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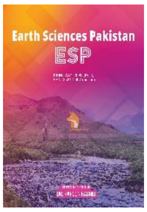

RESEARCH ARTICLE

HYDROGEOCHEMICAL, CONTAMINATION AND PROBABILISTIC ECOLOGICAL AND HEALTH RISK ASSESSMENTS OF HEAVY METALS IN WATER IN OWO METROPOLIS, SOUTHWEST NIGERIA

Popoola[a*], O.J., Adeseko, A.A[b]., Sebastine, L[a]. and Owolabi, R.R[a].

[a]Department of Geological Sciences, Achievers University, Owo, Ondo State, Nigeria
[b]Department of Remote Sensing and Geoscience Information System, Federal University of Technology, Akure, Ondo State, Nigeria
Corresponding Author Email: adewumiadeniyi27@gmail.com

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ABSTRACT

This study focuses on assessing the water quality and heavy metal contamination in surface and groundwater in the Owo metropolis. Water, a vital resource for human existence and ecosystem maintenance, plays a crucial role in various activities. The research emphasizes the significance of water quality in preventing waterborne illnesses, particularly in areas lacking proper sanitation. The physicochemical characteristics of surface and groundwater were analyzed, revealing parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3), and concentrations of various metals. The results indicate that the studied parameters generally fall below the World Health Organization (WHO) and Nigerian guidelines, suggesting a lower risk to public health. Cluster analysis revealed associations between water samples, linking certain clusters to anthropogenic activities like dumpsites, farming, and households. Correlation analysis demonstrated relationships between different hydrochemical parameters, highlighting potential sources of major ions. Geochemical assessments, illustrated through Piper and Gibbs diagrams, indicated the dominance of Ca-Cl water types and the influence of rock weathering on water composition. Bivariate plots and ion exchange processes provided insights into water-rock interactions. The study also evaluated ecological risks and water quality indices, revealing potential risks from heavy metals. Hazard and cancer risk assessments suggested the cumulative potential of heavy metals to pose health risks, particularly for children. The research emphasizes the need for urgent interventions to address water quality issues in the Owo metropolis.

KEYWORDS

Water Quality; Heavy Metal Contamination; Owo; Human Health Risk Assessment; Ecological Risk Assessment; Hydrogeochemistry

1. INTRODUCTION

Water is a limited natural resource that is vital to human existence and is necessary for a wide range of human activities as well as the maintenance of ecosystems and life (Kilic, 2020; Adewumi and Laniyan, 2021). Water quality, as defined by its chemical, physical, and biological properties, is critical to human health and the health of the environment (Akhtar et al., 2012). Water quality is important in many ways, from maintaining ecological balance to promoting public health and economic growth (Yurui et al., 2023). The direct influence of water quality on human health is among the primary factors emphasizing the significance of this issue. Preventing illnesses caused by water is mostly dependent on having access to safe and clean drinking water (Laniyan and Adewumi, 2019). When heavy metals are found in water supplies, there are major risks. Drinking polluted water can lead to waterborne illnesses including cholera, typhoid, and dysentery, particularly in areas without adequate sanitary facilities or water treatment (Laniyan and Adewumi, 2019; Shayo et al., 2023). Therefore, maintaining excellent water quality is essential to global public health programmes. Ecosystem sustainability and health are closely related to the quality of the water. Pollutants, fertilizers, and heavy metals in particular can upset the delicate equilibrium of these ecosystems (Alengebawy et al., 2021). Maintaining the overall balance of natural systems and the biological integrity of aquatic ecosystems depend on the protection of water quality. Thus, it is critical to comprehend the geochemical characteristics of water in order to comprehend the activities that influence them (Bogardi et al., 2020).

The decline in water quality can be attributed to anthropogenic activities such mineral extraction, mineral dressing, industry development, use of agrochemicals, human waste, and untreated soil discharge (Aziz et al., 2023). Studies conducted worldwide, including those in China (Deng et al. 2022), Nigeria (Egbueri et al. 2023), Bangladesh (Khan and Paul, 2023) and India (Bhardwaj et al., 2017) have revealed that metals are contaminating water supply. Although heavy metals were initially found in rocks, human activity has quickly altered the geochemical cycles (Adewumi and Laniyan, 2023). Water and rocks interact to release metals into them, and ingesting larger concentrations of metals—including copper, iron, manganese, zinc, and cobalt—may be harmful to human health. While there are no health advantages to metals like lead and mercury, they can be harmful if they are retained in the body for an extended period of time (Adewumi and Laniyan, 2023). They interfere with the body's metabolic functions and cause bioaccumulation in a number of vital organs, including the brain, kidney, liver, and heart (Priyadarshanee et al., 2022). Humans can absorb toxic metals through their food, breathe them in, or come into direct touch with polluted materials on their skin (Abbas et al., 2018).

The concept of ecological risk was created in relation to ecological risk

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assessment. It is the likelihood that an undesirable ecological outcome may materialize (Adewumi and Ogundele, 2024). It comprises defining the problem, analyzing exposure, evaluating the impacts, and characterizing the risk. Environmental research all across the world have employed ecological risk assessment as a crucial tool. To determine the possible harm that metals in the environment may cause to people's health, the human health risk assessment was created (Adewumi and Ogundele, 2024). Reports from all across the world such as Rehman et al., Tchounwou et al., and Ohiagu et al., have linked heavy metal exposure to possible health hazards for humans (Rehman et al., 2018; Tchounwou et al., 2012, and Ohiagu et al., 2022).

In Ondo state, southwest Nigeria, Owo Metropolis is a rapidly expanding city. The city is experiencing more industrialization and expansion, which has boosted the population. The amount of rubbish produced has increased along with the population. To determine the geochemistry of the groundwater in the region, several investigations have been conducted. Adewumi and Anifowose found that the Owo region is for groundwater buildup utilizing geology and remote sensing techniques (Adewumi and Anifowose, 2017). Adewumi et al., found that the area's groundwater has a good to exceptional water quality index and is less susceptible to pollution according to the DRASTIC model (Adewumi et al., 2017). Nevertheless, no research has been done to assess the area's surfacewater quality. Furthermore, no research has been done to ascertain the level of heavy metal contamination in the area's surface and groundwater. Therefore, this research was conducted to ascertain the level of heavy metal pollution in the area's surface and groundwater as well as how to assess the dangers to human well-being and the environment.

2. MATERIALS AND METHODS

2.1 Study area

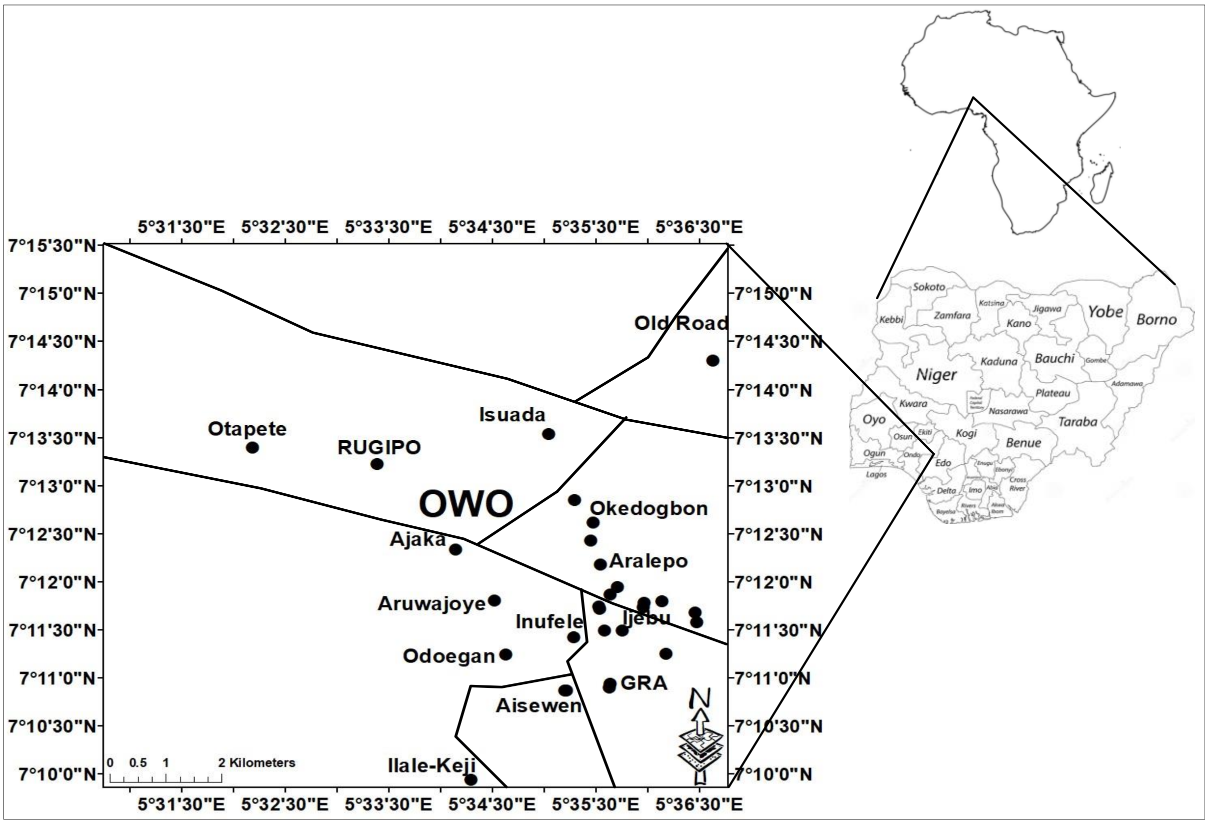

Figure 1: Location map of the study area (Use google earth for the map)

The study area is in the northern part of Ondo State, Southwest Nigeria. It lies between Latitudes 7°00’ and 7°25’N and Longitudes 5°20’ and 5°45’E and occupies an area of approximately 40 km^2 (Figure 1). The study area is bordered by towns such as Ayede-Ogbesse, Alayere, Uso-Owo, Amurin-Owo, Emure-Owo, Ipele-Owo, Ita-Ipele and Oba-Akoko which are accessible through asphaltic roads connecting the major towns, while minor roads connect settlements to the towns. The major highway in the area links Ibadan, Akure and Benin together. The study area consists typically of dendritic drainage pattern (Figure 1). The major river in the area is River Aisewen West to East which is perennial in nature. Its tributaries are mostly seasonal, reaching their maximum dryness at the peak of the dry season. The area is located within the tropical savannah belt of Nigeria. The soil belongs to the broad group Alfisol (USDA, 1975) of the Basement Complex, though, locally classified as Okemesi Series (Smyth and Montgomery, 1962). The rainfall of is between 1100mm to 1500mm per annum and mean monthly temperature of 24-32°C (Agbede and Ologunagba, 2009). Geologically, the area is underlain by the Basement Complex of Nigeria, which are classified as migmatite-gneiss-quartzite group and schist belt (Rahaman, 1971), which are Precambrian in age and is within the zone of Pan-African reactivation (Oyawoye, 1964). Rocks outcropping in the area are quartzite, schist, granite gneiss and migmatite gneiss. The quartzite/quartz schists are found in Owo and Emure areas, mostly trending from NW to SE. Joints and fractures are the most visible structures in the area, and they trend mostly in the NE-SW, ENE-WSW and NW-SE directions (Adewumi et al., 2017). Hydrogeologically, these rocks are poor aquifers, causing problems of potable groundwater supply due to the fact the underlying rocks lack pore spaces that can hold water. However, when these rocks are fractured, they can accommodate groundwater that can be used for domestic and industrial purposes (Adewumi and Anifowose, 2017). The fractured quartzite and schist that underlay this area serves as conduit through which the aquifers in the area are recharged (Adewumi and Anifowose, 2017).

