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Comparative Assessment of Seasonal Variations in the Quality of Surface water and its associated health hazards in Gold Mining Areas of Osun State, South-West Nigeria.

Awogbami Stephen Olalekan

Department of Environmental Health, Faculty of Pure and Applied Science, Kwara State University, Malete, Kwara State. Nigeria

Solomon Olayinka Adewoye

Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomosho, Nigeria

Sawyerr Olawale Henry

Department of Environmental Health, Faculty of Pure and Applied Science, Kwara State University, Malete, Kwara State. Nigeria

Morufu Olalekan Raimi (🗹 ola07038053786@gmail.com)

Department of Community Medicine, Faculty of Clinical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria https://orcid.org/0000-0001-5042-6729

Research Article

Keywords: Hydrochemistry, Sustainability assessment, Drinking water quality, Physicochemical, Irrigation water quality, Artisanal and small-scale gold mining (ASGM), Emerging contaminants, South-West Nigeria

Posted Date: November 7th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2245715/v1

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Abstract

Industrial and urban development are contributing to an increase in global environmental degradation. Therefore, the release of heavy metals from miningrelated operations into surface water is harmful to human health. But as anthropogenic influences on the environment grow, surface water characteristics are also altering, which has an impact on aquatic creatures. In order to analyze the acceptability of the surface water in the gold mining area for drinking and irrigation uses, different quality water assessment methodologies were incorporated in this research. In light of this, the purpose of the current study is to comprehend how the hydro-geochemistry and appropriateness of surface water for drinking and irrigation vary on a monthly basis. The study employed standardized analytical techniques. According to APHA recommendations, all sampling, conservation, transportation, and analysis were completed (2012). All collected samples were transported to the study lab while being kept in an icebox to prevent the degradation of the organic components. As a result, the study is focused on the contamination level in the surface water for a year. Overall, the study also highlights important pollutants that have an impact on the guality of the surface water as it passes through Osun State's gold mining regions. Finally, it has been determined that the following criteria are crucial for the stretch in each season of this research: DO, Hardness, Turbidity, Chloride, Potassium, Lead, TSS, Cadmium, Chromium, Manganese, Mercury, and Arsenic. Most of the physicochemical variables examined in this study fell within their corresponding standard limits. Based on the results of this study, the appropriate constituted authority is encouraged to continuously monitor and assess surface water quality suitability for drinking, domestic, and irrigation purposes in order to keep track of the effects of water contaminants and detect any changes in the water quality. To safeguard and maintain the groundwater quality and public health, it is advised that appropriate regulatory policies and water treatment procedures be employed in the area. Additionally, it is proposed that when enhancing water quality and investigating the sustainable use of water resources, surface water pollution should be taken into consideration. More research on report quality needs to be done in Nigeria's other mining environments in order to develop technical capacity. In the context of new contaminants and a changing climate, this study suggests additional research directions to enhance knowledge of surface water in a mining setting and sustainable surface water management in mining areas.

1. Introduction

Nigeria is fortunate to have a wealth of water resources, with an estimated 226 billion m3 of surface water and 40 billion m3 or so of ground water. According to WHO guidelines, 28% of the world's population lives in Africa and doesn't have access to better water supplies. The main factor limiting the productivity of aquatic ecosystems, particularly fish resources, is water quality. Water supply is essential in both rural and urban settings, according to the United Nations Educational, Social, and Cultural Organization. Water is a common element to the other four of the five fundamental human needs (food, health, education, and peace), making it essential to life and human growth. Water has a crucial role in the growth of settlements and in determining population density [1-10]. Furthermore, surface waters, like shallow lakes, are dynamic systems with significant spatiotemporal variation. The differences in the concentration of dissolved ions in surface water are often controlled by lithology, water flow rate, geochemical reaction types, salt solubility, and human activities. Eutrophication, which degrades water quality by encouraging excessive algal growth and elevating the concentration of suspended organic material and heavy metals, is currently one of the most prevalent ecological issues affecting inland water bodies [11-16]. Even though there is lot of water on the earth, usually surface and groundwater and it is distributed through a variety of media, including rivers, lakes, oceans, seas, glaciers, and streams [1-21], only around 0.3% of it is potable and used by people [22-25]. The fact that water doesn't exist in isolation and always has some level of contamination due to its property as a universal solvent depends on a number of variables, including the geology of the environment or the nature of aquifers, anthropogenic activities occurring nearby, and the level of sanitation and hygienic standards in the community in question [14-16, 25-27]. The increased demand for potable water for domestic, industrial, agricultural, and recreational uses, as well as other anthropogenic activities, has been linked to rapid industrialization, urbanization, and population growth worldwide [28-39]. This has resulted in a significant burden of water contamination. Surface water makes up the remaining percentage at the same time. The quantity and quality of water that is suitable for drinking, residential use, and commercial use are currently declining. The assessment and monitoring of water quality for various reasons in order to conserve, sustain, and protect water resources has piqued the interest of scholars in numerous disciplines of study across the globe [1, 8–13, 18]. Surface water contamination, however, is a major focus of study and research because of the extensive industrialization and urbanization. Water contamination risks have caused the rivers to seriously decline, which is disrupting the aquatic ecosystem, especially in developing nations like Nigeria. Water contamination is caused by small-scale and artisanal gold mining. Given that gold mining operations, in particular alluvial gold mining, take place on the river bed, this is not implausible. Toxins including lead, mercury, and arsenic are deposited in the sediments as a result of the employment of chemicals during gold mining and the extraction of gold from its ore [40]. Waste products from gold mining or processing are frequently discarded or washed into local water sources by rain or flooding. Physical, chemical, and biological indices of water quality are all significantly impacted by these contaminants. When waste from gold mining activities is dumped into water bodies, it causes an increase in both turbidity and total suspended solid. This has led to widespread adoption of these measures as markers of water pollution in mining sites [41]. As a result, as the water's temperature increased, the amount of dissolved oxygen decreased [41]. Other places, total dissolved solid and turbidity were the main indicators of artisanal mining contamination [42]. A notorious source of water pollution is mining. One of the main causes of the world's declining water supplies is the poisoning of water bodies by mining [43]. The unorganized informal mining sector known as artisanal mining has today's increased the environmental effects of mining [44]. The extraction of the minerals is done by the use of localized, affordable, and simple-to-use instruments and equipment in artisanal mining [45]. The majority of this country's poorest regions engage in this illegal mining sector, which typically operates outside of its legal and regulatory framework [46, 47]. Rapid population expansion, industrialisation, and urbanization all contribute to a worsening of this scenario by increasing demand for and pressure on mineral resources [48]. The delicate ecological systems' equilibrium, including the biotic and abiotic components of the environment, are altered by mining operations [49]. Land, soils, and water are contaminated and degraded as a result of gold mining [28, 29, 50-56]. Chemicals employed in the mining process to separate mineral resources from their ores are easily carried by runoffs into neighboring water bodies [57]. In addition, heavy metals are present in the wastewater from ore processing and other mining effluents, which contaminate water sources [58, 59]. High levels of heavy metals in rivers and streams are likely to bioaccumulate in fish and other aquatic life, posing a major health risk to humans who eat those things [60, 61]. As a result, many rural communities in Nigeria struggle to get access to drinkable water [1-21, 62, 63]. This led to a dependence on freshwater resources, such as rivers and streams, for residential water needs [25]. This claim was supported by a wide range of reliable scientific discoveries and evidence, all of which revolved around the need of water as a

