



DETERMINATION OF THE CONCENTRATIONS OF PHYSICOCHEMICAL PARAMETERS AND TRACE METALS IN THE NEW CALABAR RIVER

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Abstract

The concentration of trace metals in the surface water and sediments collected during the dry season at three different locations from the New Calabar river Port Harcourt Metropolis, Rivers State, Nigeria were determined using AAS and the physicochemical parameters were analyzed with standard methods for their corresponding mean values in the surface water and sediment samples, the heavy metals in the surface water was Cu > Zn > Pb > Cr > Ni > Cd and in the sediment Zn > Cu > Cr > Pb > Cd. These results obtained were compared to the given standards by (NESREA) and guidelines of (WHO). It was observed that the result obtained exceeded the permissible limits except those of nitrates, sulphates, dissolved oxygen, turbidity and pH. Relevant agency should put in place proactive measure in creating awareness to the public of the danger to human lives from the consumption of biota through the food chain.

Keywords: Trace metals, Physicochemical parameters, Biochemical oxygen demand, Turbidity

Introduction

Industrial development has led to rapid growth in socio-economic progress. The consequences of this growth, caused by the increase in population and the human need for survival, have led to an increase in agricultural, domestic and industrial activities, which has resulted in widespread contamination problems from spilt chemicals or product production. Wastewater resulting from the Oil processing and petrochemical industries is released into our rivers or estuaries, which are characterized by the presence of large amounts of polycyclic aromatic hydrocarbons, metal derivatives, nutrients and other chemicals (Marcus & Ekpete, 2014). The congestion of seas, coastal waters, lakes and rivers with nutrients such as nitrogen and phosphorus has led to some side effects generally termed eutrophication. In cases of severe eutrophication, a massive flowering of plankton algae occurs and some bloom is poisonous. Dead algae decompose, the oxygen in the water is depleted; seabed animals and fish die or leave the affected area. Increased nutrient concentrations can also lead to changes in aquatic vegetation. The imbalanced ecosystem and the altered chemical composition make the body of water unsuitable for recreation and other uses such as fish farming and the water is no longer drinkable.

Many social activities result in the release of nutrients into the aquatic environment like sewage discharge from households and industry. Nutrient losses from agriculture and fish farming also come from point sources and sparsely populated areas. The effects of excessive nutrient pollution are particularly evident in groundwater, lakes, large, low-flow rivers, estuaries, coastal and offshore waters (USA Environmental Protection Agency, 2015). Surface runoff due to soil erosion, logging has led to an increase in the input of domestic wastewater causing the increase in the physicochemical parameters and extensive contamination of the aquatic environment. Living organisms can be affected by the bioaccumulation of PAHs in the water depending and this can pose a threat to the lives and livelihoods of the local community (Barron, (2012). Therefore, research was undertaken to determine the levels of physicochemical parameters and trace metals in water and sediment samples from the New Calabar River.

Materials and Methods

Study Area

Sample collection for Physicochemical Parameters and Trace Metals in Surface Water

Water samples were collected under the surface film with pre-washed 1L plastic containers for analysis of physicochemical parameters and trace metals, surface water samples were collected at three locations along the river to obtain a representative sample in plastic containers of 1L that were previously leached with 1 ml HCl and rinse with distilled water.

The samples for the analysis of trace metals in water were treated with 2 ml of concentrated nitric acid before you storage to maintain stable oxidation states of the metals in the frozen state and also to avoid the adsorption of metals in the container in front of the analytical laboratory (APHA) Samples were also in Periods from low tide to medium-low tide are taken to ensure that the influence outside the point source and not the receiving water body seeks minimal changes in the sample during storage.

