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Physiochemical Properties and Levels of Selected Heavy Metals in Some Rivers around Ewekoro Local Government, Ogun State, Nigeria

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ABSTRACT: This study examines the physiochemical properties and concentrations of selected heavy metals in selected river waters around Ewekoro, an area characterized by intensive mining and industrial activities, particularly cement production. The research aims to assess the impact of these activities on water quality by analyzing parameters such as pH, electrical conductivity (EC), dissolved oxygen (DO), total dissolved solids (TDS), total hardness (TH), and alkalinity, alongside heavy metal concentrations (copper, zinc, iron, lead, cadmium, calcium, arsenic, and nickel). Twelve (12) water samples were collected from three rivers—Akinbo, Alaguntan, and Elebu using atomic absorption spectrophotometry. Results indicate that most physiochemical parameters fall within WHO, NAFDAC, and FOEN permissible limits. Elevated levels of iron (0.18–1.449 mg/L) and lead (up to 0.52 mg/L) were detected, exceeding recommended thresholds. The Heavy Metal Pollution Index (HMPI) revealed localized contamination, with values ranging from 1.14 to 6.69, indicating varying degrees of pollution, particularly in areas influenced by industrial discharges. Low dissolved oxygen levels (2.7–3.66 mg/L) suggest organic pollution, posing risks to aquatic ecosystems. Despite the general compliance with international water quality standards, the elevated concentration of Fe, Pb, TH, and alkalinity highlights potential environmental and public health risks, hence there is a need for continuous monitoring, stringent enforcement of industrial discharge regulations, and targeted remediation strategies to mitigate pollution and protect public health. These findings highlight the critical role of industrial activities in water quality degradation and emphasize the importance of sustainable water resource management in the region.

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Ewekoro is an industrial hub in southwestern Nigeria that hosts several industries, such as the cement industry, which carries out several mining activities in the area. Mining generates waste and dust, which contaminate the surface water used for industrial and domestic purposes and further expose the inhabitants to the risk of consuming contaminated water. Water quality depends on several factors, such as uncontrolled dumping of industrial waste, run-off water from mining sites, and anthropogenic activities.

The role of the environment in human health and development is germane. Any environment in which mining and cement industries are located is associated with high dust emissions that are discharged into the atmosphere aside from the wastes from the manufacturing industries. These emitted particles are deposited on the Earth's surface and further transported to rivers through rainfall (Olaleye 2005; Asubiojo *et al.,* 1991). Environmental pollution is the introduction of an impure natural environment

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that causes disadvantageous changes that can lead to damage to living systems; it can be in the form of air, water, soil, noise, or thermal damage.

Cement industries produce 5 percent of the total greenhouse gases in the atmosphere, and the pollutants emitted from cement industries in Ewekoro, which use limestone and clay as raw materials, are carbon dioxide, nitrogen oxides, sulfur dioxide, and dust. The damaging effect of the dust emitted from cement factories in the neighboring river can increase the toxicity of heavy metals, such as copper, lead, and chromium (Olaleye, 2005; Adejumo *et al.,*1994). Cement production generates highly toxic dust, which poses severe risks to nearby ecosystems Moronkola *et al.,* 2021. Furthermore, industrial and human activities significantly impact environmental quality, particularly in the water and air. Similarly, various human actions alter the river water composition. These include release of chemical and microbial substances onto land and into soil, and the direct discharge of waste into surface waters (Younger *et al.,*2002).

These practices highlight the interconnected nature of industrial processes, waste management, and environmental degradation. The presence of emerging contaminants and alterations in the physiochemical properties of river water around Ewekoro pose significant environmental and public health concerns. Rapid industrialization and urbanization in the region have led to increased pollution levels, potentially affecting the quality of the available water in the area. Despite efforts to mitigate pollution, there is a lack of comprehensive studies addressing the contamination level and physicochemical properties of river water in proximity to mining and industrial locations in the Ewekoro area. This knowledge gap hampers effective pollution control and water resource management strategies, highlighting the need for detailed investigation.