necessary component of survival [1-25]. Water is essential for human life and is important for a country's economic prosperity, well-being, and overall health [64-66]. In the meantime, heavy metal contamination is well documented in places where gold is mined. The bioaccumulation of these heavy metals in the human body can result in diseases such kidney damage, cancer, reproductive disorders, brain damage, spontaneous abortion, etc. [1-25]. Therefore, it is crucial to conduct research on the heavy metal and physico-chemical composition of water sources in gold mining towns to safeguard public health from the risks of potential chemical exposure. Additionally, this will give decision-makers in both governmental and non-governmental groups the crucial data they need to take action. As a result, the region taken into consideration for this research project is dominated by urban centers, mining industries, and agricultural lands. This work has been attempted with the main objectives of evaluating surface water aptness for irrigation and drinking practices, by computing various monthly variation in physico-chemical, radical, and heavy metal concentration in selected surface water bodies. As there is not known extensive research study carried out so far in this study area for the assessment of surface water quality and its associated health hazard in a gold mining area of Osun State, this work has been attempted. The results of this study may help the locals in this area use surface water resources wisely for beneficial agricultural practices. In agricultural settlements in Nigeria, the quality of the surface water has been in issue. The majority of these surface waters, according to reports, are unsafe for drinking and irrigation, however some may be suitable for industrial uses. According to Raimi and Sawyerr [11], background values for some components in the oil and gas environment are assessed either spatially or temporally (concentrations prior to anthropogenic activity) (concentrations in the areas not influenced by anthropogenic activity). As a result, there is an increasing need to address surface water quality issues because poor water quality has an impact on both crop output and human health. Anthropogenic and geogenic factors have a significant impact on changes in surface water quality [7, 9, 11, 12, 17]. Therefore, if anthropogenic activities are to blame for the degradation, environmental legislation can preserve the surface water. Monitoring the river's water quality is also crucial for sustainable use. However, long-term monitoring produces a huge and complex database that requires a competent method for interpretation. To better understand geographical changes in water guality, multidimensional scaling analysis will aid in the interpretation of complicated datasets. These methods are excellent resources for creating sensible plans for the efficient management of the water resources.

2. Material And Methods

The Study Area

Surface water samples analyzed in this research were collected for twelve (12) months (June 2020 to May 2021) from three surface water bodies from different locations. The surface water bodies include Aye-Oba River, Alapadi and Eti-oni stream; both Alapadi and Eti-oni stream are tributaries of Aye-oba River. All situated within gold mining activities areas across three Local Governments (Ife South, Atakumosa East, and Atakumosa West) in Osun State, Southwest Nigeria. Aye-Oba River lies between the latitude 7° 23' N and longitude of 4° 61['] E (see Fig. 1–5). The river is very significant to the socio-economic growth of the residents of Ife South Local Government area in Osun State to sustain subsistence farming such as irrigation, livestock, and fishery. The river is the major source of water supply for consumption and domestic use. The river was constructed as a dam in the year 2004. Thus, the dam served as the major source of potable water supply to more than fifteen communities in Ife South Local Government areas and its environs until it stopped the operation (Fig. 1–5).

Experimental design and description of the sampling points

The study design employed was laboratory-based experimental approach and a descriptive cross-sectional study coupled with field observations. The sampling points were: upper stream (site A), middle stream (site B) and lower steam (site C) (see Fig. 1–5 below). The division was done in relation to the discharge of effluents from mining, domestic and agricultural activities, most especially pesticide pollution through various forms of indiscriminate application on farmlands and domestic effluents particularly from the oil mills processing that enter the stream. Site A (upper stream) represent Eti-oni stream, this stream is about 500 meters from the mining site and about 1km to site B the effluent discharge point.

Site B (middle stream) represents Alapadi stream. This stream directly receives effluents discharge due to mining activities in the area. It also receives significant effluents from oil palm processing units located along the river bank and run-off water from farmlands, cassava processes, and refuse dump from homes. Site C (lower stream) represent Aye-Oba River/dam, the abandoned dam. The river is about three (3) kilometers from site B. Physical observation showed that the effluents received by the water bodies from site A and B has changed the colour of the water bodies and there was unpleasant smell emanating from the river. In addition to this, the river receives effluents from cassava processing wastes, open defecation, poultry wastes, animal dung, pesticide products, and water run-off from dumpsite. Therefore, the choice of the afore-mentioned sampling points, presented in Fig. 1–5, was based on the accessibility, the rate at which they receive effluents from different sources, the extent of their pollution, and particularly their distances from the site of mining activities. In addition, sampling sites were chosen based on the potential exposure of the surface water to different sources of agro-industrial and other sources of pollutants.

Water sample collection for heavy metal analysis

Collection of water samples was conducted between the hours of 8.00 am and 12 noon, every fourth week of the month in all the sampling points for the period of 12 months (June 2020 to May 2021). Water samples were collected into plastic bottles which were previously soaked in 3% nitric acid and washed with distilled water before sampling, this was in accordance to the method described by APHA [67]. Water samples collected for the determination of dissolved oxygen were collected in dark glass containers and fixed on the spot with Winkler reagent. The water samples were properly preserved following the water sample preservation methods described by APHA [67]. As a result, Fig. 6 displays the primary approaches for determining the composition of surface water.