Those for organic oxygen demand (BOD₅), chemical oxygen demand (COD) and dissolved oxygen (DO) had been gathered in 250 ml glass stoppered reagent bottles. The BOD₅ samples had been cautiously crammed without trapping in air and the bottles were wrapped with darkish polythene baggage and incubated for five days to exclude all light, the presence of which is capable of producing DO by autotrophs (algae) presumably present in the sample. Dissolved oxygen (DO) samples were fixed at the spot with Winkler solutions I and II. The COD samples were acidified with tetraoxosulphate (VI) acid (APHA, 2005). Sample Preparation and Extraction for Physicochemical and Trace Metals

Solvent extraction the use of ammonium pyrrolidinedithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) became hired for coaching of water samples. The samples for evaluation of the fundamental cations had been organized through acid digestion the use of 1:3:1 aggregate of HClO₄, HNO₃ and H₂SO₄ acids. Trace metals within side the floor water samples had been decided the use of a process of USEPA, (2003). Each floor water pattern became filtered the use of Whatman No.1 clear out paper and 500 ml of the filtrate became measured into six hundred ml beaker and evaporated to dryness at 105oC in an oven. The residue became dissolved in 10 ml 1:1 HNO₃, HClO₄ and located over a steam tub for half-hour and then it became quantitatively filtered right into a 25 ml popular flask the use of Whatman No.1 clear out paper.

Determination of the main cations in surface waters

water samples were treated with a 1: 3: 1 mixture of the acids HClO₄, HNO₃ and H₂SO₄ and pre-concentrated samples were used to determine the main cations in water. Serially diluted mixed standard solutions containing 1.00 mg of the metal. The ion in 1 ml of the solution was prepared by pipetting appropriate volumes of commercially purchased stock solutions (BDH Chemicals) into a standard 250 ml single flask. The concentrations of each metal ion were read against the standards on the Thermo-Elemental Solar Atomic Absorption Spectrophotometer used for trace metals.

Other water quality parameters

The determination of pH, temperature, conductivity and total content of dissolved substances in the surface water and sediment samples was carried out at the sampling point with a well-calibrated HANNA device type DI 4337 in strict compliance with the instructions in the operating instructions, COD (titrimetry), DO, BOD₅, according to the Winkler method, turbidity with the portable Hach model 2100P ISO turbidity meter, nitrate with the colorimetric method with the Harch 3900 Dr spectrometer and sulfate with turbidimetry (APHA, 2005).

Statistical Data Analysis and Quality Control studies

Numerical analysis was done using the analysis of variance (ANOVA) to examine if there was a significant difference among the three stations in the new Calabar rivers at 90% (p =0.05). Physicochemical Parameters in the surface water and sediment of the New Calabar River. As shown in Table 1 the hydrogen ion concentration of the surface water ranged from (6.45 to 6.59) across the locations with a mean pH value of 6.51 ±0.0211 respectively. The values were slightly acidic which could be accounted for the anthropogenic activities taking place at the locations. It was below the National Environmental Standards and Regulations Enforcement Agency (NESREA) acceptable limit of pH 6.0-9.0 for the discharge of wastewater into surface water. It is lower than that reported by Marcus and Ekpete, (2014) who stated a mean pH value of 7.45 ±0.31 in the effluent from the refinery area, Okrika Port Harcourt.

Results and Discussion

Table 1. Concentrations of physicochemical parameters and trace metals in surface water.

Parameters	Abonema wharf	Master Energy jetty	Pelfacoiwofe jetty	Mean water	Surface	WHO (2011)	NESREA, (2009)
pH	6.50	6.45	6.59	6.51 ± 0.071		6.5-8.5	6.0 – 8.5
Temperature °C	31°C	30.5°C	30.6°C	30.7 ± 0.265		30°C	< 40°C
Conductivity (µscm ⁻¹)	13784	30100	29800	29,156 ±	1350.11	600	400
Chloride (mg/l)	4,255	4450	3802	4169 ±	332.45	200	-
BOD ₅ mg/l	10.75	14.87	11.00	12.21 ±	2.31	10	30
COD mg/l	16.00	22.30	16.50	18.27 ±	3.502	40	250
DO mg/l	5.50	6.15	6.05	5.90 ±	0.35	<7.5	7.50
Turbidity (NTU)	14.5	16.55	18.00	16.35 ±	1.159	15	20
TDS mg/l	13784	15,050	14900	14578 ±	591.43	2000	2100
NO ₃ ⁻	0.26	4.15	1.90	2.13 ±	1.953	45	20
(SO ₄ ²⁻)	16.5	2.80	2.50	7.270 ±	7.997	200	500
Salinity %	7020.8	7345	6270	6878.6 ±	551.43	50	-
TSS mg/l	27.5	32.50	36.00	32.00 ±	4.27	30	-
Cd ²⁺ mg/l	0.108	0.81	0.75	0.56 ±	0.389	0.05	<0.10
Cr ³⁺ mg/l	3.95	2.35	2.35	2.88 ±	0.924	0.05	<0.05
Cu ²⁺ mg/l	5.7	3.55	3.20	4.15 ±	1.354	1.5	-
Ni ²⁺ mg/l	2.65	3.10	1.50	2.42 ±	0.231	0.03	<1.00
Pb ²⁺ mg/l	3.25	2.85	2.85	2.983 ±	0.231	0.05	<0.01
Zn ²⁺ mg/l	4.95	2.50	2.30	3.25 ±	1.476	0.05	<1.00

