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Pollution Evaluation Based on Physicochemical and Heavy Metal Levels of Miniokoro Stream, Port Harcourt, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author DMA designed the study, wrote the second draft of the manuscript and managed the result/discussion session. Author MEA wrote the first draft of the manuscript and managed the literature searches. Author TCO managed the literature organization, supervised and interprets the field data statistically. Author MEA designed the study area, managed all graphical designs, organized manuscript and supervised the study. All authors read and approved the final manuscript.

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ABSTRACT

Evaluation of physicochemical parameters and heavy metal levels in surface water of the Miniokoro stream, Port Harcourt, Nigeria were investigated to determine its potability and pollution status at various stations along the stream. The physicochemical parameters analyzed in the water samples were: pH, Temperature, Salinity, Electrical conductivity, TDS, DO, BOD, Alkalinity, Chloride, NH_4^+ , NO_3^- , PO_4^{3-} , SO_4^{2-} while heavy metals such as Nickel, lead, Iron, Zinc and Chromium were analyzed using atomic absorption spectrophotometer. The results from the research showed an average concentration level of the physicochemical parameters such as pH (5.79-7.01), EC (136.43 - 960.67µS/cm), TDS (90.17 - 1517.67) and the spatial distribution of heavy metals: zinc (0.07 - 1.09mg/l), chromium (0.03 - 0.09mg/l), nickel (0.07 - 0.08mg/l) and iron (12.29 - 39.95mg/l). Water samples from various stations depicts the varying level of pollution along the stream when compared with national and international permissible limit. Thus, it suggests that the government

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should develop and implement an effective waste management plans due to environmental and other anthropogenic impacts on the stream.

Keywords: Water quality index; physicochemical; heavy metals; miniokoro stream.

1. INTRODUCTION

Water is known as an essential requirement for human and industrial developments which is one of the most delicate part of the environment [1]. Availability and quality of surface water vary seasonally from place to place and stratum to stratum depending on the topography gradient, intensity of rainfall and geological formation of an area [2]. However, in the past, there has been a tremendous increase in the demand for freshwater due to rapid growth of population and the accelerated pace of industrialization [3]. Thus, water bodies have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluents, agricultural run offs and bad fishing practices [4].

Water quality index is an important parameter for the assessment and management of water quality which provide information to citizen and policy makers [5]. It is defined as a rating reflecting the composite influence of different water quality parameters [6]. Since the quality of contaminated surface water cannot be restored by stopping the pollutants from the source [3]. Therefore, it's important to regularly monitor the water quality in order to conserve it. Records of study on the quality of surface water [7,8] have attributed the deterioration of the quality of surface waters to the deposition of heavy metals and toxic organic compounds probably from surface runoffs and indiscriminate dumping of refuse at river banks.

Heavy metal pollution is also а kev environmental problem because it can be bioaccumulated by organisms. In recent times, researchers have investigated the status of heavy metal concentration in surface water which revealed a high level of contamination of water bodies as a result of heavy metals release from run-off and other industrial activities [8-11]. Furthermore, studies on the physicochemical parameters of water bodies in the Niger Delta area of Nigeria which is known for its high industrial and oil exploration activities have also been carried out by several researchers [12-16]. These investigations revealed the urgency to protect the quality of water bodies for recreational, industrial and domestic uses.

Hence, this investigation aims at providing information on the physicochemical characteristics and heavy metal content in the Miniokoro Stream, Port Harcourt, Obio-Akpor Local Government Area of Rivers State, Nigeria in order to evaluate its water quality status.

2. STUDY AREA

The study was carried out on Miniokoro stream. Port Harcourt, in Obio/Akpor Local Government Area in Rivers State, Nigeria which lies between longitude 6°55 E to 7°00 E and latitude 4°30 S to 4°55' S and is accessible through networks of linked roads (Map 1) [17]. It is locally constituted by the people of Ikwerre Ethnic Nationality. There is also high volume of commercial activities due to the location of several corporate organizations within the area. Miniokoro stream drains freshwater swamp forest into Woji creek where it usually emptied into the Bonny estuary. The entire stream stretch is degraded and built up with concrete structures and paved roads. The stream is filled with various municipal wastes from nearby market trading, fish farming, building activities etc [7,18].