3. Results And Discussion

3.1 General description of monthly variations of surface water quality

Understanding a water body's healthiness depends critically on its water quality. Numerous researchers have shown over the past few decades that the physical and chemical processes at surface water interfaces are extremely complicated and frequently interconnected. Surface water pollution by heavy metals is currently a significant environmental problem, and numerous studies have been carried out to identify rising metal concentrations that cause increased toxicity. This leads to a sharp decline in microbial activity, which is reflected in a slowing of the apparent growth rate and an extension of the lag time. Figures 7 through 34 below show a descriptive summary of all the physicochemical parameters that were analyzed. Poor mining practices have been used in the study area, which is primarily agricultural. It is thought that a number of pollutants may have had an impact on this region's surface water resource. The next section includes several physico-chemicals that are considered to be "good water." While the study documents the physicochemical characteristics of the study area's surface water. The significance of the study is to evaluate the water's appropriateness and quality for home use. Due to the study area's proximity to a residential area, the river and its tributaries serve as a source of water for domestic use. The water body passes via a mine, an abandoned dam, a processing plant for oil palm, a processing plant for cassava, and farms with cattle and fisheries.

Potable water must be flavorless, odorless, and colorless, in accordance with Morufu and Clinton [1], Olalekan *et al.* [10], and other sources. These specifications weren't met by the surface water used in this study. These might occur from microbial activity in the water. According to reports, biological processes and chemical contamination of water sources encourage the development of microbial communities and give water an unpleasant odor, look, and taste [13]. Due to its role in bodily processes, water is the most crucial nutrient for human survival, according to Raimi *et al.* [2]. In a similar vein, the author claimed that water is crucial to human nutrition, both directly as drinking water and indirectly as a food medium in addition to its many other uses. Lack of access to adequate drinking water has been linked to a number of health issues that plague developing countries like Nigeria [1–25]. About 66.3 million Nigerians [13–16, 19, 24–27] lack access to clean drinking water, which causes them to rely on surface water for both their daily needs and as a method of waste disposal. According to studies by Olalekan *et al.* [14], Raimi *et al.* [16], Olalekan *et al.* [17], and Raimi *at al.* [19], there are about 2 billion people without access to potable drinking water in their homes worldwide as of 2017. Nearly 80% of these people rely on surface water, which is unsafe for drinking as well as other domestic uses. Olalekan *et al.* [10] assertion that pure water is colourless. Therefore, any water with a distinctive color implies pollution. Figure 7 shows the monthly fluctuation in surface water's apparent color. In the months of January (1925.35), June (2030.18), July (1920.28), September (1720.52), and November, the apparent color of the surface water was high and over 1500. (1568.57). In surface water, March saw the lowest value of 447.07 and June saw the highest value of 2030.18. This study is in opposition to the study that discovered that Okpai had the highest value for color during the dry season

The receiving water bodies may experience significant DO depletion and fish deaths as a result of a high biochemical oxygen demand (BOD) level [12]. The BOD measures the quantity of organic matter in water that is biologically active. Figure 8 displays the monthly variance in the surface water's BOD. January, April, and the early to late rainy seasons saw elevated BOD levels in surface water (June – September). The maximum BOD in surface water was recorded in August (4.4 mg/L), while the lowest value was recorded at the start of the rainy season in May (0.93 mg/L). Notable high BOD levels were also recorded in January (4.27 mg/L) and June (4.00 mg/L). BOD₅ is a crucial measure for detecting contamination from organic and inorganic wastes. As a result, wet seasons had higher values than dry ones, leading to the conclusion that anthropogenic activities may have an impact on higher BOD levels in the same way as wetness in seasonality had a greater impact on BOD than dry seasons. Therefore, the discharge into surface water from industrial units engaged in gold mining accounts for this rise in BOD5 concentrations. If no action is made to address BOD5 trends, the environment of the area receiving these effluents will suffer grave effects. BOD₅ must not exceed the 40 mg/l limit for discharge into the environment. But since the BOD₅ concentrations in the surface water have gone above the permitted environmental release threshold, careful action is needed to lessen the effects of this pollution.

COD are significant indicators of organic and inorganic waste pollution [1–6]. Higher COD values were linked by Raimi *et al.* [12] to greater anthropogenic stresses on groundwater. As a result, Fig. 9 provides the chemical oxygen requirement in surface water. In instance, the mid-late dry season (January - April) and the middle of the rainy season have greater chemical oxygen demand levels (June – August). The highest value (9.60 mg/L) and lowest value (3.20 mg/L) were noted in April and July, respectively. Chemical oxygen demand levels averaged 7.47, 4.27, and 5.60 mg/L in January, February, and March, respectively, while they were 6.93, 6.67, 5.07, 5.07, 6.67, 6.67, and 6.13 mg/L in May, June, August, September, October, November, and December. Thus, it might be concluded that locations susceptible to mining operations have a greater influence on COD than those that are not affected by these activities. Additionally, it might be proven that rainy seasons had a greater impact on COD than their dry counterparts. Higher COD values were linked by Olalekan *et al.* [10] and Raimi *et al.* [9] to greater anthropogenic stresses on groundwater. However, urgent action must be taken to lessen the impact of this flow's environmental pollution. 150 mg/l is the upper limit for COD discharge into the environment. The COD trends in the surface water channels, on the other hand, are obviously below 150 mg/l.

Aquatic creatures require dissolved oxygen (DO) for their best chances of survival. The presence of low oxygen levels is a sign of biological activity, nutritional input, and organic loading [6, 13]. Large loads of organic debris are frequently the source of elevated water DO values. In extreme circumstances, oxygen loss can result in a major fish death by altering the fish population significantly [25, 31]. For good fish production, a DO level of at least 5 mg/L is advised [6, 13, 31]. So deviation from that range has an impact on fish survival in that body of water. Its concentration in surface water fluctuates depending on the trophic levels of the water. The amount of dissolved oxygen is influenced by photosynthetic activity and the microbial breakdown of both native and foreign organic materials. The surface water's generally low level of dissolved oxygen is an indication of eutrophication. The most frequent outcome of several types of water pollution is likely the depletion of DO in the water [17, 18, 20]. As a result, Fig. 10 provides the DO concentrations in surface water are greater during the rainy season (6.4–9.6 mg/L). The months with the greatest DO levels were June (9.6 mg/L) and September (9.07 mg/L), while the months with the lowest levels were March (5.33 mg/L). As a result, higher DO correspond to increased biological activity; rainy seasons had a greater impact than dry seasons, however there were no discernible variations across the different months at the p0.05 level of significance. The pH and dissolved oxygen (DO) levels, however, were within the WHO-recommended range [69] and matched the findings of Afolabi and Raimi [21]. The suggested value was not exceeded by any of the chemical

ions that were extracted from the water samples for this study. According to the study, they are less than what the WHO offers [69]. DO is therefore crucial for supporting a variety of aquatic life. Its concentration in rivers fluctuates depending on the trophic levels of the lakes. The amount of dissolved oxygen is influenced by photosynthetic activity and the microbial breakdown of both native and foreign organic materials. The river's overall low level of dissolved oxygen points to eutrophication. Most often, certain types of water pollution lead to the depletion of DO in the water. Additionally, the current trends of DO depletion in the majority of sample stations are brought on by the existence of a large organic load, which is dumped by a drain, as well as religious rituals along the river bank. Hydrogen sulfide, ammonia, nitrite, ferrous iron, and several oxidizable compounds are examples of inorganic reducing agents that tend to lessen the amount of dissolved oxygen in water. Meanwhile, the decomposition of extra nutrients and biodegradable organic materials by decomposing organisms like bacteria may be the cause of the low DO value during the dry season. These organic materials are brought in by an influx of dissolved solutes from nearby metropolitan areas, agricultural fields, and industrial wastes.