The pH of water is important because taste, corrosiveness, and the effectiveness of chlorination and coagulation in treatment processes are affected. Aquatic ecosystems also are influenced by pH and in general, pH alone is not a problem, but the combination of pH with temperature, dissolved oxygen, and the presence of various ions could pose a significant problem. Some compounds are more toxic to the aquatic organisms at different pH values, for example, the toxicity of nickel cyanide increases as the pH value decreases (Shallcross et al., 2014).

The average temperature ranged from 30.50°C to 31°C across the sampling sites, with a mean temperature of (30.7 ± 0.265°C) in the surface water. This value is within the maximum permissible limit set by the National Environmental Standards and Regulations Enforcement Agency (NESREA) at 40 °C. It is observed that the relatively high temperature affects the chemical and biological properties of the surface water and also increases the solubility as more solute dissolves and the amount of dissolved oxygen available to the water decreased promoting the overgrowth of aquatic plants and algae and thus intensifies an increase in the toxicity of pollutants (Diya 'udden et al., 2014).

The high conductivity values recorded in this study is therefore indicative of the presence of a high concentration of dissolved ions which could be attributed to a large number of chemicals due to the anthropogenic activities taking place like boat transportation. The electrical conductivities of the surface water ranged from 13784 to 30100 µs/cm. In table 2 the values are higher than the permissible limit of 600 µs/cm and the NESREA acceptable limit for the wastewater into surface water at 400 µs/cm. It has been reported that waters with conductivity values below 1000 µs/cm are fresh while those with values above 40,000 µs/cm- indicate the marine nature of the water and those between these two limits are brackish waters (Egborge, 1994).

Turbidity which is a measure of the cloudiness of a liquid as a result of particulate matter being suspended within. It is often associated with higher levels of disease-causing microorganisms such as bacteria and other parasites (Shittu et al., 2008). The turbidities of the surface water ranged from 16.0- 18.0 NTU across the sampling sites with a mean Turbidity of the surface water observed as (16.35 ± 1.759 NTU) whose value was higher than the WHO (2011) maximum permissible limit of 15.00 mg/l.

A high TDS value increases the salt content of the water and can therefore make it unhealthy for drinking and irrigation purposes (UNIDO, 2000), although fish can slowly get used to higher TDS concentrations than usual (Reddy and Subba, 2001). This makes discharges of sewage into surface water harmful, and consumption of water with high concentrations of TDS has reportedly caused digestive, respiratory, nervous, and coronary disorders, as well as miscarriages and cancer. TDS in water is a problem for water utilities as it changes the taste and a high concentration of TDS also exerts osmotic pressure in water purification systems in hospitals, industries and on the stream ecosystem (UNIDO, 2000).

The total dissolved solids (TDS) of the surface water ranged at a value of 13,784 to 15,050 mg/L across the sampling sites with a mean value of 14578 ± 591.702 mg/L as shown in Table 1. The high concentrations of total dissolved solids from the master Energy (15,050mg/L) and Abonema wharf jetty (13784mg/L) suggest intense anthropogenic solids in the activities in the water samples (UNESCO/WHO/UNED, 2001).