2.2 Sample collection

For this study, a total thirty-one (31) samples which include twenty-nine (29) surfacewater, six (06) groundwater and one (01) control ground and surfacewater samples were collected within the Owo Township in November 2020 during the dry season. The sampling locations were chosen to represent the groundwater quality in the study region (Figure 1). The physical parameters measured were measured in-situ using the multiparameter instrument package. The physical parameters measured are pH, temperature, electrical conductivity (EC), and total dissolved solids (TDS). The samples were filtered through 0.45 µm membrane filter which was acidified with nitric acid (HNO_3) to a pH of less than 2 to minimize adsorption of metals to container walls and reduces biological activity. All groundwater samples are stored at approximately 4°C in a clean unused and uncontaminated plastic. The water collection and analytical techniques used followed standard procedure (APHA, 1998). Chemical parameters measured in the water samples are SO_4, Cl, HCO_3, Na, Ca, K and Mg using flame spectrometer. Heavy metals such as Cu, Cd, Cr, Fe, Ni, As, Pb and Zn in the samples were analyzed using Atomic Absorption Spectrophotometer (AAS).

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2.3 Quality control

An internal standard was assessed for each ten samples, along with a calibration standard to gauge the efficiency and performance of the analytical tool and a blank to continually monitor for contamination. Calibration curves were updated at every step of the sample reading procedure using quality control standards. After soaking in 10% HNO_3 for the whole night, all glassware was thoroughly cleaned with distilled water and dried in an oven at 50 to 60°C. Before being used, the glassware was first dried in an oven and then dried for about 20 minutes in a desiccator. The analytical accuracy was more than 10% thanks to the use of duplicates, reagent blanks, and internal standards in quality assurance and quality control procedures.

2.4 Statistical Analysis and Spatial Map Generation

Statistical analysis employed for this study include: descriptive analysis, one-way ANOVA, bivariate correlation, hierarchical cluster analysis (HCA), and principal component analysis (PCA). All data were statistically standardized before carrying out the bivariate correlation, HCA and PCA. Statisitcal evaluation was carried out using Statistical Package for the Social Sciences (SPSS) version 22. All spatial maps used in this study were generated using krigging techniques in ARCMAP.

2.5 Hydrogeochemical assessment

In order to further examine the contribution of the mineral dissolution process to the water hydrochemistry, the saturation indices (SI) can be used to indicate the saturation status of minerals in water, when the solubility of the minerals in groundwater reaches the limit, and the ions in groundwater precipitate and reattach to the minerals. Moreover, SI can identify whether dissolution or precipitation has occurred, which was calculated by the following formula:

$$SI = log\left(\frac{IAP}{K_s}\right) \tag{1}$$

where IAP represents the value of ionic activity product, Ks represents the solubility product of different minerals. When SI is greater than 0, equal to 0 and less than 0, it denotes the oversaturation, equilibrium, and unsaturated state of minerals in water, respectively (Vinnarasi *et al.* 2021). The unsaturated state means that the minerals still have the potential to release ions into groundwater. Aqion 3.1 software was used to generate the SI values for this study.

2.6 Water-rock Interactions

Ion exchange is a crucial step in the interactions between water and rock and affects the chemistry of groundwater. An aquifer's composition varies depending on its hydrogeochemical circumstances, giving rise to specific governing elements for groundwater hydrochemistry. The cation exchange process between Na, K, Ca, and Mg has been identified by the chloro-alkaline indices (CAI-I and CAI-II) proposed by Schoeller (1977) and has been widely used to better understand the ion exchange process that takes place between water and its host environment during the process of residence or travel (Marghade *et al.* 2012). The following formulas can be used to determine CAI:

$$CAI - I = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{2}$$

$$CAI - II = \frac{Cl^- - (Na^+ + K^+)}{HCO_3{}^- + SO_4{}^{2-} + CO_3{}^{2-} + NO_3{}^{2-}} \tag{3}$$

where the units of all ions are meq/l.

2.7 Contamination assessment

The Geo-accumulation Index (Igeo), Contamination Factor (CF), Contamination Degree (CD), and Pollution Load Index (PLI) were used to assess the level of metal pollution in the water in the area. The geo-accumulation index, a metric proposed by Muller (1969), was obtained using Equation (4). Igeo was divided into five types by Muller (1969): Igeo less than zero (unpolluted); 0 ≤ Igeo less than one (unpolluted to moderately polluted); 1 ≤ Igeo less than two (moderately polluted); 2 ≤ Igeo less than three (moderately to heavily polluted); 3 ≤ Igeo less than four (heavily polluted); 4 ≤ Igeo less than five (heavily to extremely polluted); and Igeo less than five (extremely polluted):

$$I_{geo} = log_2 \frac{C_n}{1.5 \times B_n} \tag{4}$$

The background sample's metal concentration is denoted by Bn, whereas the sample's metal concentration is indicated by Cn. Any background value fluctuations that may result from lithologic changes in the water are mitigated by the constant 1.5.

The CF in Equation (5) was also used to evaluate the pollution of the water. All four classes are recognised by the single element index, CF (Hakanson, 1980). The CF categorization may be broken down into four subcategories: low contamination factor (CF<1), moderate contamination factor (CF < 3), significant contamination factor (CF < 6), and extremely high contamination factor (CF <= CF).

$$Contamination\ factor = \frac{Metal\ Concentration}{Concentration\ of\ elements\ in\ background\ soils} \tag{5}$$

The environment's CD is indicated by the total number of contamination factors for all the elements under examination (Hakanson, 1980). The CD is given to four groups. The CD may be calculated using the formula in equation (6). CD is classified into four categories: low contamination (CD < 8), moderate contamination (CD < 16), considerable contamination (CD < 32), and very high contamination (CD ≥ 32).

$$C_d = \sum_{i=1}^{n} C_f^i \tag{6}$$

The contamination factor is denoted by CF and the contamination degree by Cd.

Furthermore, PLI was developed by Tomilson et al., (1980) (Equation (7). A value of 0 indicates no pollution, 1 indicates none to medium pollution, 2 indicates moderate pollution, 3 indicates moderate to strong pollution, 4 indicates strong pollution, 5 indicates strong to very strong pollution, and 6 indicates very strong pollution (Rai et al. 2019). This provides a simple but comparable method for assessing the quality of a site.

$$Pollution\ Load\ Index\ (PLI) = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n} \tag{7}$$

where CF is the contamination factor determined according to Eq. (4) and n is the number of metals investigated. The PLI provides simple but comparative means for evaluating a site quality. It can be PLI can be measure via a scale from 1 to 6: 0 = none; 1 = none to medium; 2 = moderate; 3 = moderate to strong; 4 = strongly polluted; 5 strong to very strong; 6 = very strong (Rai et al., 2019).

2.8 Water quality index

Using the most often measured water quality variables, the weighted arithmetic water quality index approach categorised the water quality based on the level of purity. Numerous scientists such as Chauhan and Singh (2010), Chowdhury *et al.* (2012), and Balan *et al.* (2012) have employed this approach extensively. Brown *et al.* (1972) calculated WQI using equation 8:

$$WQI = \frac{\sum Q_i W_i}{\sum W_i} \tag{8}$$

Equation 9 is used to determine the quality rating scale (Qi) for each parameter:

$$Q_i = 100\left[\frac{V_i - V_o}{S_i - V_o}\right] \tag{9}$$

Where Vo is the ideal value of this parameter in pure water, Vo = 0 (unless pH = 7.0), Si is the suggested standard value of the ith parameter, and Vi is the estimated concentration of this parameter in the analysed water. Each water quality parameter's unit weight (Wi) is determined using the formula below:

$$W_i = \frac{K}{S_i} \tag{10}$$

where K, which is similarly computed using equation 11, is the proportionality constant:

$$K = \frac{1}{\sum(1/S_i)} \tag{11}$$

2.9 Water suitability for irrigation

2.9.1 Sodium adsorption ratio (SAR)

Equation 12 provided an estimate of SAR for the groundwater in the research region.

$$SAR = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}} \tag{12}$$

Excellent water has a SAR value of less than six; problems get worse with values 6–9; and significant problems arise with values >9 (Herman, 1978).

2.9.2 Permeability index

Soil permeability is impacted by irrigation water consumption over time. It relies on a number of variables, including the water's bicarbonate concentration, sodium, calcium, and magnesium contents. Equation 13 is used to compute the permeability index. Based on the Permeability Index (PI), Doneen (1964) divided irrigation fluids into three types (Doneen, 1964). It is appropriate for irrigation if the permeability index is less than 60; if it is greater than 60, it is not.

$$PI = \frac{(Na+K)+\sqrt{HCO_3}}{Ca+Mg+Na+K} \tag{13}$$

2.9.3 Magnesium adsorption ratio (MAR)

In most groundwater, the ions Ca^{2+} and Mg^{2+} keep the system in an equilibrium (Hem, 1985). When Mg^{2+} in water reaches equilibrium, it turns the soil alkaline, which lowers crop output (Kumar *et al.,* 2007). The magnesium adsorption ratio is used to quantify the impact of magnesium in irrigated water. An index was created by Paliwal (1972) to determine the magnesium danger. Equation 14 is used to compute MAR:

$$MAR = \frac{(Mg^{2+})\times 100}{(Ca^{2+}+Mg^{2+})} \tag{14}$$

2.9.4 Soluble sodium percentage (SSP)

The mineralization of water and its impact on plants and soil determine whether groundwater is suitable for irrigation (Selvakumar *et al.* 2017). Increased sodium content in irrigation water causes Na^+ to be absorbed by clay particles, which in turn displaces Mg^{2+} and Ca^{2+} ions and decreases soil permeability (Selvakumar *et al.* 2017). Equation 15 represents the SSP.

$$SSP = \frac{(Na^{+}+K^{+})\times 100}{Ca^{2+}+Mg^{+}+Na^{+}+K^{+}} \tag{15}$$

If the percentage of sodium in the groundwater is less than 20, it is ideal for irrigation; if it is between 20 and 40, it is suitable for irrigation; if it is between 40 and 60, it is acceptable; if it is between 60 and 80, it is questionable and might be hazardous to use as irrigation water; and if it is more than 80, the water is not suitable for irrigation.

2.9.5 Residual sodium bicarbonate (RSBC)

When the bicarbonate (HCO_3) level of irrigation water is higher than the calcium (Ca) content of the water, residual sodium bicarbonate (RSBC) is present. Equation 16 presents the calculation of RSBC.

$$RSBC = HCO_3 - Ca^{2+} \tag{16}$$

A release of sodium (Na) in the soil will result from prolonged irrigation in areas where the water's relative soil pH (RSBC) is high (>2.5 meq/l). This could lead to three possible outcomes: (1) direct toxicity to crops; (2) excessive soil salinity (EC) and related poor plant performance; and (3) loss of soil structure due to pore space clogging caused by silt or clay content in the soil, which prevents air and water movement (Naseem 2022).

2.9.6 Kelly ratio

Based on the ratio of Na to Ca and Mg, Kelley (1946) developed this crucial metric. Equation 17 expresses it.

$$KR = \frac{Na}{Ca+Mg} \tag{17}$$

Kelly ratios less than 1.0 indicate that groundwater is appropriate for irrigation; KR values between one and two indicate marginal quality and may indicate impending threat to the groundwater; and KR values more than two indicate that the groundwater is not suitable for irrigation.

2.10 Evaluation of ecological risks

An ecological receptor's exposure, the presence of a physical or biological agent, the amount of a chemical, a mixture of chemicals, or an emission released into a particular environment, and the agent's inherent toxicity are all factors considered in the scientific decision-making process known as ecological risk assessment (Tian *et al.* 2020). To evaluate heavy metal pollution in water and establish a connection between the toxicity of the metals and their effects on biology and the environment, the toxic-response factors (TRi) of Cu, Zn, Cd, Cr, Ni, and Pb are 5, 1, 30, 2, and 5 (µg/g), respectively (Hakanson 1980). ERI is represented by equation (18):

$$E_r = T_r \times C_f \tag{18}$$

where Tr stands for the toxic reaction factor and Cf stands for the contamination of a single element factor. The Potential Ecological Risk Index is used to determine a semi-quantitative study of the level of regional pollution (PERI). It may be represented by equation (19) (Wang *et al.* 2015).

$$RI = \sum_{i=1}^{n} E_r \tag{19}$$

where ER is the potential ecological risk (TR for Zn = 1, Cr = 2, Cu = 5, Pb = 5, Cd = 30) for each particular element.