Figure 11 displays the electrical conductivity (EC) level in surface water. Surface water EC values were typically higher from the months of February (206.67 S/cm) and March (210.00 S/cm) through April (224.90 S/cm) and May (224.97 S/cm) until the end of the dry season and the beginning of the rainy season. As a result, it takes into consideration the nutrient load of rivers, which are highly impacted by anthropogenic activities such wastewater discharges and agricultural runoff. The month of May saw the highest EC value of 224.97 S/cm, while the month of July saw the lowest value at 103.33 S/cm. As a result, an increase in EC in water can result in aesthetic issues and annoyances, such as an unwelcome taste and color [22]. The 500–600 mg/L range corresponds to the WHO's recommended threshold for drinking water [22]. Afolabi and Raimi [13] asserted that poor water quality is not related to a greater level of EC. In addition, the presence of dissolved salts and other organic resources may be the cause of increased conductivity readings. Olalekan *et al.* [25] also pointed out that conductivity readings higher than 100 S/cm were a sign of human activity. Water conductivity between 150 and 500 S/cm is optimum for fish culture, according to Olalekan *et al.* [10]. This showed that the EC values found in the current study were higher than those considered ideal for fish culture. This could be as a result of the high conductivity agricultural drainage and the solutions of the majority of inorganic compounds and more numerous ions produced by industry [67].

Figure 12 depicts the surface water's hardness. Surface water's hardness peaked in April at 182.94 mg/L before dropping precipitously and reaching its lowest point in June (7.54 mg/L). The readings for the months of July (73.21 mg/L), August (71.61 mg/L), September (89.30 mg/L), October (74.55 mg/L), November (74.90 mg/L), and December (78.13 mg/L) showed little variation. Alkaline earth, which includes calcium and magnesium ions, is what causes the total hardness (TH) of water (it measures the sum of calcium and magnesium ions). According to the classification system, water with a TH of less than 60 mg/L is categorized as soft, 60 to 120 mg/L is moderately hard, 120 to 180 mg/L is hard, and more than 180 mg/L is very hard (Fig. 12). The water used for this investigation is categorized as soft and moderately hard according to the chart. According to this study's TH values, divalent metallic ions, calcium, and magnesium ions are dissolved in low to moderate amounts [9–12].

Total dissolved solids (TDS) originate from natural sources, sewage, urban runoff, and industrial wastewater (WHO, 2017). A high level of TDS affects aquatic life (APHA, 2012). Thus, higher ionic concentration, which is less palatable and causes an undesirable physicochemical reaction in consumers, is indicated by high TDS in water [6, 13]. TDS levels in surface water were measured between 89 mg/l and 158 mg/l (Fig. 13), with the lowest value occurring in the rainy (monsoon) month of July (89 mg/l) and the highest in the dry season of March (158 mg/l). Due to the significant concentration of dissolved organic matter and dissociate electrolyte, which entered the surface water through a variety of point and non-point sources, upward trends in TDS were seen during each monitoring month.

The total organic carbon (TOC) and total organic matter (TOM) level in surface water is given in Fig. 14. The TOC and TOM trends were identical as TOM was estimated from TOC. The peak values of TOC were recorded between June (21.88 mg/L) and July (21.04 mg/L). In mid-late dry season, the range of TOC was between 3.04–7.11 mg/L. In rainy season, it was between 6.58–21.88 mg/L. For TOM, highest value was observed in the month of June (38.0mg/L), July (36.5mg/L), April (10.0mg/L) during rainy season. While in the months of January, October, November and December the values are 10.2, 10,2, 10.2 and 10.0mg/L respectively.

The true colour of surface water is given in Fig. 15. The values were higher for most part of the study period, particularly mid-dry season (January) and Midrainy season (July), where it reached a peak of 1037.73 and 1331.28 respectively. Its lowest value was in March (253.01). The value of surface water true colour decreases toward the beginning of the dry season in the month of October (294.37). Good and potable drinking water has been characterized by a number of chemical, physical, radiological and biological parameters. In general, the appearance, taste, colour, and odour of drinking water are used to determine its quality [9–12]. Hence, the true colour of water samples in the present study were extremely high in the month of January, June, July and September and when compared to the WHO standard; this maybe as a result of effluents from industries, mining activities and homes around the study area [1, 25].

Turbidity restricts light penetration and limits photosynthesis in the aquatic environment. The turbidity degree of the water is an approximate measure of the intensity of the pollution [22, 23]. High turbidity indicates the presence of organic suspended material, which promotes the growth of microorganisms [9, 11]. Also, the level of water turbidity describes the cloudiness of the water as a result of precipitation of chemical, suspended particles, faunas and flora debris in the water bodies [29]. Turbidity in surface water is shown in Fig. 16. The turbidity level in surface water in some of the months was markedly higher, most especially in the months of the rainy season, this may be related to flood water originating from surrounding of the research area. The highest value of turbidity could be the presence of high biodegradable organic matter that comes from wastes of surrounding urban and discharged from mining related activities and agricultural fields. There is inclination of turbidity level from the month of June, July, August, and September. Surface water was high in most part of the rainy season between, June and September (163.38–222.94 NTU). Its lowest point was recorded in May (35.43 NTU). Thus, turbidity could be due to continuous and impactful predisposition to receiving large quantities of organic and inorganic materials emanating from mining related activities contaminating the surface waters of the study area. Raimi *et al.*, [9], Olalekan *et al.*, [10], Raimi and Sawyerr [11] and Raimi *et al.*, [12] attributed high values of turbidities in the dry season to decreased vegetation and evapotranspiration during cooler months. Thus, the present study reports high level of turbidity in all

the water samples; this makes the water not suitable for human consumption. All the water samples collected along the course of the river, in both dry and wet seasons were higher in surface water, especially in the dry season. This indicates the possibility of the water bodies containing hazardous chemicals and microorganisms (bacteria and protozoa) which are pathogenic to human [23]. The results of the turbidity level recorded from this study falls within the turbidity value reported by Olalekan *et al.* [25], which is higher than the WHO recommended value.