Water is a vital natural resource for economic, human, and plant purposes and can be sourced from surface water such as rivers, wells, streams, springs, lakes, and boreholes. In many urban and rural environments in developing nations, surface water is the water source for domestic and agricultural purposes. Water from these sources can be contaminated through domestic, industrial, and agricultural discharges, which may have adverse effects on inhabitants (Ayeni *et al.,*2009; Ojekunle, 2000). River water is among the oldest surface water bodies in the world (Higler, 2012). and is experiencing an increasing threat of emerging contaminants from agriculture, urbanization, mining activities, and industrial development. This necessitates an extensive assessment of the aquatic ecosystem, leading to practical actions to protect the natural quality of river water available for use. The importance of physiochemical (both metal and non-metal) concentrations in water can be understood from recent studies. Adejuwon and Adelakun (2012) conducted physiochemical analyses in three different rivers in the Ewekoro area. Parameters such as pH, TDS, TH, EC, chloride, calcium, nitrate, and fecal coliforms were analyzed. Their research concluded that only one of the three selected rivers (Lala River) was free from contamination. Denkok *et al.,* (2021) determined heavy metals in various water samples, including groundwater and factory-packaged sachet water, in the Jos Plateau state. The authors found that the levels of Pb, Cd, Cr, and Cu in drinking water were higher than their respective WHO allowable limits. Adeyemi and Ojekunle, (2021) investigated heavy metal concentrations in underground waters (which provide drinking water to people) around industrial estates in Ogun state. High concentrations of Pb, Fe, Ni, and Cr were measured in the samples, with the total hazard index (HI) showing high risk across different age groups, particularly for infants. On the other hand, Gray (2005) determined the quality of well water samples collected from limestone mining sites around Ibeshe and Ewekoro in Ogun state. It was established that the concentration of TDS, Cr, Pb, Zn, Fe, and Mn are within the permissible limit of NSDWQ while Cd and Ni were not detected in the analyzed water samples.

The continuous release of dust and other anthropogenic activities into the rivers around mining areas has led to an increase in water pollution. Therefore, this study aimed to investigate the physiochemical properties and the levels of copper, zinc, iron, lead, cadmium, calcium, arsenic, and nickel in selected river water around mining and industrial sites in the study area and compare the water quality with national and international standards to provide further information.

MATERIALS AND METHODS

Study Area: The study areas of the Akinbo, Alaguntan, and Elebu rivers are located within the Ewekoro Local Government in Ogun State. Ewekoro is one of the local governments in Ogun State bounded in the north and south by Abeokuta North and Abeokuta South local governments, respectively, while in the east and south by Yewa South and Ifo local governments, respectively, and in the west by Obafemi Owode local government (Figure 1).