2.11 Risk assessment for human health

Equation 20 was used to estimate the chronic daily intake (CDI) of drinking water, using modifications made by Muhammad *et al.* (2011). There are several ways that metals may enter the human body, but the most dangerous one is oral ingestion.

$$CDI\left(\frac{\mu}{kg.day}\right) = \frac{C_{MW}\times I_R}{B_W} \tag{20}$$

where C_{MW} denotes the amounts of heavy metals in water, and IR and BW stand for the daily water intake rate and body weights, respectively.

Equations 21 and 22 (USEPA 2023) were also utilised to determine the yearly exposure resulting from ingestion and cutaneous exposure:

$$EXP_{ing} = \frac{CM_o\times I_R\times E_F\times E_D}{B_W\times A_T} \tag{21}$$

$$EXP_{derm} = \frac{CM_o\times I_R\times E_F\times E_D}{B_W\times A_T} \tag{22}$$

This means that AT=EF×ED.

In this case, EF is the exposure frequency (days/year; 365 days for adults and children), and IR is the water intake rate (L/day; 2.20 and 1.10 for adults and children, respectively). The terms exposed skin area (cm^2), average exposure time (h/day) (0.52 for both adults and children), exposure duration (years), average body weight (kg) (70 kg for adults and 15 kg for children), exposure time (days) (10,950 and 2,190 for adults and children, respectively), and unit conversion factor (l/cm^3) (0.001 for both adults and children) are all represented by the acronyms EA, AT, and ED. The dose rates of exposure (in grammes per kilogramme per day) by ingestion and the skin, respectively, are denoted as EXP(ing) and EXP(derm). For permeability coefficient, use the symbol PC. For Pb, Cr, Cd, Fe, Mn, Cu, Zn, and 1×10^{-3}, 2×10^{-3}, 1×10^{-3}, 1×10^{-3}, 1×10^{-3}, and 6×10^{-4}, respectively, the Pc (cm/h) values are as follows.

2.11.1 Risk assessments for non-carcinogens

Equations 23 and 24, which were adopted from USEPA (2023), were used to create the hazard quotient (HQ) for non-carcinogenic health risk assessment for cutaneous and oral exposure pathways.

$$HQ(ing) = \frac{EXP(ing)}{RD(ing)} \tag{23}$$

$$HQ(derm) = \frac{EXP(derm)}{RD(derm)} \tag{24}$$

The ingestion and dermal contact hazard quotients are HQ(ing) (unit less) and HQ(derm) (unit less), respectively. RD(ing) and RD(derm) are reference doses (RD) for cutaneous exposure and ingestion, respectively, expressed in units of (µg/kg/day).

The hazard index (HI) is produced if the HQ comes from n different metals. The non-carcinogenic consequences were determined by adding together all of the HQ due to individual metals. The HI was calculated using equations 25 and 26 for ingestion and cutaneous exposure:

$$HI(ing) = \sum_{i=1}^{n} HQ(ing)n = \sum_{i=1}^{n} \frac{EXP(ing)n}{RD(ing)n} \tag{25}$$

where HI(ing) is the HI (unitless) from consuming various metals.

$$HI(derm) = \sum_{i=1}^{n} HQ(derm)n = \sum_{i=1}^{n} \frac{EXP(derm)n}{RD(derm)n} \tag{26}$$

HI(derm) is the hazard index (unit less) from skin contact with each of the n different metals. Table 1 displays the values for each metal, which are HI(derm), Exp(derm), and RD(derm).

2.11.2 Calculations of the risk of cancer

The cancer slope factor (CSF), which is used to represent carcinogenic health concerns, is shown in Table 1 and converts the expected exposure from metal consumption into an incremental risk of cancer over time (USEPA 2023). Equation 27 was used to determine the carcinogenic health risks associated with the water from different sources:

$$Risk\ (ing) = \frac{EXP(ing)}{CSF(ing)} \tag{27}$$

3. RESULTS AND DISCUSSIONS

3.1 Physicochemical properties of water

The research region's surface and groundwater physicochemical characteristics are described in detail in Table 1. Surface water in this area has a pH ranging from 6.21 to 7.03, with an average of 6.69; the amount of EC varies from 269 µS/cm to 287 µS/cm, with an average of µS/cm. With an average of 319.28 mg/l, the total dissolved solids (TDS) level varies from 306.50 to 332.67 mg/l. The surface water in Owo City has a mean concentration of 1.97 mg/l of chloride (Cl) and a range of 0.18 to 5.48 mg/l of sulphate (SO_4) between 10.29 and 38.98 mg/l, calculated from the data. While the concentration of sodium (Na) varies from 8 to 17.20 mg/l with a mean of 12.44 mg/l, the bicarbonate (HCO_3) content ranges from 17.28 to 27.48 mg/l with a mean of 21.43 mg/l. The samples' average potassium (K) content is 51.19 mg/l, ranging from 43.90 to 57.70 mg/l, while their average calcium (Ca) concentration is 18.98 mg/l, ranging from 13.94 to 22.70 mg/l. With a mean value of 25.14 mg/l, the water's magnesium (Mg) concentration ranges from 2.24 to 25.14 mg/l. The amount of physicochemical traits found in groundwater in the study area is displayed in Table 2. The amount of EC in groundwater varies from 261 µS/cm to 289 µS/cm, with a mean value of 278.33 µS/cm, while the pH ranges from 6.00 to 6.38, with a mean value of 6.18. TDS values have an average of 286.72 mg/l and vary from 269.11 to 301.19 mg/l. In groundwater, the concentration of Cl varies from 0.64 to 5.18 mg/l, with an average of 2.96 mg/l, while the concentration of SO_4 varies from 20.25 to 33.17 mg/l, with an average of 23.88 mg/l. Whereas the concentration of Na varies from 0.10 to 2.41 mg/l with a mean of 1.25 mg/l, the concentration of HCO_3 ranges from 20.11 to 23.03 mg/l. While the concentration of Ca varies from 16.90 to 20.30 mg/l with an average of 19.19 mg/l, the concentration of K ranges from 33.80 to 41.20 mg/l, with an average of 38.04 mg/l. Water contains 6.84 to 25.21 mg/l of magnesium, with a mean of 17.01 mg/l. The results of this investigation showed that the concentrations of all the physicochemical parameters (pH, EC, TDS, Cl, SO_4, HCO_3, Ca, Mg, Cu, Cd, Cr, Fe, Ni, As, Pb, and Zn) evaluated in the city's surface and groundwater were lower than those found in background samples, the Nigerian guideline (SON 2007), and the WHO (2011). The research area's groundwater had lower pH, Cl, Na, K, and Fe concentrations than those reported by Taiwo *et al.* (2023) in Abeokuta, Nigeria; nevertheless, the study area's groundwater had greater concentrations of EC, TDS, Ca, Mg, Cu, Ni, and Zn. The groundwater of Owo has lower levels of pH, EC, TDS, Cl, HCO_3, Ca, and Mg than the groundwater of Wa municipal in Ghana, according to Saana *et al.* (2016). The research area's groundwater had greater levels of Fe and As than Wa City's stated levels. While the levels of TDS, SO_4, and Mg in the surfacewater of the Owo region were greater than those reported in that of South Africa, the pH, EC, Cl, HCO_3, Na, K, and Ca in the area's surfacewater were lower than those discovered in the Mutangwi River, South Africa by Elumalai *et al.* (2020).

The water around the glass quarters area had the lowest pH levels, while the Inufele area had the highest values, according to spatial distribution maps of physicochemical water parameters in this region (Figure 2). The water from this region had the lowest Total Dissolved Solids (TDS) content around the Mabena junction area, while the highest TDS levels were found in the Odoegan, Aruwajoye, Ajaka, Ogbomo, and Ecobank areas. The Okedogbon region had the lowest Electrical Conductivity (EC) rating, while the Old Road region had the greatest value. Arsenic (As) distribution was lowest in RUGIPO, Okedogbon, Odoegan, Ecobank, and GRA neighbourhoods, and greatest in the Otapete neighbourhood. Furthermore, the Okedogbon area had the lowest quantity of sulphate (SO_4), whereas the Ijebu area had the highest amount. The regions along Okedogbon, Alafia, and Old Road had the highest concentrations of magnesium (Mg), while Inufele had the lowest. Moreover, the Odoegan, RUGIPO, and Old Road sectors have the lowest concentrations of bicarbonate (HCO_3). Additionally, this study showed that the Odoegan area had the highest concentration of calcium (Ca), whereas the Ijebu area had the lowest concentration. The regions of Okedogbon and GRA had the lowest levels of cadmium (Cd), while the areas of Ijebu and Ecobank had the highest levels. The locations with the lowest amounts of chloride (Cl) were Inufele, Ecobank, Old Road, and Ijebu; the places with the highest amounts were Odoegan and Aralepo. The Okedogbon region had the lowest zinc (Zn) content in this research, whereas the Old Road and Ijebu areas had the highest concentrations. The Okedogbon region had the lowest concentration of sodium (Na), whereas Old Road, Ajaka, Inufele, and Ilale-Keji had the highest concentration. The places with the lowest concentration of chromium (Cr) were Okedogbon, Glass Quarters, and GRA; the ones with the highest concentration were Mabena Junction and Aralepo. The locations with the least quantity of copper (Cu) were Okedogbon, Glass Quarters, Aisewen, and Ijebu; the place with the most amount was RUGIPO. The locations with the lowest amounts of iron (Fe) were Ajaka, Okedogbon, Ijebu, Glass Quarters, GRA, and Aisewen; the ones with the highest amounts were Old Road, Aralepo, and Odoegan. The Glass Quarters region had the lowest concentration of potassium (K), whereas the areas of RUGIPO, Isuada, Aruwajoye, and Inufele had the greatest concentration. The regions with the greatest lead (Pb) concentrations were Isuada and Inufele, while the lowest amounts were identified in RUGIPO, Ecobank, Ijebu, Dominion, and GRA. The Okedogbon area had the lowest concentration of nickel (Ni), whereas the Odoegan, Otapete, and Isuada regions of Owo had the greatest concentration.