Temperature plays a vital role in determining the effectiveness of digestive enzymes, reproductive activities, and life cycles in the fish [23, 39]. A study by Afolabi and Raimi [13] showed that temperature influences fish growth, specifically in the sensitive fingerling stage. Olalekan et al. [25] found that high water temperature is an optimum condition for various mesophilic bacteria to grow, thus playing an important role in influencing their presence in fish. Thus, the water temperatures generally fluctuate naturally both daily and seasonally with air temperature. Surface water bodies are capable of buffering water temperature; even moderate changes in water temperature can have serious impacts on river ecosystem due to narrow temperature tolerance by aquatic organisms. High amounts of sewage discharges as well as religious ritual activities along the river bank significantly change river water temperature. Thus, temperature plays a vital role in controlling the chemical and biological composition of a freshwater body. In aquatic environment, temperature is the most significant ecological factor. In Osun state, rivers show seasonal variation in temperature. The temperature of surface water is given in Fig. 17. There was slightly difference in temperature across the months in the surface water. The range of value were 24.93-30.13°C. No clear peak was observed. The slightly low temperature from this study was recorded in the month of July with 24.93°C which is not too obvious from other value of temperature recorded from other months. Afolabi & Raimi [13] and Odipe et al., [22] stated that areas prone to discharge of industrial wastes usually have temperature ranges above those of their surrounding environments. Thus, the operational presence must have influenced an increase in surface water temperature, correspondingly reflecting in the result as seen above. This is indicative of surface water pollution since organisms that initially depend on surface water could find the temperature ranges no longer suitable for their continued stay and could migrate to areas with favourable temperature ranges. Moreover, in the present study, were higher than the values reported in the studies by Raimi et al. [12] and Olalekan et al. [14], who reported the 23.5 ± 1.8°C and 21.23°C, respectively. Morufu and Clinton [1] recommended a desirable temperature range of 20-30⁰C for aquaculture water quality. Afolabi and Morufu [6] also recommended a temperature range of 20 to 35°C for surface water. This indicates that the temperature values were within the recommended limits and that the same temperature range is also sufficient for the proliferation of most pathogenic bacteria [10].

The TSS concentrations in surface water is given in Fig. 18. The levels of TSS were generally low in the month of February (29.17 mg/L), March (80.00 mg/L), and May (24.33 mg/L). However, in the rainy season, they reached a peak of 2547.33 mg/L and in September. The range of values were 24.33–2547.33 mg/L. Thus, excessive influx of suspended solids in surface water could be attributed to discharge of large quantities of substances directly into surface water bodies or out rightly onto terrestrial areas from where they leach into surface water bodies. Hence, the value of total suspended solid (TSS) reported by Raimi *et al.* [2] is comparable to those of this present study as they both exceeded the recommendation of the WHO guideline for drinking water quality WHO [69].

The levels of TS in surface water are given Fig. 19. The concentrations in surface water sources are low between mid-dry season (February) – early rainy season (June). However, the values increased and peaked in September (2647.33 mg/L), levelling off in late rainy season to the early dry season. Thus, the report of their research shows that the concentration of solids dissolved in the water determine the concentration of water conductivity. The recommended EC for drinking water according to WHO [69] should not exceed 400 μ S/cm. The EC recorded from this study is found below this value, and this agreed with the result published by Odipe *et al.* [22].

The pH is a general measure of the acidity or alkalinity of a water sample and is indicated on a scale of 0-14. It influences many biological and chemical processes in water. The natural or human-induced process may elevate or decrease the pH of water. Due to its influence on nutrients' solubility and availability as well as their utilization by aquatic organisms, pH becomes an important factor. It varied significantly throughout the seasons. The monthly variations of pH levels in the surface water source are presented in Fig. 20. pH level almost similar through the dry season with a range of 6.10-6.82. However, pH levels of surface water levels increased, reaching a peak of 7.8 in September. Using the maximum permissible range of 6.0-8.5 as limit for pH as benchmark [67]. It is seen that the water is acidic. Thus, signifying some level of pollution throughout the seasons. The pH range from 6.10 to 7.8 indicates productive nature of the water body. This agrees with the discovery by Nwankwo and Ogagarue [70], that areas prone to mining area have pH levels that are within acidic ranges. In addition, the month of September showed higher acidities during rainy seasons, this could be attributed to large amounts of water received by rainwater which tends to increase the level of acidity within the study area. Hence, it is necessary to take appropriate measures to stop this increase. These results agreed with Olalekan *et al.* [10], Raimi and Sawyerr [11], Raimi *et al.* [12] and Afolabi and Raimi [13] who indicated that pH value lies in the acidic side. Morufu and Clinton [1] concluded that the suitable pH range for aquatic organisms especially for groundwater can be set at 5.5-9.0, implying that the pH value of water recorded during this research was not within the limit, especially during rainy and dry season.

3.2 Monthly variation of free radicals in surface water

The Ca²⁺ content of the surface water is presented in Fig. 21. The range of Calcium ion (Ca²⁺) in surface water was found between 1.29 mg/L obtained in the month of June and 37.08 mg/L in the month of May. The concentration of Ca²⁺ increases with respect from the onset of the dry season toward the onset of the rainy season. There is decrease in Ca²⁺ concentration at the peak of rainy season. Thus, the presence of Ca and Mg ions in the water supplies is attributed to the occurrence of calcic and ferromagnesian mineral-bearing rocks [70].

Cl⁻ levels in surface water is given in Fig. 22. The values of Cl⁻ in surface water in the dry season is low. However, surface water Cl⁻ increase dramatically in the mid-rainy season (July) reaching a peak of 496.3 mg/L only to plummet in August (21.27 mg/L) and remain steady for the rest of the season. Thus, higher value of chloride during rainy season could be due to large quantities being leached into surface water from adjoining lands due to contaminated rain falling onto such surface water than dry counterpart and settling on such surface waters. Higher chloride values could be due to chloride existing as a natural resource where there was limited quantity of water to neutralize available chloride compared to the lower value during other months where there are enormous

quantities of water to cause massive chloride neutralization. Thus, seasonal variations were also needed wherein it was found that chloride values were higher during rainy season than dry seasons.