The stretch of the Miniokoro stream under study was divided into three sampling stations: upstream (station A latitude 04°52'15.7"N and longitude 007°59'64.7"E), midstream (station B latitude 04°52'12.8"N and longitude 006°59'58.8"E) and downstream (station C 04°52'14.6"N latitude and lonaitude 06°59'50.8"E) as shown in Map 1. The upstream reach is filled up with green algae with little or no wastes deposit in the water. The water surface of the midstream are filled with some waste as a result of anthropogenic activities around the stream. In the downstream, there were particles of disposed materials found on the water surface with some aquatic organisms. The geology of the area comprises basically of alluvial sedimentary basin and basement complex. The vegetation found in this area includes raffia palms, thick mangrove forest and light rain forest. The soil is usually sandy or sandy loam underlain by a layer of impervious pan which is leached due to the heavy rainfall experienced in this area [19].

3. METHODOLOGY

3.1 Sampling

Three sampling stations were established for the collection of surface water, the stations include the upstream (station A); midstream (station B) and downstream (station C). The water samples were collected at each station in triplicates into clean plastic sample bottles (2-liter and 30ml) once monthly for three months from October,

November and December, covering the dry season period. Few drops of concentrated HNO_3 were added for the preservation of each water sample prior to its heavy metal analysis. Eighteen (18) Amber Bottles were also used in collecting water samples for both the Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD). At each sampling station the DO is fixed at the field with five (5) drops of Winkler solutions respectively.



Map 1. Map of Rivers State showing the study area

3.2 Determination of Physicochemical Parameters

Quantitative analysis carried out on the water samples includes the following physicochemical parameters; Temperature (mercury filled Celsius thermometer), Electrical Conductivity (EC-TDS meter), Total Dissolved Solid (EC-TDS meter), Salinity and pH (Extech instrument DC 700 model). Phosphate (PO₄) (Stannous Chloride method). sulphate concentration (SO₄²⁻) (Turbidometric method), ammonium (NH₄), and nitrate (NO₃) (Brucine method), alkalinity was determined using sulfuric acid with a digital titrator while Chloride (CI⁻) concentration was determined by the argentometric titration method [20]. The Winkler method [20] was used in the determination of Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) levels in the water samples.

3.3 Heavy Metal Determination

The ion concentrations of heavy metals (Zn, Pb, Cr, Ni and Fe) of the water samples were determined using the Atomic Absorption Spectrophotometer (AAS) – Agilent AA SPECTRA 55B model. Stock solutions from which standards were prepared by serial dilution as reported by [21]. Standard graphs for the detected elements were prepared following procedures given by [22] and [23].

3.4 Calculation of Water Quality Index

This index was calculated using the Weighted Arithmetic Index method [5]. In this study, the WQI for drinking purposes is considered and permissible as 100 [6].

Overall
$$WQI = \frac{\sum Q_i W_i}{\sum W_i}$$

The Quality rating scale for each parameter (Q_i) were calculated using this expression:

$$Q_i = \left(\frac{C_i}{S_i}\right) \times 100$$

Where (C_i) is the concentration of each parameter and its respective standard (S_i) in the water sample. Also, the relative weight of parameter (W_i) was calculated using the expression below:

$$W_i = \frac{1}{S_i}$$

3.5 Statistical Analysis

The statistical analysis was done using Microsoft Excel 2013. Water quality index was calculated from the point of view of its suitability for human consumption [6].

4. RESULTS AND DISCUSSION

The average values of the physical parameters (pH, temperature, salinity, total dissolved solid, electrical conductivity), chemical parameters (alkalinity, phosphate, chloride, sulphate and nitrates) and biological/organic parameters (dissolved oxygen saturation and biochemical oxygen demand) of the surface water samples obtained from three stations (station A-C) along Miniokoro stream were analyzed and results presented in both Tables and Figures.

Table 1 shows the pH values of the stream ranging from 6.79 to 7.01 making station A slightly acidic than station C. pH of the stream water were within the acceptable limits required for potable water (6.5-8.5). [24-26] stated that microorganisms frequently change the pH of their own habitat by producing acidic or basic metabolic waste products.

Mean temperatures of the surface water ranged from 28.80 to 28.97° C. The highest temperature was recorded at station B. The temperature of the water samples were within permissible limit (25-30°C) which implies that there is no thermal pollution of the stream that could have affected the aquatic organisms inhabiting it.