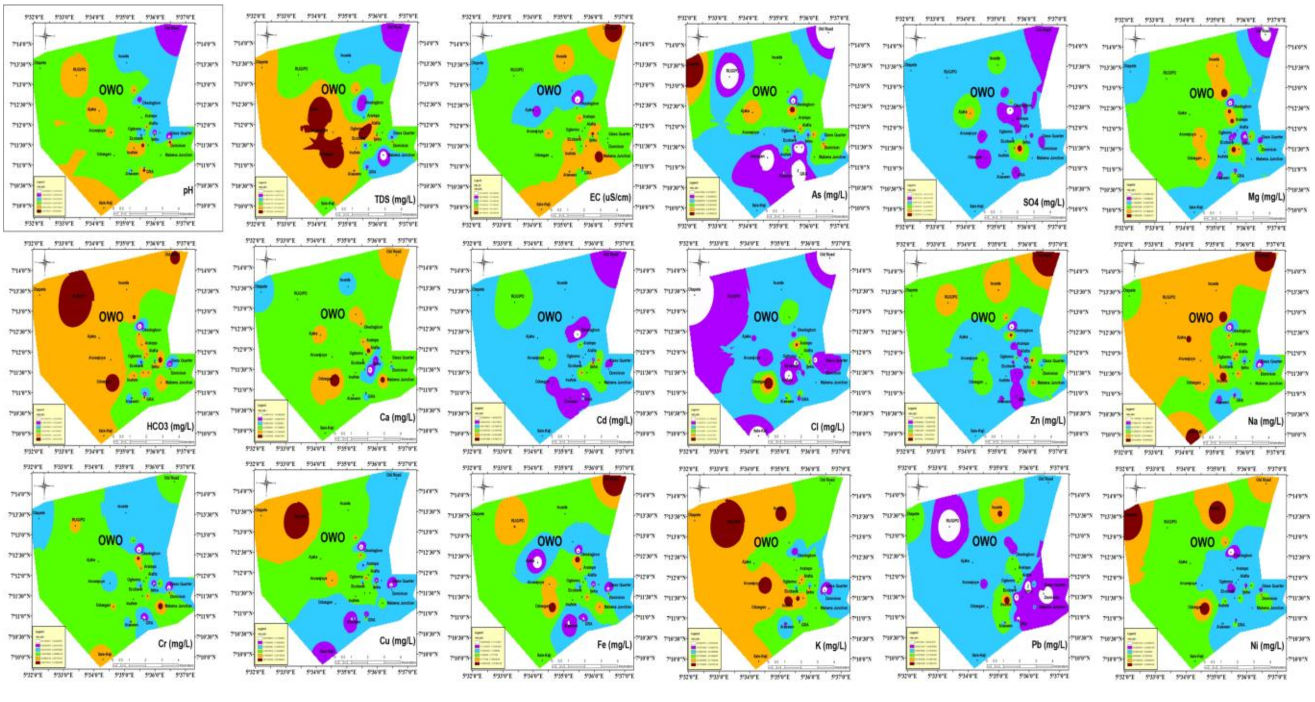

Figure 2: Spatial distribution maps of physicochemical parameters in water

Table 1: Physicochemical parameters in surface and groundwater in the study area

	Surfacewater				Groundwater								
	Min.	**Max.**	**Avg.**	**Control**	**Min.**	**Max.**	**Avg.**	**Control**	**WHO (2011)**	**Nigerian Guideline SON (2007)**	**Abeokuta Nigeria (Taiwo *et al.* 2023) Groundwater**	**Ghana (Saana *et al.* 2016) Groundwater**	**South Africa (Elumalai *et al.* 2020) Surfacewater**
pH	6.21	7.03	6.69	7.10	6.00	6.38	6.18	6.60	6.50-8.50	6.50-8.50	7.40	6.87	6.70
EC (µS/cm)	269.00	287.00	277.95	164.00	261.00	289.00	278.33	169.00	1500	1000	144.28	373.32	344
TDS (mg/L)	306.50	332.67	319.28	82.00	269.11	301.19	286.73	79.00	1000	500	72.60	218.21	220.00
Cl (mg/L)	0.18	5.48	1.97	1.10	0.64	5.18	2.96	1.90	250	250	53.50	13.97	49.00
SO_4 (mg/L)	10.29	38.98	22.97	19.75	20.25	33.17	23.88	17.38	500	100	-	-	6.40
HCO_3 (mg/L)	17.28	27.48	21.43	4.40	20.11	23.03	21.37	3.10	100	-	-	178.07	105.00
Na (mg/L)	8.00	17.20	12.44	27.00	0.10	2.41	1.25	17.50	200	200	7.53	-	18.00
K (mg/L)	4.39	5.77	5.11	4.58	3.38	4.12	3.80	2.94	12	-	4.68	-	9.00
Ca (mg/L)	13.94	22.70	18.98	16.40	16.90	20.30	19.19	17.50	250	-	12.88	55.28	21.00
Mg (mg/L)	2.24	25.14	16.18	5.99	6.84	25.21	17.01	6.02	250-350	20	0.30	29.84	15.00
Cu (mg/L)	0.13	0.25	0.19	0.13	0.08	0.10	0.09	0.08	1.20	1.00	0.06	-	-
Cd (mg/L)	0.0001	0.02	0.01	1.00E-4	0.0001	0.005	0.003	1.00E-4	0.003	0.003	-	-	-
Cr (mg/L)	0.03	0.08	0.06	0.03	0.011	0.015	0.01	0.01	0.05	0.05	-	-	-
Fe (mg/L)	0.10	0.22	0.17	0.10	0.08	0.10	0.09	0.06	0.30	0.05	0.15	0.06	-
Ni (mg/L)	0.05	0.10	0.07	0.05	0.02	0.04	0.03	0.03	0.10	0.02	< 0.01	-	-
As (mg/L)	0.0001	0.006	0.003	1.00E-4	0.0001	0.002	0.0005	1.00E-4	0.01	0.01	-	0.00	-
Pb (mg/L)	0.0001	0.02	0.009	1.00E-4	0.0001	0.004	0.002	1.00E-4	0.01	0.01	-	-	-
Zn (mg/L)	0.89	1.45	1.15	0.15	0.76	1.05	0.87	0.24	5.00	3.00	0.55	-	-

3.2 Hydrogeochemical facies

Plotting the principal ions in the Piper trilinear and Durov diagrams allowed researchers to better understand the hydrochemical development of the water in the study region (Figures 3 and 4). All groundwater is classified as Ca-Cl water according to the piper diagram (Figure 3). According to Mondal and Singh (2012), the dominance of Ca-Cl water types is a sign of mineral dissolution, which is mirrored in the interaction between rock and water and the recharging of freshwater. Sulphate accounts for 100% of the total anion burden in the lower right triangle (Figure 3). The samples in the lower left triangle are of the magnesium water type (59%) and the calcium water type (OWG4 and OSW4), which together account for 7% of the total samples. This reveals the causes of surface pollution, which include irrigation return flow with existing water followed by the ion exchange process (Selvakumar *et al.* 2017), residential wastewater, septic tank effluents, and liquid and solid waste released into the neighbouring land and channel (Jeyaraj *et al.* 2019). All of the water samples were plotted along the dissolving or mixing line, according to the Durov plot (Figure 4). Lloyd and Heathcoat (1985) suggest that this pattern may be explained by recently recharged fresh water that shows straightforward dissolving or mixing without a prominent major anion or cation (Figure 4).

3.3 Factors influencing the properties of hydrochemistry The process of hydrochemical evolution

The Gibbs diagram (Gibbs 1970) is a commonly used tool for understanding the creation process of hydrogeochemistry and is helpful in identifying the components that govern the hydrochemical features of water (Adewumi *et al.* 2018; Marandi and Shand 2018; Nazzal *et al.* 2014). The Gibbs diagram splits the variables governing the groundwater chemical processes into three aspects: precipitation, rock weathering, and evaporation crystallisation (TDS versus $(Cl^-/Cl^- + HCO_3^-)$ and TDS versus $(Na^+/Na^+ + Ca^{2+})$ (Zhang et al. 2021).

According to Luo *et al.* (2018), Figure 5 illustrates that every sample of surface water and groundwater falls into the "rock dominance" zone. This indicates that the Basement Complex rocks, which include migmatite, schist, and quartzite, are primarily responsible for the release of minerals into the water. Moreover, Table 2 demonstrated that all samples are located in the rock weathering zone with low TDS (< 1000 mg/L), indicating that the primary hydrogeochemical production process in the region is likely the result of water-rock interactions.

Bivariate diagrams are used to describe which lithological minerals (carbonate, silicate, and evaporite) are dissolved in order to better decode the primary weathering and dissolution mechanisms of the water-rock interaction processes (Luo et al. 2018). The Mg/Na, HCO_3/Na, and Ca/Na sodium normalised ratios were computed. The Gaillardet diagram illustrates the correlations between (Mg/Na) and (Ca/Na), (HCO_3/Na), and (Ca/Na) (Gaillardet et al. 1999). The majority of samples lie close to the silicate weathering zone, as seen by the Gaillardet diagram (Figure 6), indicating that silicate dissolution dominates groundwater chemistry.