 Mg^{2+} concentrations in surface water are given in Fig. 23. In surface water, the highest levels of Mg^{2+} were observed between the late dry season and the start of the rainy season, i.e., April (23.80 mg/L) and May (19.07 mg/L). However, the lowest point Mg^{2+} concentration was in June (1.049 mg/L). Thus, it could be deduced that seasonal variations have significant influences upon the concentrations of magnesium during both seasons and this seasonal influence was stronger.

 NO_3^{2-} levels in surface water are shown in Fig. 24. NO_3^{2-} was low in surface water in both the early rainy season and some months in the dry seasons. Its highest point was toward the end of the rainy season in the month of September (7.37 mg/L) and October (7.82mg/L). On the other hand, it was somewhat steady between January and August. Nitrates are naturally occurring or anthropogenically incepted environmental pollutants. It is essential for human health but excessive intake may cause adverse health challenges [9–12]. Nitrate is essential in the production of inorganic fertilizers. Its release into water bodies may be through agricultural activities [31, 33–38, 72, 73], fossil fuel combustion, and the release of domestic and industrial sewages [4, 7, 8, 12, 74–77]. Methemoglobinemia (also known as blue baby syndrome) and stomach cancer are associated health hazards of excessive intake of nitrate. Also, high NO_{3-} value could be due to the deamination of ammonium nitrogen from nitrogenous materials and raw wastes that can be oxidized to nitrate by the action of microbiological agents, wastewater disposal, and agricultural activity [2–7, 70]. Henry *et al.* [23] reported that the results of the high rate of microbial activity are associated with a high organic compound and in turn high nitrogen content. Regarding the toxic nature of NO_3^- , the World Health Organization (WHO) and the Standard Organization of Nigeria (SON) defined its acceptable limit in water as 50 mg/L. Additionally, seasonal usage of nitrate fertilizers could also explain this trend. Availability of nitrogen fixing bacteria that penetrate atmospheric nitrogen into the soil could account for the very level of nitrate within the study area and consequent higher amount in ground waters.

 PO_4^- is an essential plant nutrient that stimulates the growth of algae and macrophytes in lakes. It is a proxy indicator of lake productivity. PO_4^- concentrations of the surface water are given in Fig. 25. There is fluctuation in the concentrations of the ions throughout the months of the study. However, in July, October and November there was a notable difference between surface water (0.34 mg/L, 0.33 mg/L and 0.34 mg/L was observed). Thus, phosphate groups have been discovered to play a crucial role in the binding of Ni to the cell wall of gram-negative bacteria. PO_4^- enters the river through domestic wastewater and gold mining activities accounting for the accelerated eutrophication. In addition, phosphate levels were observed to increase from dry season to wet season. Rainy season tends to influenced phosphate concentration more than dry season. The higher values in the rainy season at the expense of dry season could be due to the fact that farmers in the study area usually engaged in seasonal farming where rain is seasonally targeted before crops could be planted and the soil had to be nourished with fertilizers of which phosphate fertilizer is one [31].

 $SO_4^{2^-}$ levels in surface water are presented in Fig. 26. $SO_4^{2^-}$ concentrations in surface water reached its peak in June (12.50 mg/L) and lowest point in December (2.36 mg/L). It was low at the onset of the rainy season in the month of April (2.87 mg/L) and toward the mid of the dry season in December (2.36 mg/L) and January (2.56 mg/L). Thus, it could be stated that sulphate are very unstable in the atmosphere from where they are converted into forms suitable for their stay in surface and groundwater. Additionally, it could be stated that agricultural contamination from fertilizers which latter seeped underground to mix with ground water, gold mining in the study area must have increased the concentration of sulphate during the rainy season as against the low levels during dry season. Hence, surface water acts as receiving ends from rain constituents and contaminants emanating from gold mining activities. This shows the interrelationship existing between the rain and surface water within the study area.

Na⁺ levels in surface water are given in Fig. 27. The surface water had higher Na⁺ in the dry season, were it reached a peak of 18.2 mg/L in December and January, its lowest point in July (3.8 mg/L). The range of values of surface water was 3.3–18.17 mg/L and no clear peak was observed. Thus, as it can be seen in the graphs below (Fig. 27), the concentrations is low between July, August, October and November but starts to rise sharply until December – June, thence to plummet, thus giving a more or less symmetric shape. The reason behind is the adequate water flow in the river during rainy season. Quick decisions should be taken to reduce this concentration for the sake of environmental protection and public health.

In Fig. 28, the K⁺ concentrations in surface water are shown. In both the dry and wet seasons, the K⁺ concentrations in surface water are less than 10 mg/L, with the exception of the dry season's February (20.03 mg/L) and the wet season's July (12.0 mg/L), when they reach their highest levels. A range of values between 1.6 mg/L and 20.03 mg/L were discovered. Therefore, elevated potassium levels may be caused by farmers using potassium fertilizers, which later settle below and permeate into ground water. Additionally, potassium might be a naturally occurring resource in the study location. Additionally, it might be concluded that greater potassium levels during wet seasons may be caused by soil potassium leaking from potassium fertilizers into nearby surface waterways. Meanwhile, the discharge of effluents from gold mining industrial units accounts for the rise in potassium concentration as one approaches the area. Due to the abundance of industrial activity related to gold mine in the area, this becomes much more significant when we are there. All industrial gold mining facilities must be required to treat their effluent before discharging it into the environment in order to protect the ecosystem by minimizing the negative effects.

3.3 Monthly variations in heavy metal concentration in surface water

Heavy metal pollution has developed as a result of human activity, which is the main cause of pollution. This activity frequently results in metal mining, smelting, foundries, and other industries that are based on metal, as well as the leaching of metals from special repositories like landfills, waste dumps, excretion, cattle manure, runoffs, vehicles, and roadwork. The secondary source of heavy metal pollution in the agriculture sector includes the use of herbicides, insecticides, fertilizers, and other heavy metal-containing products. Natural factors such as volcanic activity, metallic corrosion, metallic evaporation from soil and water and sediment re-suspension, soil erosion, and geological weathering can also result in the growth of heavy metallic

pollutants. In surface waterways, substantial sources of contamination are therefore thought to be trace metals. Trace metal contamination in surface water is a serious global problem due to its toxicity, ubiquity, and environmental durability.