The total suspended solids (TSS) of the surface water were highest for the Pelfaco Iwofe jetty 36mg/L and lowest at the Abonema wharf with a value of 27.5mg/L. The Pelfaco Iwofe Jetty values are higher than the WHO maximum permissible limit of 30mg/L. The value of salinity in water sample was higher than the values of the WHO permissible limit of 50mg/l which could be attributed to the high TDS values which increase the salinity of the water and thus rendered it unhealthy for drinking and irrigation purposes.

Nitrate and nitrite ions are naturally part of the nitrogen cycle. Nitrate values of the studied areas were well within the permissible limits of WHO (2011) that is 45mg/L and 10mg/L for NESREA (2009). The mean concentration was observed as 2.103 ± 1.953 mg/l. Most of the nitrates and nitrites found in the water were a result of biological activity going on in it. Under the right condition, most of the organic nitrogen is decomposed into ammonia which then oxidizes the ammonia to nitrite and finally to nitrate by bacteria thus nitrates are very often the most predominant nitrogen compound in any water body (Okieimen et al., 2012). Nitrate ion in water is undesirable because it can cause methaemoglobinaemia in infants less than 6months old as reported by UNESCO/WHO/UNEP, (2003).

The concentration of sulphate which is naturally present in surface water as SO_4^{2-} in Abonema wharf, Master Energy and Pelfaco Iwofe jetties are 16.5, 2.80 and 2.50 mg/L respectively. These values are below the NESREA and WHO values of 200mg/L. A high concentration of sulphate is associated with respiratory illness and laxative effect which may contribute to the corrosion of distribution systems (Shivaraju, 2012; Subin & Husna, 2013). The mean results obtained in the present study (7.27 ± 7.997 mg/L) showed that sulphate content in surface water was low and discharges into the flowing water may not pose serious adverse health effects.

The high concentration of chloride observed in all the sampling points is worrisome because high chloride makes the water unpalatable and therefore, unfit for drinking or livestock watering. The chloride of the surface water ranged from 3802 to 4450mg/l across the sampling sites with a mean chloride value of 4169 ± 332.45 mg/L as shown in Table 1, this value is higher than the WHO maximum permissible limit of 200mg/L.

The dissolved oxygen (DO) of the surface water ranged from 5.50 to 6.15 mg /l at the sampling points, with a mean DO in the surface water of 5.90 ± 0.35 mg / L as shown in Table 1, whose value was higher than the observed 3.73 ± 0.29 mg /l in wastewater from the Okrika Port Harcourt refinery area (Marcus & Ekpete, 2014). The DO reported was below the acceptable limits of the National Environmental Standards and Regulatory Enforcement Agency (NESREA) of 7.5 mg / L. Oxygen molecules dissolve in water and are measured as dissolved oxygen. The presence of dissolved oxygen in lakes and rivers is good for the survival of most aquatic plants as they depend on adequate oxygen levels. It is therefore a good indicator of healthy water quality (Bhiyan et al., 2010).

From Table 1, the Biochemical Oxygen Demand (BOD) of the surface water ranged at a value of 10.75 to 14.87mg/L across the sampling sites with a mean BOD in surface water observed as 12.21 ± 2.31 mg/L, whose value was higher than the reported value of 3.30 mg/L by Okieimen et al., (2012) and WHO permissible limits of 10mg/L. BOD which is a very important water quality parameter that is used to evaluate organic pollution of surface water or pollution potential of effluent depends on the; concentration of organic matter, extent of biological activities, temperature and other related factors and the desirable limit for BOD is 4.0 mg/L, while values below the 3 mg/L is required for the best use of water (Kumar et al., 2010). Discharge of effluent with a

high oxygen demand directly into surface water, overloads the sensitive balance maintained in the water and oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to live so therefore, dissolved oxygen depletion in water can encourage microbial reduction of nitrates to nitrites and sulphate to sulphide giving rise to odour problems (Udiba et al., 2014).