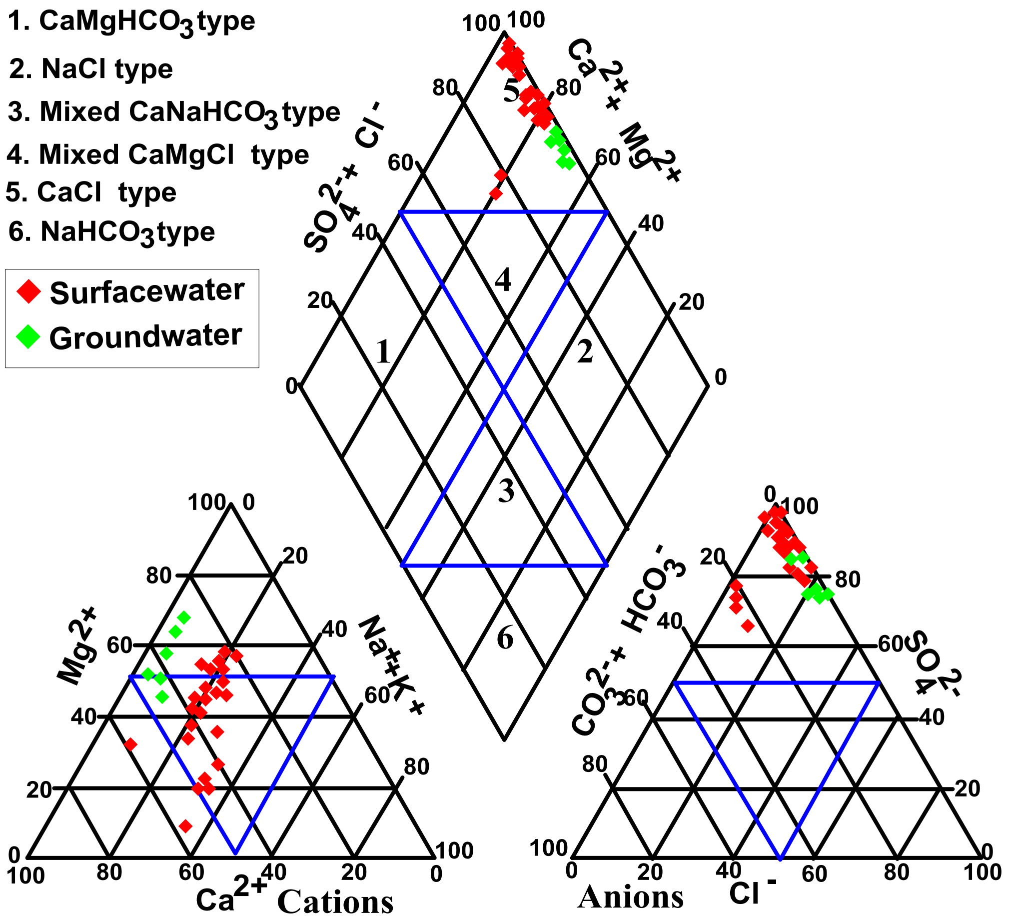

Figure 3: Trilinear pipers plot for surface and ground water in the area

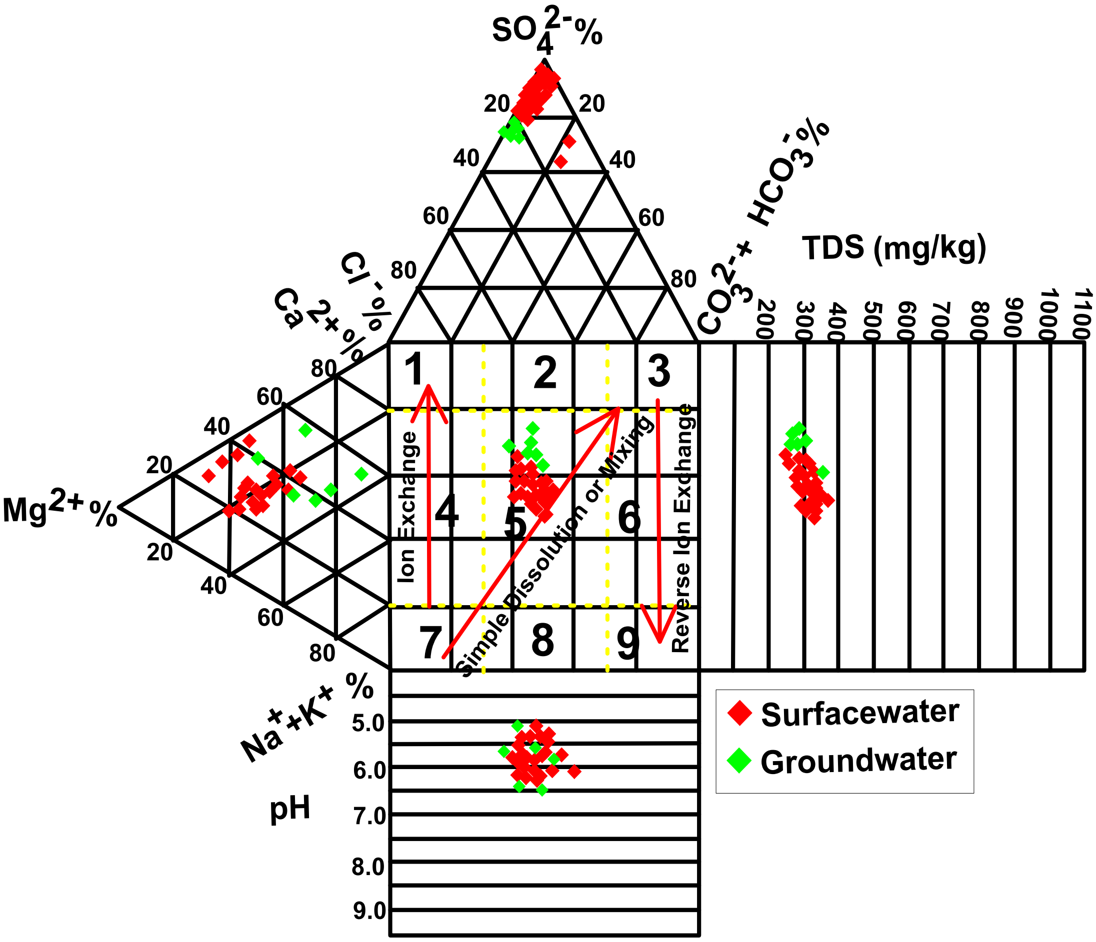

Figure 4: Durov diagram of physicochemical parameters in surface and ground water

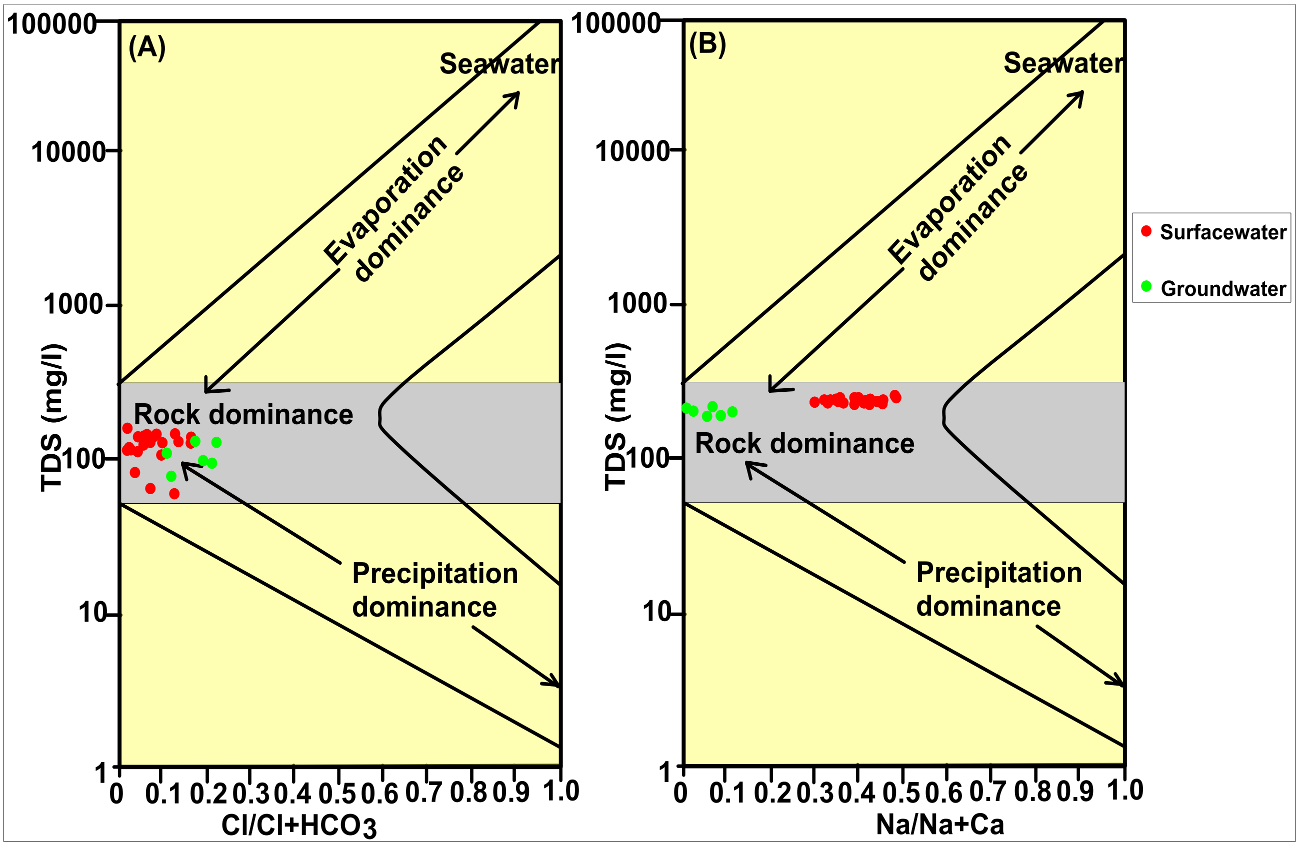

Figure 5: The plot of (A) TDS versus $Cl^-/(Cl^- + HOC_3^-)$ and (B) TDS versus $(Na^+)/(Na^+ + Ca^{2+})$

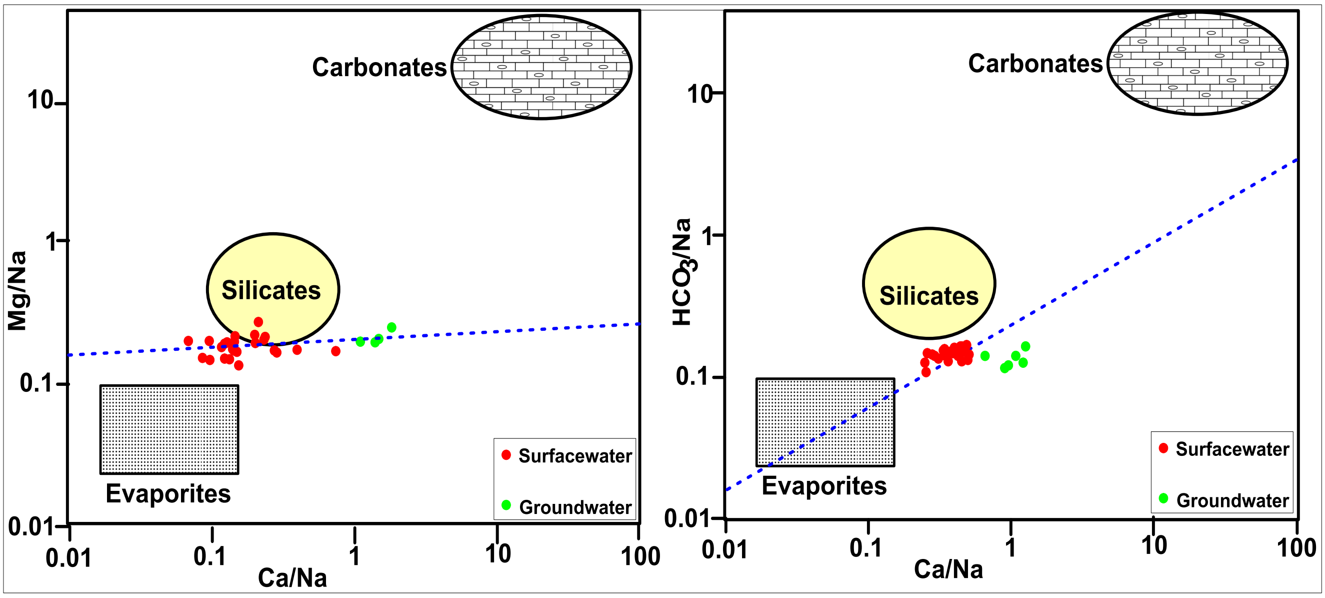

Figure 6: The sodium normalized bivariate plots (a) Mg/Na vs Ca/Na and (b) HCO_3/Na vs Ca/Na

Table 2: Water classification according to total dissolved solids (TDS).

S/N	Water class	TDS Range (mg/l)	Number of Samples		Sample Number
			In. No.	In %	
1.	Fresh Water	<1000	29	100	All Samples
2.	Slightly Saline	1000-3000	-	-	-
3.	Moderately Saline	3000-10000	-	-	-
4.	Very Saline	10000-30000	-	-	-
5.	Brine	>30000	-	-	-

3.4 Water-rock interactions

3.4.1 Ion exchange chloro-alkaline indices (CAI)

Schoeller (1977) states that the reverse ion exchange occurs when the Na^+ in groundwater is replaced by the Ca^{2+} or Mg^{2+} absorbed in the aquifer media (Zaidi *et al.* 2015). The content of Ca^{2+} or Mg^{2+} in groundwater decreased as a result of CAI-I and CAI-II being less than 0. Negative values for CAI-I and CAI-II indicate that Na^+ absorbed on the aquifer media has replaced Ca^{2+} or Mg^{2+} in groundwater, indicating that ion exchange may be the source of the rise in Na^+ in groundwater. The ions Na^+-Cl^- and Ca^{2+}-Mg^{2+}-HCO_3^--SO_4^{2-} were created to investigate the exchange of ions between sodium and calcium. The slope of the fitted line that depicts the connection above should be near to 1 if there is a cation exchange (Fisher and Mullican, 1997). The fitted line of (Na^+– Cl^-) /(Ca^{2+} + Mg^{2+}–HCO_3^-–SO_4^{2-}) in this investigation has a slope of 0.667, and all the water samples fall within the zone of reversal (Figures 7a and b), further confirming that Na has replaced Ca and Mg in the aquifer matrix.

Ion ratio

The primary ion source in groundwater may be determined using the stoichiometric connection between several ions (Liu et al. 2020). If the halite is the only source of Na^+ and Cl^-, then the connection between the two would be found on the 1:1 line. As seen in the figure, 35% of the samples come close to the 1:1 correlation line, suggesting that the chemistry of the water is caused by the halite dissolving. This suggested that ion exchange and silicate weathering may have released Na+ from these samples (Figure 7a). There may be silicate weathering, according to the sodium normalised bivariate plots (Figure 7b). As reflected in Figure 7b anthropogenic activities might have also played important roles in releasing ions into the water in the area.

Additionally, excess Na^+ from the ion exchange might be the cause of the decreased Ca^{2+} over SO_4^{2-} (Figures 7c and 7d). This suggests that the water chemistry may be caused by the weathering of silicate and ion exchange (exchange of Ca^{2+} and Mg^{2+} in groundwater with Na^+ on clay minerals) (Han *et al.* 2013). The (Na^+-Cl^-) against (Ca^{2+} + Mg^{2+}-HCO_3^--SO_4^{2-}) scatter plot (Figure 7a) clarifies the possibility of the reverse ion exchange since several of the samples lie beyond the 1:1 line. Nonetheless, 100% of the groundwater samples and 65% of the surfacewater samples fall below the 1:1 lines, indicating that human activity in the region may have been the source of the Na in these samples (Zhou et al. 2023).