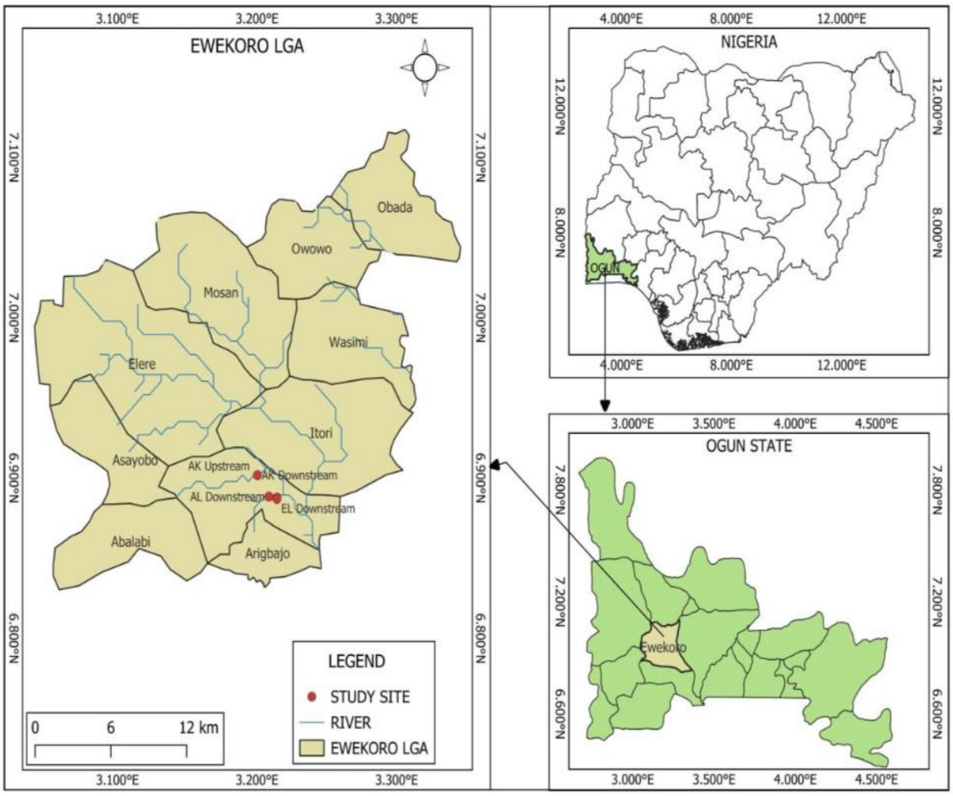

Fig 1: Location map of the study area

The coordinates of the study areas are Akinbo River (Lat 6.901855°, 6.901934° N Long 3.200255°, 3.200264° E), Alaguntan River (Lat 6.888491°, 6.888499° N Long 3.208463°, 3.208583° E), and Elebu (Lat 6.887939°, 6.887032°N) Long (3.214306°, 3.214243° E), all within the tropical rainforest belt of Nigeria. Ewekoro is known for its concentration of manufacturing, processing, and, majorly, mining activities. Geologically, the Ewekoro area is part of the sedimentary basin known as the Dahomey Basin. This basin is characterized by layers of sedimentary rocks deposited over millions of years. The predominant rock formations in the area include limestone, shale, and sandstone.

Water sample collection and Preparation: The sample collection was carried out in three (3) different rivers in Ewekoro using systematic random sampling techniques. All possible contamination sources were taken into consideration during the analysis. As part of the quality assurance carried out, the residue of the previous sample was removed from the container to minimize error. A total of twelve (12) plastic containers, consisting of four for each of the three rivers, were used for sample collection, and they were initially washed with detergent and then rinsed thoroughly with 5% HCl and left to dry overnight. The samples were then placed in a cool environment immediately after each collection, and each container was tagged with different labeling to differentiate them from each other. Two samples each were collected at upstream and downstream areas of the Alagunta (samples A to D), Akinbo (samples E to H), and Elebu rivers (samples I to L). Afterward, the collected water samples were transported to the laboratory for analysis. All the analyses were carried out in duplicate to ensure accuracy in the measurement.

Evaluation of Selected Physicochemical Parameters: The physio-chemical parameters analyzed are pH, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), and total alkalinity. pH was measured through potentiometry, total dissolved solids measurement was carried out through gravimetry, electrical conductivity through conductimetry, alkalinity, total hardness, and dissolved oxygen were measured through titrimetry. The result of the total hardness was categorized by the report of Twort and Dickson (1994) (Table 1). The quality control measures, according to Batley and Gardner, were strictly adhered to during the sampling and analysis processes. Samples were analyzed in the laboratory within 3 hours of collection.

Table 1: Comparison of total hardness level as adapted from Twort and Dickson (1994)

Hardness	Level
0.5	Soft
50-100	Moderately soft
100-150	Slightly hard
150-200	Moderately hard
Over 200	Hard
Over 300	Very hard

Source: Adejuwon and Adelakun (2012)

Heavy Metal Analysis: A total of two hundred milliliters (200 mL) of the sample was digested using a 9:4 mixture of nitric acid (HNO□) and perchloric acid (HClO□) on a hot plate to ensure a complete breakdown of contaminants. The solution was filtered through Whatman No. 42 filter paper to remove particulates. The filtrate was quantitatively transferred into a 50 mL volumetric flask and diluted with double-distilled water to achieve the desired concentration for analysis. The concentrations of heavy metals were subsequently determined and compared against regulatory standards established by the World Health Organization (WHO), the National Agency for Food and Drug Administration and Control (NAFDAC), and the Federal Office for the Environment (FOEN). This methodology ensures accurate quantification of trace metal contaminants, providing essential data for the assessment of water quality and potential environmental or health risks.

Evaluation of Contaminant Index: Contaminant indices were evaluated using the Heavy Metal Pollution Index (HMPI) and partial contamination index (PCI). The HMPI was calculated for each sample using Equation 1:

$$HMPI = \sum_{p=1}^{n} PCI_i \qquad 1$$

Where PCI_i is the partial contamination index (PCI_i)

The partial contamination index of heavy metals is calculated using Equation 2:

$$PCI_i = \frac{\sum_{n=1}^{1}[WF]_i \times MS_i}{\sum_{1}^{n} WF_i} \qquad 2$$

Where MS_i and $[WF]_i$ are metal subscript and unit weighting factor defined using equation 3 and 4 respectively

$$M_s = \sum_{n-1}^{n} \frac{|MC_i - AD_i|}{|AL_i - AD_i|} \times 100 \qquad 3$$

$$[WF]_i = \frac{1}{AL_i} \qquad 4$$

Where n is the number of heavy metals;MC_i is the measured concentration; AL_i is the maximum allowed concentration; AD_i Is the maximum admissible concentration.