The Chemical Oxygen Demand (COD) of the surface water ranged from 16 to 22.30mg/L across the sampling sites with a mean COD in surface water observed as 18.27 ± 3.502 mg/L. It is another parameter used to assess the Oxygen demands of wastewater (Noorjahan & Jamuna, 2012). COD does not differentiate between biologically available and inert organic matter, since nearly all organic compounds are oxidized in the COD test, the results are always higher than BOD results; this was confirmed in this study and, also higher value was observed as 896.3 mg/l for brewery effluents from Ibadan, Nigeria (Alao et al., 2010). Discharge of effluent with high oxygen demand into receiving waterbodies impact it adversely.

The concentrations of cadmium is 0.108, 0.81 and 0.75mg/L for Abonema Wharf, Master energy and PelfacoIwofe Jetties respectively. These values are however above the permissible limit of NESREA (2009) and WHO (2011) of <0.10 and 0.05mg/L respectively. The concentration of chromium in the surface water was 2.35 to 3.95mg/L. these values were higher than those reported by WHO (2011). The concentration of copper (Cu) in the surface water was observed as 3.20 to 5.70mg/L with a mean value of 4.15 ± 1.354 mg/L. These values were lower than the values obtained by Kpee et al., (2009) 18.48 from water from Ipo stream, Rivers State.

Nickel concentration varied from 1.50 to 3.10 mg/L with mean values of 2.42 ± 0.23 mg/L. these values were higher than the recommended value of 0.03mg/L by the World Health Organization (2011). Nickel is necessary in many organisms' diets but can be carcinogenic and toxic in high doses. Women are more commonly allergic to nickel exposure than men. Exposure to skin can cause dermatitis upon contact.

Textural Quality (Silt, Sand and Clay)

The sediment samples in this study were determined by sand particles of fine and medium size. The percentage levels of silt, sand, clay in sediment samples ranged at a value of 9 to 10%, 78 to 81% and 11 to 13% respectively with a mean level of 9 ± 1 , 79.33 ± 1.53 and 11.204 ± 3.101 respectively as shown in Table 2, and the distribution pattern is silt > clay > sand, these particle size play an important role in nutrient accumulation in the sediments, because fine- grained particles often have greater surface to volume ratio and more organic matter. Sediment grain size and organic matter content are two critical factors that affect their distribution and the level of pollution.

Total Organic Carbon (TOC), Total Organic Matter (TOM), Total Nitrogen

The estimated values of organic matter were at a value of (13.99%) in the sediment samples as shown in Table 2, the sediment samples in this study were determined by total organic carbon (TOC), total organic matter (TOM), total nitrogen and the percentage levels were observed as 3.65 to 5.261 %, 7.484 to 9.511% and 0.233 to 0.263% respectively with a mean level of 4.554 ± 0.82 , 8.1903 ± 0.8071 and 0.241 ± 0.0202 respectively and the total mean of 13.99 ± 1.6344 . This is considered to be low, and its implication can be the reason for the general high levels of the trace metals in the sediment, since organic matter content of river sediments has been shown in literature to be an important factor to determine the extent of sorption and low organic matter content is also attributed to low pH (Marcus et al., 2013).

Metal Concentration of the surface water and sediment

Trace metal levels are very important in pollution studies and in setting up water quality criteria. The mean levels of trace metal in surface water and sediment across sampling locations varied from one point to another and the results are presented in Table 1 and 2 respectively. The distribution pattern of the total mean levels of trace metals in surface water was Cu > Zn > Pb > Cr > Ni > Cd and in the sediment Zn > Cr > Cu > Pb > Cd.

Concentrations of Zinc in Surface Water and Sediment Samples

The mean zinc levels at the sampling sites varied by a values of 3.25 ± 1.476 mg / L to 11.204 ± 3.101 mg / L as shown in Tables 1 and 2. The zinc observed in this study was lower than the observed value of 2.670 to 6.417 mg / kg by Ekpete and Festus, (2013). The relative low concentration in water sample of the river may indicate low agricultural activity, car emissions and the lack of propagation of strong winds in the sites. In sediment samples, Zinc (Zn²⁺) had a high concentration in all examined locations with a range of 7.811 to 13.891 mg / kg and a mean value of 11.204 ± 3.101 , the highest concentration was recorded at Abonema Wharf Jetty,