If groundwater was solely the result of gypsum dissolving, the Ca/SO_4 ratio would be 1:1. The majority of samples strayed from the 1:1 line, suggesting that SO_4^{2-} is more prevalent than Ca^{2+}. In the meanwhile, excess SO_4^{2-} displays the same traits in the interaction between Mg^{2+} and SO_4^{2-} (Fig. 7e). On the one hand, gypsum's negative saturation indices help to explain why gypsum dissolution is important for groundwater chemistry.

Groundwater chemistry is caused by the dissolution of silicate minerals from the Basement Complex rocks, as shown by the ratio of (Ca^{2+}+Mg^{2+}) to (HCO_3^- + SO_4^{2-}), which is almost equal to one (Edmunds *et al.* 2002). The majority of samples shown in Figure 7f are below the 1:1 line of the (Ca^{2+} + Mg^{2+}) versus (HCO_3^- + SO_4^{2-}) scatter plot, with the deficient Ca^{2+}+Mg^{2+} over HCO_3^- + SO_4^{2-}. This suggests that groundwater chemistry may be caused by silicate weathering dissolution and ion exchange (exchange of Ca^{2+} and Mg^{2+} in groundwater with Na^+ on clay minerals) (You et al. 2024). A scatter plot of (Na+-Cl) versus (Ca^{2+}+Mg^{2+} - HCO_3^- + SO_4^{2-}), (Fig. 7b) illustrates the potential of reverse ion exchange, but only a small number of samples fall beyond the 1:1 line.

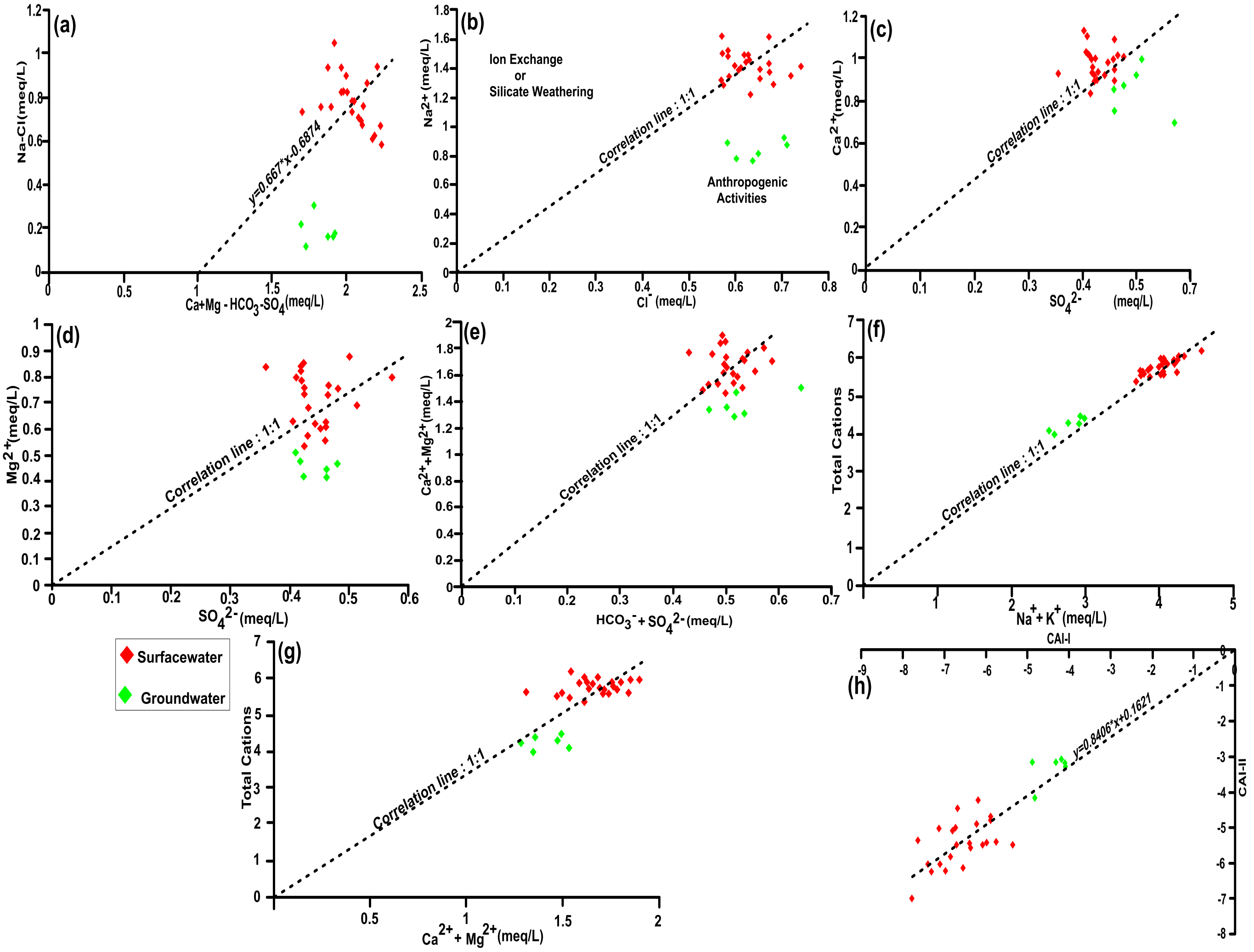

Figure 7: Binary diagram: (a) (Na^+ + Cl^-) versus (Ca^{2+}+Mg^{2+}–HCO_3^-–SO_4^{2-}), (b) Na versus Cl, (c) Ca versus SO_4, (d) Mg versus SO_4, (e) (Ca + Mg) versus (HCO_3 + SO_4), (f) total cation versus Na + K, (g) total cation versus Ca + Mg and (h) CAI-II versus CAI-I

3.5 Mineral Dissolution Processes

3.5.1 Saturation Index

Based on the hydrogeochemical properties, the usual minerals are chosen to compute the SI of different minerals. Figure 8b illustrates that all groundwater samples had SI values more than zero for goethite, hematite, magnetite, cuprous-ferrite, and tenorite, whereas all surfacewater samples have SI values greater than zero for the same minerals (Figure 8a). This implies that certain minerals are oversaturated in the water.

On the other hand, the smaller than zero SI of antlerite, gypsum, portlandite, anglesite, scorodite, halite, mirabilite, and anhydrite indicates that groundwater is unsaturated (Figures 8a and 8b). Specifically, the saturation index (SI) of halite is significantly lower than zero (– 7.97 to -7.66), suggesting that halite may be dissolved by both surface and groundwater. Anglesite ($PbSO_4$) has a SI that is also below zero (-11.57 to -10.083), indicating that Pb may be absorbed in water. In a similar vein, the SI values of antlerite ($Cu_3(SO)_4(OH)_4$), mirabilite ($Na_2SO_4.10H_2O$), and scorodite ($FeAsO_4.2H_2O$) are all significantly below zero (-18.65 to -16; -9.082 to -8.36, and -13.364 to -9.8), indicating that these minerals have the ability to release As, Na, and Cu into the surrounding water. According to García *et al.* (2001), the dissolving processes of different minerals are as follows:

$$NaCl \rightarrow Na^{+} + Cl^{-} \qquad (28)$$

$$FeSO_4.2H_2O \rightarrow Fe^{3+} + AsO_4 \quad + 2H_2O \qquad (29)$$

$$Na_2SO_4.10H_2O \rightarrow 2Na^{+} + SO_4{}^{2-} + 10H_2O \qquad (30)$$

$$CaSO_4.2H_2O \rightarrow Ca^{2+} + SO_4{}^{2-} + 2H_2O \qquad (31)$$

$$CaSO_4 \rightarrow Ca^{2+} + SO_4{}^{2-} \qquad (32)$$

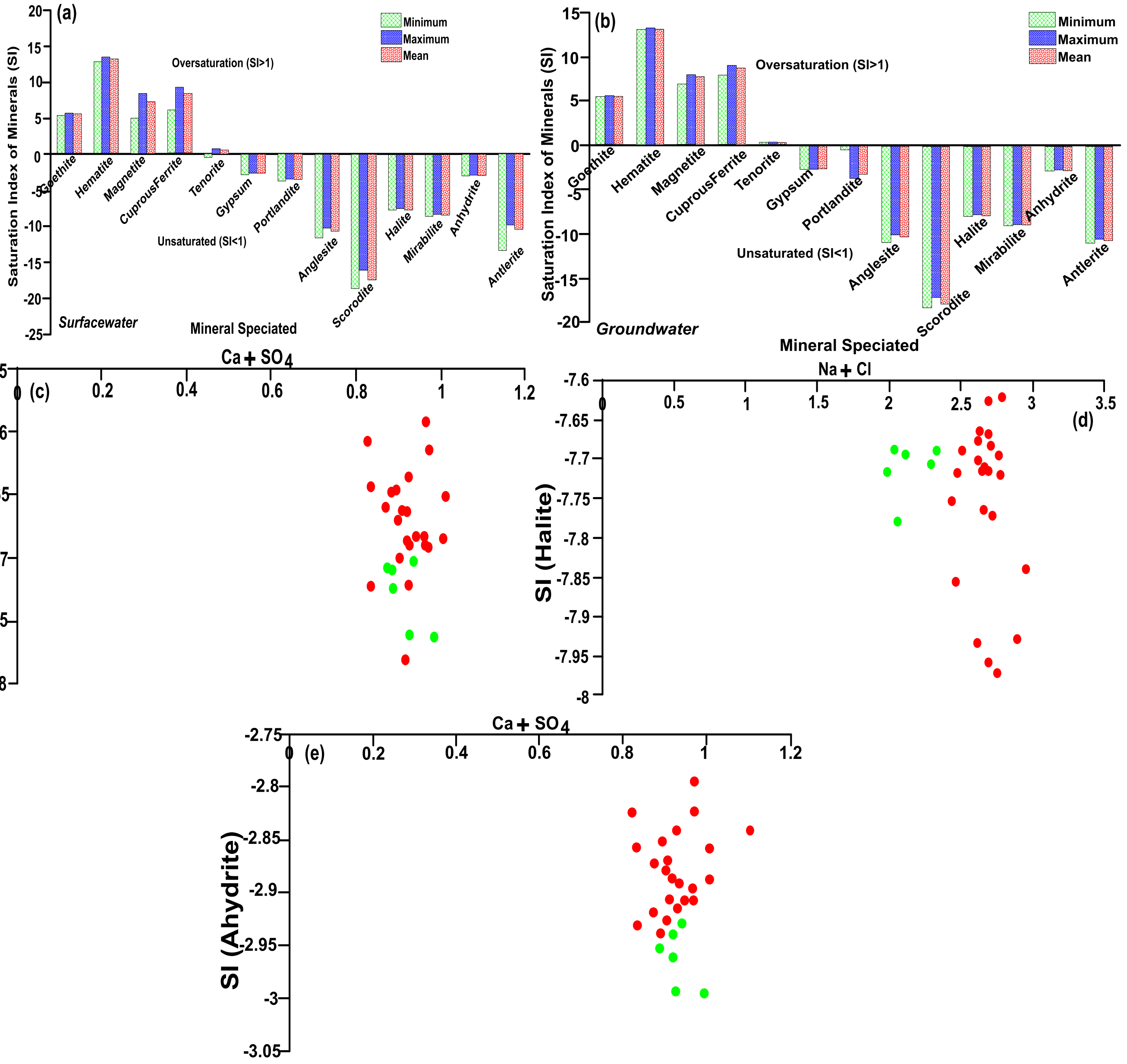

Figure 8: (a) Saturation indices of different minerals in surfacewater; (b) Saturation indices of different minerals in groundwater a saturation; (c) gypsum versus ($Ca^{2+} + SO_4{}^{2-}$); (d) halite versus ($Na^{+} + Cl^{-}$), (e) anhydrite versus ($Ca^{2+} + SO_4{}^{2-}$)

3.6 Statistical Analysis Of Data

3.6.1 *Correlation Analysis*

The identification of similar sources of significant ions with good correlation was accomplished by the use of correlation analysis, which illustrates the dependency between various hydrochemical parameters (Pant *et al.* 2018; Yin *et al.* 2021). As can be seen in Table 3, Na^+ and Cl^- have a significant positive association with a correlation value of 0.756, suggesting that halite may dissolve. Na^+ and $SO_4{}^{2-}$ have a positive link (correlation value of 0.533), suggesting that salt dissolution is a contributing factor (Liu *et al.* 2019). This city's water contains salts that might have come from industrial and domestic trash. With a correlation value of 0.596, Mg^{2+} and $SO_4{}^{2-}$ both exhibit a positive association, suggesting the dissolution of minerals containing sulphur. Significant associations among heavy metals in the water from this region suggested that the build-up of harmful metals in the samples may have been largely influenced by both geological processes and human activity.