From Table 1, the salinity of the water ranging between 0.06 - 1.04 showed an increased value at station B. This implied that there may be salt containing substance deposited at station B which possibly settles or decompose as the water flows along the stream. However, station A is less influenced by contaminant as compared to station B and C. Salinity affects water density i.e. the higher the dissolved salt concentration, the higher the density of water. Also, the higher the salinity level, the lower the dissolved oxygen concentration. These results also correspond to electrical conductivity (EC) of the study area which ranged from 136.43 to 960.67µS/cm. In terms of spatial distribution, these values were comparatively higher at the midstream stretch (station B) than at the downstream stretch (station C). Significant changes in the electrical conductivity of the stream could be attributed to: anthropogenic activities, temperature, dissolved salts and other inorganic chemicals which could

be an indicator that a discharge or some other source of pollution has entered the stream. This implies that station B is highly contaminated while station A has less contaminants thereby making it a preferred source of water for domestic and animal consumption.

The total dissolved solid (TDS) of the stream water varies between 90.17 -1517.67mg/L. There is a significant TDS deviation across the stations, station B and C have TDS above WHO permissible limit. [27] noted that high concentration of dissolved solids tends to increase the density of water, reduce solubility of gases in water and affect osmoregulation of aquatic organisms. Total dissolved solids increase the hardness of water, which in natural water is usually made up of carbonates, calcium sulphate. magnesium sulphate, potassium sulphate and sodium sulphate. The higher the TDS, the higher the electrical conductance of the water [28,29]. The trend of TDS values obtained correlates with the trend of results obtained from the electrical conductivity across the stations. Thus, there is a general linear relationship between electrical conductivity and total dissolved solids (TDS) as represented in Fig. 1b.

Considering the chemical parameters of the water sample presented in Table 1, the research reveals that the total alkalinity across the stream ranged between 0.10-1.07mg/l. Alkalinity is caused by dissolved bicarbonate salt along the stream [29]. The spatial distribution of nutrients parameters in Fig. 1a revealed: NH_4^+ (1.05 to 1.77mg/l); NO_3^- (3.00 to 1.93); SO_4^{-2} (5.60 to 5.67); PO₄³⁻ (0.06 to 0.05); Cl⁻ (2.57 to 8.37). Although all the samples were within the permissible limit except ammonium ion (NH_4^+) which could be due to leachates from waste disposal, sanitary landfills, over application of inorganic nitrate fertilizer or improper manure management practice [30]. However, the distribution of nitrate, sulphates, phosphates and chloride were within the permissible limit. The analysis confirmed that there are less salt containing compounds in station A compared to station B and C. This implies that water collected at station A (upstream) along Miniokoro stream is less polluted. The qualitative inorganic analysis shown in Fig. 2 (a & b) confirmed the presence of Cl⁻, $SO_4^{2^-}$, NO_3^- and $PO_4^{3^-}$ suggesting the possible occurrence of the metals in combination with these anions.

Based on the biological activities along Miniokoro stream, the concentration of Dissolved Oxygen

(DO) ranges from 1.00 to 1.20mg/l making station A the highest. whereas the Biochemical Oxygen Demand (BOD) concentrations ranged between 0.40-0.47mg/l. BOD were generally lower than DO levels in the water body. The BOD is slightly higher in Station C than in Station B and A. The BOD measure only the biodegradable part of the organic waste concentration [31]. The result depicts that station A offers a better support to aquatic life as it does not contain oxygen demanding waste or pollutant as compared to station B and C.

Generally, the level of physicochemical parameters of the water bodies showed some fluctuations when compared to the standard permissible limits for drinking water [32]. Thus, the water obtained at various station (A-C) along the stream must be treated before it can be set for human consumption. For water potable, the concentration of desirable substance must not exceed the levels set by standard organization [33,34].

Furthermore, the quantitative level of heavy metals such as Zinc, Lead, Chromium, Nickel and Iron were also analyzed and their results presented in Table 2.