followed by Pelfaco, Iwofe Jetty and Master Energy, Saipem Jetty. The high concentration of zinc ion (Zn^{2+}) is expected since it readily hydrates and combines with other metals to form its ores and a higher concentration value of Zn^{2+} was observed in this study than those value reported by Okezie et al., (2020) observed as (1.215 to 1.185mg/kg). A one-way analysis of variance showed a significant difference at $p < 0.05$ in the mean value of Zinc ion (Zn^{2+}) in the surface water and sediment sample across the three sampling locations. Zinc is a natural component of the earth's crust and most zinc compounds found in nature are water-soluble. The metal is vital for plants and animals, but is poisonous in high concentrations. It is configured to minimize the potential phytotoxicity of irrigation waters due to the presence of zinc and is also an intestinal irritant, meaning that the first sign of zinc poisoning is usually intestinal discomfort such as vomiting, stomach cramps, diarrhea, and nausea, but other symptoms of zinc poisoning is low blood pressure, urinary retention, jaundice, seizures, joint pain, fever, cough and metallic taste in the mouth as well as induced copper deficiency (Udiba et al., 2014).

Concentrations of Lead in Surface Water and Sediment Samples

The concentration values of lead ion (Pb^{2+}) observed as 2.85 to 3.25mg/kg with mean values of 2.983 ± 0.231 for the surface water as shown in Table 1 and in sediment the concentration values of lead ion (Pb^{2+}) observed as 4.611 to 9.511mg/kg with mean values of 7.335 ± 2.496 mg/kg. The concentration of lead was observed to be higher than 1.51 to 1.890mg/kg reported by Okezie et al., (2020) and 1.472 ± 1.314 mg/kg reported by Ekpete and Festus, (2013). A one-way analysis of variance showed no significant difference at $p > 0.05$ in the mean value of lead ion (Pb^{2+}) in the surface water but showed a significant difference at $p < 0.05$ in the sediment sample across the three sampling locations. Lead is a natural constituent of the earth crust, it is the most abundant among the heavy metals with an atomic number > 60 and given the evidence from solution culture of potential direct lead toxicity to plants, the long-term trigger values and Short-term trigger values have been set in order to minimize these risks of lead exposure in young children which has been linked to learning disabilities. Lead affects both the male and female reproductive systems. When blood lead levels exceed 40 mcg / dL, sperm count is reduced, resulting in changes in sperm volume, motility and morphology, while high blood lead in a pregnant woman can cause miscarriages. Premature labor, low birth weight, and developmental difficulties in childhood. In addition, kidney damage, pain, muscle weakness, paresthesia occur with high levels of lead exposure and acute poisoning (Pearce, 2007).

Concentrations of Chromium in Surface Water and Sediment Samples

The concentration values of Chromium ion Cr^{2+} in the surface water was observed as 2.35 to 3.95mg/kg as shown in (Table 1) with mean values of 3.25 ± 1.476 and the concentration values in the sediment sample was observed as 6.587 to 9.694mg/kg with mean values of 7.931 ± 1.667 as shown in (Table 2). The concentration levels of chromium observed at 2.35 to 3.95mg/kg, were higher than those reported at by Marcus and Ekpete, (2014) observed as 0.1mg/kg and were above the World Health Organization (WHO) permissible limits while, in the sediment the concentration levels of Chromium ion Cr^{2+} was observed as 7.931 ± 1.667 were higher than those reported by Ekpete and Festus, (2013) observed as (0.049 to 1.354mg/kg). A one-way analysis of variance showed a significant difference at $p < 0.05$ in the mean value of Chromium ion Cr^{2+} in the surface water but showed no significant difference at $p > 0.05$ in the sediment sample across the three sampling locations. Chromium is known in all oxidation states from -2 to +6, with +3 (chromic) and +6 (chromate) being the most common. There is no evidence that the metal is essential to plants, although traces of it are essential for humans and animals. In general, there should be few problems associated with discharges to land of wastewaters (e.g., from tanneries) containing chromium (III) because this form of chromium is reported to be relatively non mobile and studies with nutrient solutions indicate that there may be some direct phytotoxic effect on irrigated crops of chromium in irrigation waters. Concentrations of 1–10 mg/L in nutrient solutions reduce crop yield, depending on the tolerance of different plant species and there is limited evidence that chromium (III) and chromium (VI) in nutrient solutions are about equally available to plants (ANZECC, 2009).