Seasonal analyses of the amounts and distribution of metals revealed that lead (Pb) concentrations in surface water are shown in Fig. 29 for the analyzed surface waters. Pb levels in surface water reached their highest point in December (2.23 mg/L), during the dry season. The lowest amount in surface water, nevertheless, was recorded in February (0.75 mg/L). Sources of lead contamination include mining, paint, battery waste, coal burning, pesticides, herbicides, and emissions from the burning of leaded fuel. According to research on the health consequences of Pb, accumulation of the metal in humans would have negative effects on the heart, blood pressure, incidence of hypertension, kidney function, and reproductive issues [1–3]. Children are most susceptible to the harmful effects of Pb, which is a severe hazard to public health. Children's nervous systems and brain development are impacted by Pb hazardous drinking water [12, 78, 79]. According to Brown & Woolf's [80] survey findings in Zamfara, children who live near Pb mines are more likely to develop hemorrhagic encephalopathy due to high Pb levels. Additionally, Gyamfi *et al.* [81] revelation of increased Pb concentrations in Ghanaian mining site soil and water supported the findings of the current investigation. Therefore, Pb in surface water may come from sources such as gold mining, the plastic and rubber, paint, metal, and alloy industries, battery, fabric, and solid waste disposal industries, among others. Surface waters nearby get untreated industrial wastewater that has been discharged along with sewage from the city. While research on lead exposure in drinking water have been widely documented over the past few decades as the number of lead contamination cases has increased [25], lead continues to be a deadly heavy metal. Nearly every physiological system may be distressed, although the hematologic, gastrointestinal, and neurological systems are most commonly impacted. Furthermore, exposure to lead harms children's behavioral and mental health, mak

Figure 30 shows the monthly fluctuations in surface water cadmium (Cd) concentration. Surface water Cd concentrations were generally higher, peaking at 2.73 mg/L in December and declining to 0.061 mg/L in May. While the preparation of Cd-Ni batteries, electroplating, control rods, and shields inside nuclear reactors leak Cd into the river, so do stainless steel production facilities, electroplating factories, and vehicle batteries. Under adequate physico-chemical conditions, the predominance of an exchangeable fraction of Cd indicates anthropogenic origin and strong mobility between aqueous (water) and solid (sediment) phases. Therefore, under proper physico-chemical conditions, the prevalence of an exchangeable fraction of Cd indicates anthropogenic origin and high mobility between aqueous (water) and solid (sediment) phases [9, 11, 31, 32]. Cadmium is another dangerous element that has been designated as Group B1 by the US EPA (probable human carcinogen). Industrial waste and agricultural fertilizers generate cadmium pollution in drinking water. Renal failure, liver damage, muscle cramps, diarrhea, nausea, and vomiting are a few examples of specific medical conditions that may be brought on by cadmium exposure [1–10].

In Fig. 31, the levels of chromium (Cr) in surface water are depicted. Particularly during the dry season and the beginning of the rainy season, the levels of Cr in surface water were greater (May). Surface water chromium concentrations peaked in December (2.09 mg/L) and ranged from 0.32 to 2.09 mg/L. Surface water samples with greater Cr concentrations are the result of the metal building up over time in the area. According to Fagbenro *et al.* [82], Osun State had greater chromium (Cr) concatenation. However, despite both exceeding the WHO-recommended level, the concentration of Cr found in this study was not higher than that reported by Fagbenro *et al.* [82].

Figure 32 shows the manganese (Mn) concentration in surface water. Over the course of the study's twelve months, there was a noticeable variation in focus. December saw the highest Mn levels (1,802) while March saw the lowest (0.35 mg/L). When compared to the rainy season, the concentration of Mn was found to be greater in the dry season. Although manganese is a vital element and is more abundant in surface water, an excessive amount can be detrimental. Our study's high Mn concentration was consistent with reports by Omotola *et al.* [83] regarding a gold mining site in Zamfara and Fagbenro *et al.* [82] regarding the heavy metal profile of sediments in gold mining towns in Osun State. Also. In comparison to the WHO-recommended standard, Cr and Cd are greater in all samples taken from the study site [68, 69].

Figure 33 displays the concentrations of mercury (Hg) in surface water. In the months of February (1.39 mg/L), April (1.61 mg/L), August (1.73 mg/L), and December (1.97 mg/L), the concentration of Hg was obviously high. The highest level was recorded in the month of December (1.97 mg/L), while the lowest level (0.13 mg/L) was recorded in the month of October. Surface water that was collected along the river's course had an extremely high hg content. This might be due to a long-term buildup of mercury in the sediment of the local river and its tributaries. According to Veiga *et al.* [84], gold mining causes 20–30% of the Hg pollution. This is because mercury is used in the process of extracting gold. Water and soil pollution result from the indiscriminate release of metal into water bodies during the mining process. A higher concentration of Hg was found in the soil taken from various artisanal gold mining sites in Ghana, according to Mantey *et al.* [85]. The findings of their investigation were consistent with those of the current study. Additionally, the considerable positive association between mercury and temperature supports the finding that mercury toxicity increases as temperature rises [84, 85], leading us to record extraordinarily high mercury levels in water samples. As a result, the discovery of mercury in the surface water suggested that untreated sewers transporting trash from urban and industrial effluent may have been the cause of the pollution. Therefore, it is crucial to analyze the amounts of mercury in surface water, such as rivers and lakes, because it is a hazardous element with no biological or physiological purpose in humans. Leukemia, neuro-pathological deterioration, kidney disease, renal system failure, and other health issues are all caused by it, though [29].

The toxicity of arsenic depends on its chemical state; the inorganic forms are thought to be more dangerous than the organic ones since they have quite different impacts and metabolic processes. Arsenic is a common contaminant throughout the world. Figure 34 shows the amount of arsenic (As) in surface water. Surface water contained As concentrations ranging from 0.04 to 7.36 mg/L. Surface water As levels were consistently low and constant throughout the other months, with a definite high in February (7.37 mg/L). It was interesting to note the elevated As concentrations, which affected both the river and its tributaries. This result was most likely related to anthropogenic activity as well. These heavy metals, however, accumulated throughout the dry season due to human activity in the mining region. Additionally, the discharge of urban and industrial waste water, particularly sewage from gold mining operations, is to blame for considerable increases in arsenic concentrations in surface water.