3.6.2 *Principal Component Analysis*

Four principal components (PCs) with eigenvalues greater than one were identified using principal component analysis (PCA), as Table 4 illustrates. The cumulative explained variance accounted for 76.62% of the original complicated hydrochemical datasets, suggesting that PCA greatly decreased their dimensionality. The Table 4 shows that most parameters and PCs have a positive or negative connection, whereas certain parameters do not significantly correlate with the PCs. The factor PC1 governs the growth of various physicochemical parameters in the water samples, as evidenced by its substantial correlation with HCO_3, pH, Na, K, Mg, Cu, Cd, Cr, Fe, Ni, As, Pb, and Zn and its explanation of 45.26% of the total variance. PC2, PC3, PC4, and PC5, on the other hand, account for 10.62%, 7.65%, 7.17%, and 5.93% of the overall variation, respectively. While PC2 has a negative correlation with $SO_4{}^2$, PC2, PC3, and PC4 have positive correlations with Ca, EC, and Cl. Based on preliminary findings, PC2, PC3, and PC4 might be influenced by a combination of anthropogenic and geogenic activity variables.

Table 3: Bivariate correlation of physicochemical parameters in water

	EC	**TDS**	**Cl**	**SO_4**	**HCO_3**	**pH**	**Na**	**K**	**Ca**	**Mg**	**Cu**	**Cd**	**Cr**	**Fe**	**Ni**	**As**	**Pb**	**Zn**
EC	1																	
TDS	0.313	1																
Cl	0.429	**0.671**	1															
SO_4	**0.801**	0.287	**0.806**	1														
HCO_3	**0.870**	0.108	**0.800**	**0.896**	1													
pH	0.191	0.302	**0.509**	**0.898**	**0.677****	1												
Na	**0.715**	0.029	**0.756**	**0.533**	**0.887****	**0.643****	1											
K	**0.567**	0.411**	**0.889**	0.132	**0.782****	**0.606****	**0.825****	1										
Ca	**0.875**	**0.745**	0.271	-0.336	**0.897**	**0.849**	**0.902**	**0.595**	1									
Mg	**0.734**	0.466	**0.587**	**0.596**	**0.754****	**0.668****	**0.657****	**0.584****	**0.506**	1								
Cu	**0.960**	0.365*	0.470	0.432	**0.774****	**0.654****	**0.788****	**0.810****	**0.550**	**0.656****	1							
Cd	**0.981**	0.299	-0.074	0.387*	**0.601****	**0.519****	**0.536****	**0.680****	0.286	0.493**	**0.610****	1						
Cr	0.416	0.178	**0.933**	**0.538**	**0.808****	**0.676****	**0.797****	**0.663****	**0.528**	**0.708****	**0.730**	**0.612**	1					
Fe	0.284	0.488	**0.815**	**0.965**	**0.779****	0.435**	**0.780****	**0.732****	**0.973**	**0.608****	**0.747****	**0.517****	**0.808****	1				
Ni	**0.935**	0.086	**0.912**	**0.659**	**0.758****	0.431*	**0.756****	**0.630****	**0.620**	0.497**	**0.555****	0.434**	**0.520****	**0.630****	1			
As	**0.918**	0.261	**0.720**	**0.680**	0.411*	0.355	0.480**	0.362*	**0.514**	0.349	0.497**	0.313	0.487	0.327	0.358	1		
Pb	0.477	0.295	**0.881**	**0.957**	0.445*	0.261	**0.504****	0.444**	0.251	**0.518**	0.406*	**0.852**	**0.517****	0.414*	0.371*	0.491*	1	
Zn	0.258	**0.731**	0.463	0.318	**0.668****	0.259	**0.629****	0.485**	0.524	0.421	**0.609****	0.354	**0.593****	**0.730****	**0.713****	0.476*	0.383	1

Table 4: Principal component loadings and explained variance for the first five components

Parameter	**Component 1**	**Component 2**	**Component 3**	**Component 4**	**Component 5**
EC	-0.062	0.356	**0.764**	0.229	0.152
TDS	0.390	-0.295	-0.400	0.380	0.456
Cl	-0.064	0.186	0.043	**0.804**	-0.358
SO_4	0.130	**-0.661**	0.303	0.411	0.188
HCO_3	**0.931**	0.022	0.005	-0.066	-0.140
pH	**0.711**	-0.229	-0.392	-0.082	-0.296
Na	**0.931**	0.010	0.002	0.016	0.046
K	**0.870**	-0.190	0.104	0.127	0.060
Ca	-0.024	**0.690**	-0.317	0.307	-0.166
Mg	**0.764**	-0.047	-0.090	0.056	0.406
Cu	**0.885**	-0.117	-0.022	-0.080	0.022
Cd	**0.667**	-0.447	0.145	0.031	-0.106
Cr	**0.874**	0.136	0.016	0.095	-0.134
Fe	**0.846**	0.177	0.279	-0.094	-0.114
Ni	**0.763**	0.300	0.091	-0.081	0.109
As	**0.557**	0.255	-0.263	-0.018	0.350
Pb	**0.540**	0.400	-0.185	0.205	0.423
Zn	**0.706**	0.413	0.234	-0.282	0.108
Total	8.147	1.912	1.376	1.290	1.068
% of variance	45.260	10.624	7.645	7.169	5.931
Cumulative%	45.26	35.885	63.329	70.696	76.621

The absolute values of the loading values larger than 0.50 are in bold

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3.6.3 Hierarchical cluster analysis

In HCA, all water samples are divided into three clusters based on the hydrogeochemical characteristics using the ward's linkage approach and Euclidean distance (Figure 9). As can be seen in Figure 9, the dendrogram reveals that the three clusters are made up of 16, 7, and 6 samples, in that order. Although the hydrochemistry features of each cluster are similar, there are variations among them. The study found that similar human activities, such as farming, dwellings, and dumpsites, are situated in and have an impact on samples, mostly surface water in cluster I. Waste discharged from human settlements has a key influence on the release of metals into samples, primarily surface water from cluster II. Cluster III revealed that all groundwater samples include metals that are discharged from human waste and agriculture. According to the boxplots shown in Figure 10, the order of EC, pH, and Ca is Cluster II > Cluster IIII > Cluster I. In comparison, the mean pH value for clusters I, II, and III was 6.73, 6.93, and 6.19, respectively. The average EC values were 176.50 µS/cm, 181.29 µS/cm, and 178.30 µS/cm. In clusters I, II, and III, the average Ca value was 18.64 mg/l, 19.74 mg/l, and 19.19 mg/l. The grouping shown by the piper's plot in Figure is reflected in this version. The area's slight acidity indicated that geogenic interactions between the water and the silicate rocks of the basement complex nearby released these physicochemical properties. The clusters for Mg, Fe, Ni, and As are arranged as follows: CII > CI > CIII. Clusters I, II, and III had mean values of 8.67 mg/l, 8.75 mg/l, and 0.09 mg/l for magnesium, and 0.17 mg/l, 0.19 mg/l, and 0.09 mg/l for ferrous. While the average value for As is 0.002 mg/l, 0.004 mg/l, and 0.0005 mg/l, the average value for Ni was 0.07 mg/l, 0.06 mg/l, and 0.03 mg/l in clusters I, II, and III. The anthropogenic activities in the region are reflected in this cluster. The clusters for HCO_3, Na, K, Cu, Cd, and Zn are arranged as follows: CI > CII > CIII. Clusters I, II, and III have average HCO_3 values of 4.39 mg/l, 4.33 mg/l, and 2.57 mg/l, respectively, whereas clusters Na have average values of 29.50 mg/l, 31.70 mg/l, and 38.04 mg/l. Clusters I, II, and III have mean values of 52.93 mg/l, 47.23 mg/l, and 38.04 mg/l for K, whereas the clusters' average values for Cu are 0.19 mg/l, 0.18 mg/l, and 0.09 mg/l, respectively. Moreover, clusters I, II, and III had average values of Cd of 0.01 mg/l, 0.009 mg/l, and 0.003 mg/l, and clusters Zn of 1.11 mg/l, 1.26 mg/l, and 0.87 mg/l, on average. These clusters show the combined effects of anthropogenic and geological processes on the metals released into the local water.

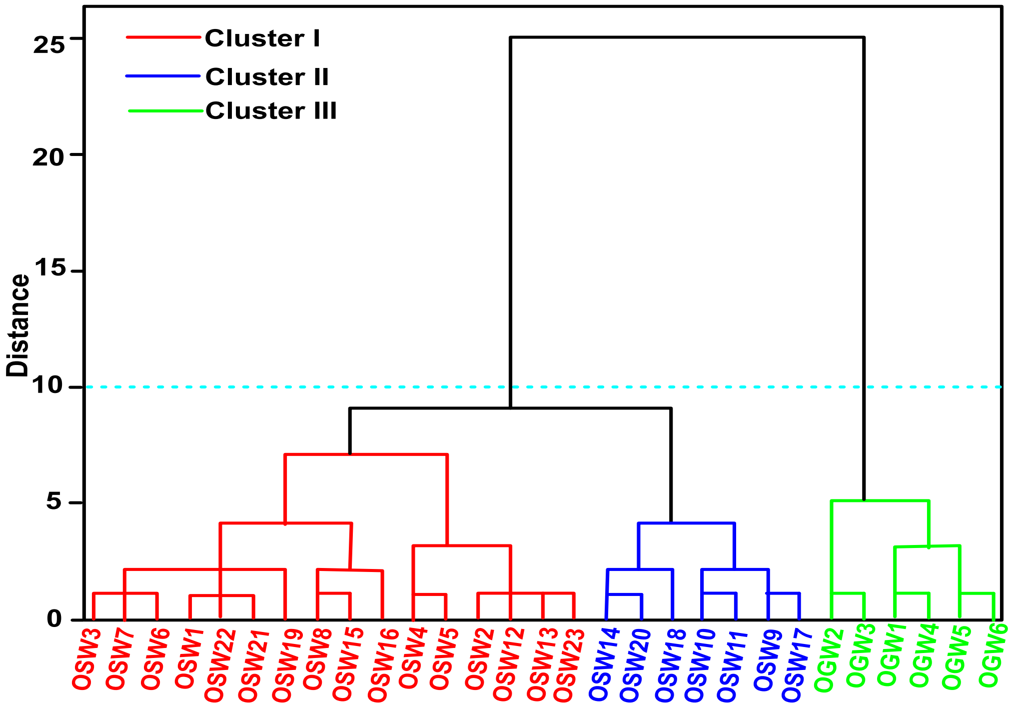

Figure 9: Classification results of groundwater samples using hierarchical cluster analysis