Concentrations of Cadmium in Surface Water and Sediment Samples

The concentration values of Cadmium ion Cd^{2+} concentrations in the surface water were observed as 0.108 to 0.81mg/kg with mean value of 0.56 ± 0.389 as shown in Table 1 and the concentrations values of Cadmium ion Cd^{2+} in the sediment was observed as 1.497 to 2.801mg/kg with mean value of 1.996 ± 0.704 as shown in Table 2. The concentration values of cadmium observed at 0.56 ± 0.389 , were higher than those reported by Marcus and Ekpete, (2014) observed as (0.13mg/kg) and it was above the World Health Organization (WHO) permissible limits of 0.05mg/L while, in the sediment the concentration values of cadmium ion were observed as 1.996 ± 0.704 were higher than those reported by Ekpete and Festus, (2013) observed as (0.049 to

1.354mg/kg). A one-way analysis of variance showed no significant difference at $p > 0.05$ in the mean value of Cadmium ion Cd^{2+} in the surface water but showed a significant difference at $p < 0.05$ in the sediment sample across the three sampling locations. Cadmium salts with strong acids are easily soluble in water a toxic to both animals and plants at minute concentration. Research also suggests that carcinogenicity is also possible. Consumption of food or drinking water with a high concentration of cadmium irritates the stomach causing vomiting, and diarrhea. Chronic exposure can also cause irreversible damage to the lungs (Udiba et al., 2014).

Concentrations of Copper in Surface Water and Sediment Samples

From Table 1, the concentration of copper ion (Cu^{2+}) in the surface water was observed as 3.20 to 5.70mg/kg with a mean value of 4.15 ± 1.354 . The highest concentration was recorded at the Abonema Wharf Jetty followed by Master Energy, Saipem Jetty before Pelfaco, Iwofe Jetty. Higher concentration level of Cu^{2+} was observed in this study than that reported by Ekpete and Festus, (2013) observed as (0.046 to 2.723mg/kg). Copper ion (Cu^{2+}) concentration values in the sediment was observed as 5.891 to 10.711mg/kg with mean levels of 7.991 ± 2469 as shown in Table 2. The concentration values of copper observed was higher than those reported by Okezie et al., (2020) observed as (1.51 to 1.890mg/kg) and those reported by Ekpete and Festus, (2013) observed as (1.124 ± 0.672 mg/kg). The relatively high concentrations observed could be attributed to higher levels of automobile emission and of heavy wind dispersion around the locations. A one-way analysis of variance showed a significant difference at $p < 0.05$ in the mean value of Copper ion (Cu^{2+}) in the surface water and sediment sample across the three sampling locations.

Concentrations of Nickel in Surface Water Samples

The concentration of Nickel ion Ni^{2+} in the surface water was observed as 1.50 to 3.10mg/kg with mean values of 2.42 ± 0.231 as shown in (Table 1), The concentration values was observed to be lower than those reported by Marcus and Ekpete, (2014) observed as (57.194 ± 16.929) and were above the permissible limits of the World Health Organization (WHO). A one-way analysis of variance showed a significant difference at $p < 0.05$ in the mean value of Nickel ion Ni^{2+} in the surface water across the three sampling locations.

Conclusion

This study does indicate serious pollution or contamination risk on the new Calabar river and the relatively high concentration of heavy metals which affects the physicochemical quality of the river by energy generation and the incomplete combustion of fossil fuel which is a continuous exercise and this should be checked so as to prevent bioaccumulation by aquatic organism thereby causing harm to humans when it enters into the food chain.

Recommendation

It is recommended that all the activities contributing to the increased pollution in the area should be brought under control, so as to keep the environment safe for aquatic organisms and human lives that benefit from them along the food chain.

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