In conclusion, the concentrations of several physicochemical parameters, such as DO, Hardness, Turbidity, Chloride, Potassium, Lead, TSS, Cadmium, Chromium, Manganese, Mercury, and Arsenic, among others, are influenced by the ions (cations and anions). The primary sources of trace elements are mining activities, the aerospace sector, solid rocket fuels, end-of-life vehicle waste, different dyes, and pigments [9–12]. Increased levels of these hazardous metals in the environment reduce agricultural output and soil microbial activity, endangering human health through the food chain. Additionally, these metals may cause problems for human reproduction, biotransformation, and growth [28–32]. By interfering with numerous metabolic processes, including inhibition of photosynthesis and respiration and degeneration of main cell organelles, heavy metals accumulate in various plant tissues and have an adverse effect on their growth and development. These effects include stunted growth, delayed germination, chlorosis, premature leaf fall, senescence, decreased crop yield, and loss of enzyme activities [78–80]. Consuming heavy metals like Cd and Zn in humans can lead to a variety of illnesses, including acute gastrointestinal, musculoskeletal, and respiratory problems, as well as harm to the brain, heart, and kidney [1–10]. Chronic bronchitis, lung cancer, immunotoxicity, neurotoxicity, genotoxicity, infertility, and skin conditions are only a few of the harmful impacts that Ni can produce [11–25]. While excessive Al is extremely neurotoxic for animals and is suspected to be linked to a number of skeletal abnormalities and neurodegenerative diseases, the toxic effects of Cd include kidney and lung damage, fragile bones, gastrointestinal disorders, carcinogenic, mutagenic, and Itai-Itai disease [9–12].

4. Conclusion And Implications Of The Study

The buildup of heavy metals poses long-term repercussions of the threat created by these metals on aquatic life and those who depend on rivers for domestic use and as a source of drinking water. Heavy metals can exist naturally in the environment or through manmade causes. Thus, many governments must set goals to fulfill their pledges to protect water quality in order to reduce anthropogenic activities in accordance with the 2015 Paris Agreement. While the research region is marked by practices that promote the buildup of heavy metals. Different heavy metals were found in the surface water samples taken from the study sites, according to the report. The deposition of run-off and garbage from mining sites, residences, agro-processing facilities, and herbicide and pesticide residues from farmers are to blame for the buildup of heavy metals [33–39]. According to Salazar-Camacho et al. [85], residential, industrial, and mining waste are the main causes of heavy metal pollution in water. High concentrations of elements including Cd, Cr, Hg, As, Pb, Fe, Mn, Ni, Zn, and Cu are a result of mining. The majority of these substances could be harmful to human health as well as aquatic life. The investigation found dangerous levels of lead (Pb), cadmium (Cd), chromium (Cr), manganese (Mn), mercury (Hg), and arsenic (As), all of which are determined at high concentrations shove WHO recommended limits. As a result, it has been determined that most surface water used in mining environments is unfit for human consumption. According to the most deviating biological and radiological indicators compared to norms set by reputable local and international organizations, this was attributable to the high amount of contamination from various sources. The relatively high concentration of heavy metal loading in the water is a substantial barrier to rural residents' access to potable water in the mining environment. As a result, the appropriate constituted authority shall continuously monitor the surface water to identify any changes in t

5. Recommendation

The various findings on the surface water quality in the gold mining areas of Osun State, South-West Nigeria, have been given and addressed in this paper. Therefore, future study should focus on the following issues:

- 1. To protect the citizens of this community from the risks of chemical exposure and poisoning brought on by the use of surface or groundwater for irrigation, local authorities like the local government must first offer an alternate supply of water.
- 2. Significant remediation activities are required to clean up the environment, including the soil and water, and artisanal and small-scale miners must be educated on safer and more environmentally friendly techniques of mining. As a result, the environmental concerns connected with the usage and release of hazardous substances like mercury will be reduced.
- 3. Surface water samples from urban, rural, industrial, and remote locations need to have their chemical composition, speciation, and abundance of metal contaminants, as well as their physico-chemical properties, better characterized. To do this, advancements in analytical techniques and equipment are needed.
- 4. In order to improve our understanding of how physico-chemical and heavy metal properties affect surface water processes, we urge further research in the following areas: (a) more characterizations of experiments are needed to provide specifics about the effects of physicochemical and heavy metal properties on surface water; and (b) more research is encouraged because knowledge of these parameters is crucial for more accurate modeling studies and predictions.
- 5. Encourage the development of technology for safe and effective water usage, particularly with regard to the reuse and recycling of waste water.
- 6. Encourage private sector investment and the development of suitable water and sanitation technologies as well as waste management infrastructure by promoting environmental health impact analysis (EHIA) as a component of environmental impact assessments (EIA) for all developmental undertakings.

Declarations

Acknowledgements

The authors are thankful to the Department of Environmental Health Sciences, Kwara State University for the encouragement of research activity and for providing necessary laboratory facilities.

Authors' contributions

All of the authors have the same contribution, having read and approved the final manuscript.

Grant Support Details

The present research did not receive any financial support.

Conflict of Interest

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

Life Science Reporting

No life science threat was practiced in this research.

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Area map showing sampling Aye-Oba River and its tributaries.



Map showing sampling points at Aye-oba River and in Ife South.



Map showing sampling points and LULC Classes in Ife South.



Map showing sampling sites in Atakumosa East.



Map showing sampling points in Atakumosa West.



Figure 6

A diagram depicting the quantification methods used in the current investigation.

Adapted from Raimi et al., [9], Olalekan et al., [10], Raimi & Sawyerr [11], Raimi et al., [12]





Monthly variation of apparent colour in surface water





Monthly variation of Biological Oxygen Demand (BOD) in Surface water



Monthly variation of Chemical Oxygen Demand (COD) in Surface water



Figure 10

Monthly variation of Dissolved Oxygen (DO) in surface water



Figure 11

Monthly variation of electrical conductivity (EC) in Surface water





Monthly variation of hardness in Surface water



Monthly variation of total dissolved solids (TDS) in surface water









Monthly variation of true colour in surface water



Monthly variation of turbidity in surface water





Monthly variation of surface temperature



Figure 18

Monthly variation of total suspended solid (TSS) in surface water



Monthly variation of TS in surface water



Figure 20



Monthly variation of hydrogen ion concentration (pH) in surface water

Figure 21

Monthly variation of Ca²⁺ in surface water



Monthly variation of $\mbox{Cl}^{\mbox{-}}$ in surface water



Figure 23

Monthly variation of Mg²⁺ in surface water



Figure 24

Monthly variation of NO32- in surface water



Monthly variation of PO_4^{3-} in surface water



Figure 26

Monthly variation of SO_4^{2-} in surface water

Sodium ion (Na⁺) Concentration (mg/L)



Monthly variation of Na⁺ in surface water



Figure 28

Monthly variation of $\mathsf{K}^{\!+}$ in surface water







Figure 30





Figure 31

Monthly variation of chromium (Cr) concentration in surface water





Monthly variation of manganese (Mn) concentration in surface water

Figure 33



Monthly variation of mercury (Hg) concentration in surface water

Figure 34

Monthly variation of Arsenic (As) concentration in surface water.