The HMPI was determined for the river water collected in Ewekoro. Any metal with no maximum concentration allowed in WHO was not considered. Nickel and arsenic were not considered since no concentration was recorded. If HMPI values is less than 15, the samples are considered to be less contaminated, if it is between 15 and 30, it is medium contamination. However, if the HMPI recorded is greater than 30, it is regarded as high contamination (Arcentales-Ríos *et al.,*2022; Mahato *et al.,*2014).

RESULTS AND DISCUSSION

Physiochemical Analysis: The results of the physicochemical parameters from the selected samples from three different rivers within the Ewekoro Local Government in Ogun State, Nigeria are presented in Table 2. The parameters include pH, conductivity, dissolved oxygen (DO), total dissolved solids (TDS), alkalinity, and total hardness. The pH values range from 6.7 to 7.31, with a mean of 7.03, indicating that the water is slightly alkaline. This is within the acceptable range set by the World Health Organization (WHO, 2011) and the National Agency for Food and Drug Administration and Control (NAFDAC, 2007), which recommend a pH range of 6.5-8.5 for drinking water. However, the values approach FOEN's upper limit (9.0), suggesting generally neutral conditions with minor variability. The conductivity, which measures the water's ability to conduct electricity due to the presence of ions, ranges from 230 to 342 µS/cm, with a mean of 302.75 µS/cm. This is below the NAFDAC (2007) standard of 1000 µS/cm, suggesting low ionic content in the water. However, the values exceed FOEN's limit (70 µS/cm), indicating elevated dissolved ions, possibly from agricultural runoff or industrial discharges. Dissolved oxygen (DO) levels range from 2.7 to 3.66 mg/L, with a mean of 2.71 mg/L. DO is crucial for aquatic life, and the observed levels are below the WHO (2011) guideline of 6 mg/L, indicating potential stress for aquatic life. Total dissolved solids (TDS) range from 113 to 171 mg/L, with a mean of 18.32 mg/L, which is relatively low and within acceptable limits. Alkalinity, measured as mg CaCO3/L, ranges from 99.8 to 143 mg/L, with a mean of 12.27 mg/L, indicating moderate buffering capacity. Total hardness, also measured as mg

CaCO3/L, ranges from 132 to 299 mg/L, with a mean of 53.93 mg/L, suggesting that the water is moderately hard. These parameters collectively indicate that the water quality is generally within acceptable limits, although the low DO levels may pose a risk to aquatic organisms.

Table 2: Physicochemical parameters in water samples from the three Rivers within the Ewekoro Local Government in Ogun State, Nigeria

Parameters	Range (min-max)	Mean ($\bar{x}$)	Standard deviation (STD)	WHO 2011, 2007	NAFDAC 2007	FOEN 2011
pH	6.78-7.31	7.03	0.53	6.6-8.5	6.5-8.5	6.0-9.0
Conductivity ($\mu s/cm$)	230-342	302.75	37.34	-	1000	70
Dissolved Oxygen (mg/L)	2.07-3.66	2.71	0.53	≥ 6	-	≥ 4
Total Dissolved Solids (mg/L)	113-171	18.32	149.08	-	-	-
Alkalinity (mgCaCO3/L)	99.8-143	12.27	116.32	100	100	-
Total Hardness (mgCaCO3/L)	132-299	53.93	195.67	100	100	-