The mean concentrations of Zinc (Zn), Lead (Pb), Chromium (Cr) and Nickel (Ni) varies between 0.07-1.09mg/L, 0.00-0.25mg/L, 0.03 to 0.09mg/L and 0.07-0.08mg/L respectively across the stations (Fig. 2a). The mean concentrations of Zinc (Zn), were within the acceptable permissible limits in water. Lead (Pb) was detected in station C which may be traced to the anthropogenic activities around the sampling point. It has been reported that bioaccumulation of lead in human can result to poisoning. The value of Chromium (Cr) concentration at station A constitute health hazard as it was not within the standard permissible level of 0.05 mg/L. This must be totally removed from water because they are carcinogenic [35,36]. Furthermore, the presence of Nickel (Ni) is above the permissible limit and that calls for review of activities within the area. Earlier, researches have established that the absorption of Nickel in humans may result into respiratory disorder. Iron (Fe) concentration ranged between 12.29-39.95mg/L exceeds the National and International Standard permissible limits of 0.03mg/l [34,37]. Excess intake of iron could result in gastrointestinal tract (GIT) disorder. The study shows decreasing trend of Iron (Fe) concentration from station A to station C (Fig. 2b). This element leads to

coloration of the water thus initiating sedimentation in the system [31].

In addition, these metals affect the organoleptic quality of water as do other metals such as copper and aluminum [31]. The level of the heavy metals across Miniokoro stream might be due to the anthropogenic activities prevalent in this area and the inability of government to control the possible disposal of solid and liquid waste into the stream.

The overall WQI of the stations along Miniokoro stream were presented in Table 3 and classified based on their overall WQI in Table 4. The results obtained from this study revealed that station A can be categorized as a poor water and it can only be fit for animal consumption subject to microbial screening. However, water from station B and C are classified as a very poor water which is neither good for consumption by human nor animal. Furthermore, the need to treat water obtained from station B and C along the stream should be encouraged to forestall the progressive worsening of the water quality which is a direct function of the industrial and human development across the stream. If this is not could serious done. it emanate into environmental and health problem for surrounding communities [6].

The high value of WQI has been found mainly from higher value of Salinity, Ammonium, Chromium, Nickel and Iron in the water samples. This could be attributed to improper disposal of wastes, cottage activities, large quantity of agricultural and urban run-off, sewage, over application of inorganic fertilizer, improper operation and maintenance of septic system [38,30].

Table 1. Water physicochemical parameters at sampling stations from miniokoro stream

| S/N | Parameter | Station A | Station B | Station C | WHO |
|-----|--------------------------|-----------------------|--------------------------|------------------------|---------|
| 1 | pН | 6.79 <u>+</u> 0.23 | 6.81 <u>+</u> 0.35 | 7.01 <u>+</u> 0.05 | 6.5-8.5 |
| 2 | Temp. ⁰C | 28.80 <u>+</u> 1.08 | 28.97 <u>+</u> 0.90 | 28.83 <u>+</u> 1.04 | 25-30 |
| 3 | Salinity (mg/L) | 0.06 <u>+</u> 0.02 | 1.04 <u>+</u> 0.73 | 0.49 <u>+</u> 0.18 | 0.4 |
| 4 | EC (µS/cm) | 136.43 <u>+</u> 35.39 | 960.67 <u>+</u> 532.36 | 303.10 <u>+</u> 320.01 | 1000 |
| 5 | TDS (mg/L) | 90.17 <u>+</u> 23.74 | 1517.67 <u>+</u> 1106.18 | 709.33 <u>+</u> 252.80 | 500 |
| 6 | DO (mg/L) | 1.20 <u>+</u> 0.00 | 1.00 <u>+</u> 0.00 | 1.00 <u>+</u> 0.00 | 10 |
| 7 | BOD (mg/L) | 0.40 <u>+</u> 0.20 | 0.41 <u>+</u> 0.01 | 0.47 <u>+</u> 0.12 | 10 |
| 8 | Alkalinity(mg/L) | 0.10 <u>+</u> 0.00 | 1.07 <u>+</u> 1.06 | 0.20 <u>+</u> 0.10 | 500 |
| 9 | Chloride(mg/L) | 2.57 <u>+</u> 0.65 | 12.47 <u>+</u> 3.66 | 8.37 <u>+</u> 2.83 | 250 |
| 10 | NH4 ⁺ (mg/L) | 1.05 <u>+</u> 0.78 | 1.80 <u>+</u> 0.15 | 1.77 <u>+</u> 0.09 | 0.5 |
| 11 | NO_3^- (mg/L) | 3.00 <u>+</u> 0.53 | 3.04 <u>+</u> 3.53 | 1.93 <u>+</u> 1.35 | 10 |
| 12 | PO4 ³⁻ (mg/L) | 0.06 <u>+</u> 0.02 | 0.07 <u>+</u> 0.01 | 0.05 <u>+</u> 0.00 | 5.0 |
| 13 | SO4 ²⁻ (mg/L) | 5.60 <u>+</u> 4.41 | 6.30 <u>+</u> 1.89 | 5.67 <u>+</u> 1.18 | 250 |

