment, however, its highest concentrations of 2.108 mg/L in water and 8.114mg/kg in sediment were below the 3 mg/L and 121 mg/kg WHO standard for drinking water and USEPA (1999) standard for sediment respectively. Metal concentrations in the sediment and in the water were subjected to correlation analysis, the coefficient of correlation (r) was 0.752. This high positive correlation suggests that sources of metals in sediment and in water were somehow the same (Uzairu, 2009; Okon *et al*., 2021).

4.0 Conclusion

This study assessed the physicochemical parameters and heavy metals of surface water and sediment from the Issiet Ekim stream in Uruan Local Government Area, Akwa Ibom State, Nigeria. The results showed that most of the physicochemical parameters were within the WHO recommended limits except for pH (6.98), which was slightly above the recommended range (6.5-8.5). The overall water quality index (WQI) value of 17.5421 indicated that the stream water was safe for drinking concerning the physicochemical parameters studied.

The concentrations of heavy metals in the sediment were higher than those in the water except Mn and Ni. Although some of the metals (Pb, Fe, Cd, Cr, Mn and Ni) in the water exceeded WHO limits, their concentrations in the sediment were within the USEPA Threshold Effect Level (TEL) except for Cu. The high positive correlation between the metal concentrations in the water and sediment suggests a common source for the metals. The higher levels of some heavy metals in the sediment could be due to accumulated effects from continuous release of pollutants from anthropogenic activities.

The results suggest that the Issiet Ekim stream is slightly polluted with some heavy metals, but the water is still safe for drinking based on the physicochemical parameters. However, continuous monitoring of the stream is recommended to assess the long-term impact of these pollutants.

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Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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