Heavy Metal Concentration: Table 3 represents the concentrations of heavy metals in water samples from the different rivers around the Ewekoro area. The heavy metals analyzed include copper, zinc, iron, lead, cadmium, calcium, arsenic, and nickel. Copper levels range from 0.015 to 0.063 mg/L, with a mean of 0.04 mg/L, which is well below the WHO (2011) guideline of 2 mg/L. Zinc concentrations range from 0.72 to 3.11 mg/L, with a mean of 1.77 mg/L, also below the WHO (2011) standard of 3 mg/L. Iron levels range from 0.18 to 1.449 mg/L, with a mean of 0.75 mg/L, exceeding the WHO (2011) and FOEN guidelines of 0.3 mg/L and 0.3 mg/L respectively, indicating potential contamination from industrial/mining effluents or anthropogenic sources. Lead concentrations range from 0.00 to 0.52 mg/L, with a mean of 0.01 mg/L, which is within the WHO (2011) guideline of 0.01 mg/L, but has a maximum of 0.52 mg/L in some samples, posing acute toxicity risks. Cadmium levels are very low, ranging from 0.00 to 0.007 mg/L, with a mean of 0.00 mg/L, well below the WHO (2011) standard of 0.003 mg/L. Calcium levels range from 21.05 to 35.32 mg/L, with a mean of 25.91 mg/L, which is not regulated by WHO or NAFDAC. Arsenic and nickel concentrations are both below detectable limits, with means of 0.00 mg/L, which is within the WHO (2011) guidelines of 0.01 mg/L for arsenic and 0.07 mg/L for nickel. The heavy metal analysis suggests that the water is generally safe for consumption, although the elevated iron levels may require further investigation to determine the source and potential health risks.

Table 3: Heavy Metals Levels (mg/L) in water samples from the three Rivers within the Ewekoro Local Government in Ogun State, Nigeria

Parameters	Range (min-max) (mg/L)	Mean ($\bar{x}$)	Standard deviation (STD)	WHO 2011, 2007	NAFDAC 2007	FOEN 2011
Copper	0.015-0.063	0.04	0.02	2	-	1.5
Zinc	0.772-3.11	1.77	0.86	3	-	1
Iron	0.18-1.449	0.75	0.41	0.3	-	0.3
Lead	0.00-0.52	0.01	0.02	0.01	-	0.04
Cadmium	0.00-0.007	0.00	0.00	0.003	-	0.003
Calcium	21.05-35.32	25.91	4.54	-	-	-
Arsenic	0	0.00	0.00	0.01	-	0.01
Nickel	0	0.00	0.00	0.07	-	0.02

Heavy Metal Pollution Index (HMPI) Evaluation: The Heavy Metal Pollution Index (HMPI) values range from 1.14 to 6.69, with a mean of 2.59 (Table 4), indicating varying degrees of heavy metal contamination in the study area. Locations with HMPI values exceeding 4 suggest significant pollution, with the highest value (6.69) pointing to critical contamination that necessitates immediate remediation. The variation in HMPI implies localized pollution sources, likely stemming from industrial activities. Supporting water quality parameters, such as high hardness, alkalinity, and conductivity, suggest mineral-rich conditions, potentially influenced by the cement industry. Low dissolved oxygen levels indicate organic pollution from industrial and domestic waste. Elevated iron, zinc, and lead concentrations surpass safe limits, highlighting pollution from industrial processes, corrosion, and runoff. These findings underscore the need for continuous monitoring and regulatory intervention to mitigate heavy metal contamination and protect water quality. These findings correlate with elevated Iron and Lead levels (Table 3), emphasizing cumulative toxicity risks. Prolonged exposure to such pollutants could harm aquatic ecosystems and human populations.

Table 4: The HMPI of the study areas

Samples	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
HMPI values	2.29	4.74	2.29	6.69	2.29	2.29	2.29	2.29	1.47	1.14	1.61	1.63

Conclusion: The study highlights that while most physicochemical parameters and heavy metal concentrations in the selected river waters around the Ewekoro area, adhere to WHO, FOEN, and NAFDAC permissible standards, elevated levels of iron, lead, total hardness, and alkalinity pose notable environmental and public health risks indicating localized contamination. The Heavy Metal Pollution Index (HMPI) attributes this localized contamination to industrial and mining activities. The low dissolved oxygen levels further suggest organic pollution which may further endanger the aquatic ecosystems. These findings underscore the need for continuous monitoring and targeted remediation strategies to mitigate pollution sources and preserve the water quality. Addressing these challenges is crucial for ensuring the long-term sustainability of water resources and protecting public health in the area. Therefore, stringent enforcement of industrial discharge regulations, routine water quality monitoring, and targeted remediation strategies are imperative. Public awareness campaigns on pollution risks and in-depth investigations to identify the sources of the contamination are recommended for ensuring sustainable water management in the region.

Declaration of Conflict of Interest: The authors declare no conflict of interest.

Data Availability Statement: Data are available upon request from the first corresponding author.

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