 Table 2. Average concentration of heavy metals (mg/l) at sampling stations along miniokoro stream

| S/N | Heavy metals | Station A (mg/L) | Station B (mg/L) | Station C (mg/L) | WHO (mg/L) |
|-----|-----------------|----------------------|---------------------|---------------------|------------|
| 1 | Zinc | 0.07 <u>+</u> 0.04 | 0.27 <u>+</u> 0.07 | 1.09 <u>+</u> 1.55 | 3.0 |
| 2 | Lead | ND | ND | 0.25 <u>+</u> 0.00 | 0.01 |
| 3 | Chromium | 0.09 <u>+</u> 0.02 | 0.03 <u>+</u> 0.01 | 0.04 <u>+</u> 0.02 | 0.05 |
| 4 | Nickel | 0.08 <u>+</u> 0.00 | 0.08 <u>+</u> 0.00 | 0.07 <u>+</u> 0.02 | 0.02 |
| 5 | Iron | 39.95 <u>+</u> 12.30 | 20.19 <u>+</u> 2.03 | 12.29 <u>+</u> 4.32 | 0.3 |



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(a)

(b)

Fig. 1. Chart of the physicochemical parameters along Miniokoro stream



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Fig. 2. Chart of the heavy metals concentration along Miniokoro stream

| Parameter | Wi | W _i Q _i Station A | W _i Q _i Station B | W _i Q _i Station C |
|-------------|----------|---|---|---|
| рН | 0.153 | 16.071 | 16.118 | 16.592 |
| Temp. 0C | 0.040 | 4.608 | 4.635 | 4.613 |
| Salinity | 2.500 | 37.500 | 650.00 | 306.250 |
| DO | 0.200 | 4.800 | 4.000 | 4.000 |
| BOD | 0.100 | 0.400 | 0.410 | 0.470 |
| Alkalinity | 0.002 | 0.00004 | 0.00043 | 0.00008 |
| Chloride | 0.004 | 0.041 | 0.200 | 0.134 |
| Ammonium | 2.000 | 420.000 | 720.000 | 708.000 |
| Nitrate | 0.100 | 3.000 | 3.040 | 1.930 |
| Phosphate | 0.200 | 0.240 | 0.280 | 0.200 |
| Sulphate | 0.004 | 0.009 | 0.101 | 0.091 |
| EC | 0.001 | 0.014 | 0.096 | 0.030 |
| TDS | 0.002 | 0.036 | 0.607 | 0.283 |
| Zinc | 0.333333 | 0.778 | 3.000 | 12.111 |
| Lead | 100 | 0 | 20000.000 | 25000.000 |
| Chromium | 20 | 3600.000 | 1200.000 | 1600.000 |
| Nickel | 50 | 20000.000 | 20000.000 | 17500.000 |
| Iron | 3.333333 | 4438.889 | 2243.333 | 1365.556 |
| Σ | 178.974 | 28526.466 | 44845.821 | 46520.260 |
| Överall WQI | | 159.389 | 250.572 | 259.928 |

Table 3. Computed water quality index values for miniokoro stream

Table 4. Water quality classification based on wqi value

| WQI value | Water quality |
|-----------|------------------------|
| < 50 | Excellent |
| 50-100 | Good Water |
| 101-200 | Poor Water |
| 201-300 | Very Poor Water |
| > 300 | Heavily Polluted Water |

5. CONCLUSION

Physiochemical parameters and level of heavy metals were used in evaluating the pollution and water quality index of three different sampling point (Station A-C) along Miniokoro stream. The result obtained from the various stations revealed the quality of the surface water which necessitate the need for its treatment prior to consumption and sensitization of the public on the impending environmental hazard. The water quality index calculated ranges between 159.389 - 259.928 across the stream which forms the basis of judgement on the quality of the water at various station. However, Station A upstream could serve as a preferred source of water, irrigation, swimming and as a tourist center compared to station B and C. It is suggested that the government should control activities along developing Miniokoro stream by and implementing an effective waste management plans. It is also essential to measure and monitor levels of pollution due to environmental and other anthropogenic impacts on a continual basis. This

ensures the protection of the surface water to meet the rapid population growth and rate of urbanization.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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