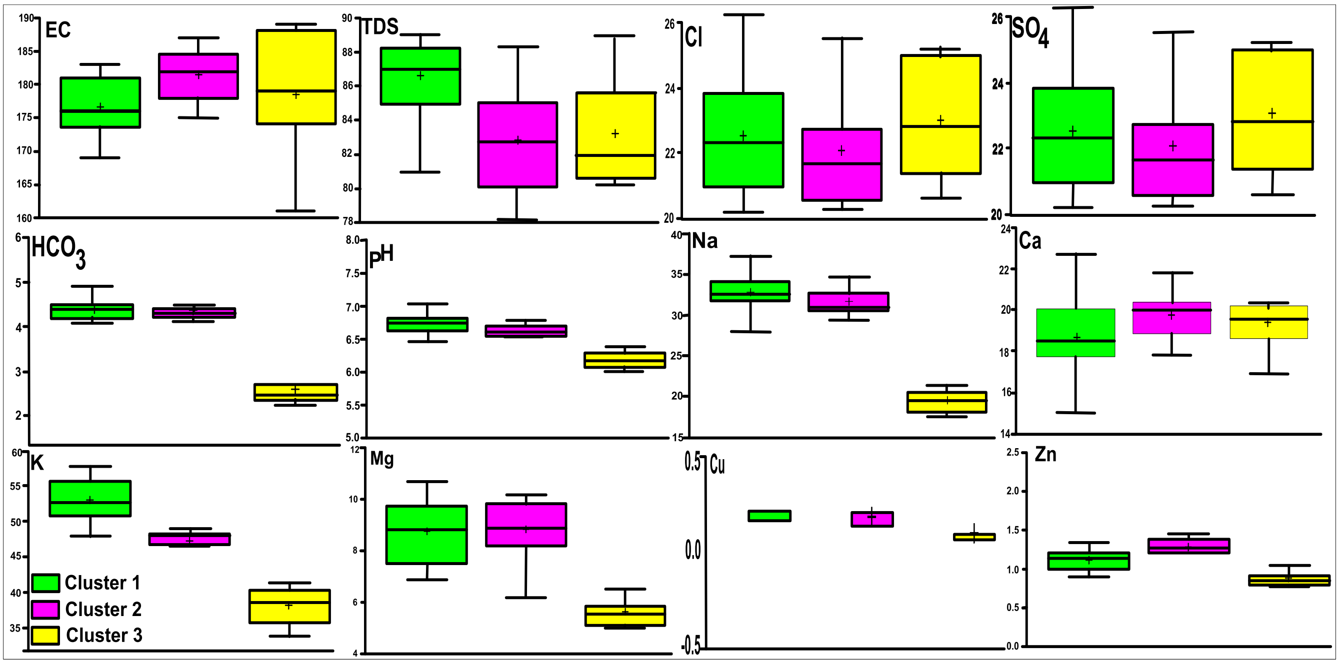

Figure 10: Boxplots of clusters based on the relationships of physicochemical parameters in water

3.7 Contamination Assessment

The area's average Igeo values for Cu, Cd, Cr, Fe, Ni, As, Pb, and Zn are -0.07, 5.91, 0.10, 1.16, -0.21, 3.40, 1.65, and -0.41 for surface water, and -0.07, 5.91, 0.10, 1.16, -0.21, 3.40, 1.65, and -0.41 for groundwater (Table 5). According to the Igeo, 59% of the samples had moderate to mild Cu pollution, whereas 61% of the surfacewater samples had no Cu pollution at all. Additionally, Igeo showed that 96% of the surfacewater samples had extremely high levels of cadmium pollution, while just 4% of the samples had moderate to high levels of the metal. Igeo went on to show that 66% of the samples had moderate to moderate levels of Cr pollution, whereas 44% of the samples had no pollution at all. The area's average Igeo values for Cu, Cd, Cr, Fe, Ni, As, Pb, and Zn are -0.07, 5.91, 0.10, 1.16, -0.21, 3.40, 1.65, and -0.41 for surface water, and -0.07, 5.91, 0.10, 1.16, -0.21, 3.40, 1.65, and -0.41 for groundwater. According to the Igeo, 59% of the samples had moderate to mild Cu pollution, whereas 61% of the surfacewater samples had no Cu pollution at all. Additionally, Igeo showed that 96% of the surfacewater samples had extremely high levels of cadmium pollution, while just 4% of the samples had moderate to high levels of the metal. Igeo went on to show that 66% of the samples had moderate to moderate levels of Cr pollution, whereas 44% of the samples had no pollution at all. Furthermore, 33% of the groundwater samples had heavy to extremely high levels of Cd pollution, whereas 17% of the samples were neither substantially nor excessively contaminated by the metal. According to Igeo's findings, 67% and 33%, respectively, of the groundwater samples from this region are free of pollutants and/or moderately contaminated by Cr, while 50% of the samples are free of pollutants and/or moderately polluted by Fe. Additionally, the study revealed that, whereas 67%, 17%, and 17% of the samples were unpolluted, moderately to severely, strongly to very contaminated by Pb, 17% and 83% of the samples were heavily and extremely polluted by As.

To ascertain the extent of water pollution in the area, the pollution load index (PLI), contamination degree (CD), and contamination factor (CF) were implemented. The findings indicate that the surface water in the region is low to extremely highly contaminated by As and Pb and low to moderately contaminated by Cu, Cr, Fe, Ni, As, Pb, and Zn. For these elements, the corresponding CF values are as follows: 1 to 1.95, 10 to 200, 1.12 to 2.15, 1 to 2.22, 0.95 to 1.93, 1 to 60, 0.1 to 20, and 0.88 to 1.43. Moreover, there is a significant amount of cadmium pollution in the surface water. The following ranges of CF values for groundwater: 0.95 to 1.27, 1 to 50, 1.22 to 1.67, 1.27 to 1.57, 0.67 to 1.31, 1 to 20, 1 to 40, and 1 to 1.37 for Cu, Cd, Cr, Fe, Ni, As, Pb, and Zn. lead, arsenic, and mercury pollution ranging from moderate to severe. The study found that the degree of heavy metal contamination (CD) in the area's surface water ranges from 68.78 to 247.64, while the CD in the groundwater ranges from 17.71 to 106.78. This implied that, whereas heavy metals are a major and highly polluting factor in groundwater, they are also highly contaminated in surface water. The heavy metal pollution load index (PLI) for surface water varies from 1.59 to 5.49, per the research. This implies that heavy metal contamination of surface water ranges from mild to severe. In addition, the PLI for heavy metals in groundwater varies from 1.44 to 4.42, suggesting that they have an impact on pollution that is medium-to-strong to extremely powerful.

Table 5: Geo-accumulation index (Igeo), contamination factor (CF), contamination degree (CD) and pollution load index (PLI) of metals in surface and groundwater of the study area

			Cu	Cd	Cr	Fe	Ni	As	Pb	Zn	CD	PLI
Igeo	**Surface Water**	**Min.**	-0.59	2.74	-0.43	0.36	-0.68	-0.59	-3.91	-0.77		
		Max.	0.38	7.06	0.67	1.51	0.36	5.33	3.74	-0.07		
		Avg.	-0.07	5.91	0.10	1.16	-0.21	3.40	1.65	-0.41		
	Ground Water	**Min.**	-0.66	-0.59	-0.30	-0.25	-1.17	3.88	-0.59	-0.58		
		Max.	-0.25	5.06	0.16	0.06	-0.21	4.85	3.74	-0.13		
		Avg.	-0.39	3.80	-0.09	-0.07	-0.59	4.47	0.69	-0.41		
CF	**Surface Water**	**Min.**	1.00	10.00	1.12	1.00	0.95	1.00	0.10	0.88	68.78	1.59
		Max.	1.95	200.00	2.15	2.22	1.93	60.00	20.00	1.43	247.64	5.49
		Avg.	1.46	101.82	1.61	1.78	1.35	32.10	8.84	1.15	150.06	3.89
	Ground Water	**Min.**	0.95	1.00	1.22	1.27	0.67	1.00	1.00	1.00	17.71	1.44
		Max.	1.27	50.00	1.67	1.57	1.31	20.00	40.00	1.37	106.78	4.42
		Avg.	1.16	33.50	1.43	1.44	1.04	5.67	23.67	1.15	69.02	2.65

3.8 Water quality Index (WQI)

Table 6 displays the findings of the computed WQI, which provides an indicator of the water quality in the research region. The readings for surface water fell between the excellent and inappropriate groups, ranging from 59.64 to 403.79. Thirty percent of the surfacewater samples fall into the low water quality class, and just one sample (OSW10), or 4% of the samples, is classified as having high water quality. Furthermore, 57% of the samples are classified as having extremely bad water quality, while the remaining 8% are classified as having inappropriate water quality. It may be concluded that the surface water in this region is typically of extremely low quality, which may be attributed to an increase in human activity in the area. According to WQI, 33% of the tests for groundwater have poor water quality, while the remaining 77% have satisfactory water quality. This demonstrates that both geogenic and anthropogenic processes have a greater effect on the area's groundwater quality.

Table 6: Calculated water quality index (WQI) and classification.

S/N	Samples Code	Water Type	WQI Variables		WQI	Remark
			∑wi	∑qiwi		
1.	OSW1	Surfacewater	567.93	126632.90	222.97	Very Poor
2.	OSW2	Surfacewater	567.93	80372.26	141.52	Poor
3.	OSW3	Surfacewater	567.93	155907.90	274.52	Very Poor
4.	OSW4	Surfacewater	567.93	115832.70	203.96	Very Poor
5.	OSW5	Surfacewater	567.93	124063.00	218.44	Very Poor
6.	OSW6	Surfacewater	567.93	120819.40	212.73	Very Poor
7.	OSW7	Surfacewater	567.93	147899.30	260.41	Very Poor
8.	OSW8	Surfacewater	567.93	134880.30	237.49	Very Poor
9.	OSW9	Surfacewater	567.93	68741.76	121.04	Poor
10.	OSW10	Surfacewater	567.93	33872.34	59.64	Good
11.	OSW11	Surfacewater	567.93	152444.00	268.42	Very Poor
12.	OSW12	Surfacewater	567.93	98637.44	173.63	Poor
13.	OSW13	Surfacewater	567.93	106687.10	187.85	Poor
14.	OSW14	Surfacewater	567.93	156022.00	274.72	Very Poor
15.	OSW15	Surfacewater	567.93	169566.00	298.56	Very Poor
16.	OSW16	Surfacewater	567.93	131800.50	232.07	Very Poor

Table 6: Calculated water quality index (WQI) and classification.

17.	OSW17	Surfacewater	567.93	148136.60	260.83	Very Poor
18.	OSW18	Surfacewater	567.93	108650.40	191.31	Poor
19.	OSW19	Surfacewater	567.93	229325.80	403.79	Unsuitable
20.	OSW20	Surfacewater	567.93	183669.60	323.39	Unsuitable
21.	OSW21	Surfacewater	567.93	113187.00	199.29	Poor
22.	OSW22	Surfacewater	567.93	115736.00	203.78	Very Poor
23.	OSW23	Surfacewater	567.93	104837.10	184.59	Poor
24.	OGW1	Groundwater	567.93	59778.89	105.26	Poor
25.	OGW2	Groundwater	567.93	60549.57	106.61	Poor
26.	OGW3	Groundwater	567.93	48593.42	85.56	Good
27.	OGW4	Groundwater	567.93	51489.82	90.66	Good
28.	OGW5	Groundwater	567.93	3131.46	5.51	Good
29.	OGW6	Groundwater	567.93	23399.83	41.20	Good

3.9 Water suitability for irrigation purposes

Table 7 displays the findings of the irrigation parameters, including SAR, PI, MAR, SSP, RSBC, and KR, that were investigated. Because there are fewer possible sodium hazards, the results indicated that SAR for the water range of 1.35 to 2.92 and indicated that all the samples can be used for agricultural purposes (Herman 1978). According to Doneen's (1964) proposal, PI ranges from 0.68 to 0.82 and indicates that the water samples are appropriate for irrigation. The local MAR of water ranges from 20.78 to 41.19. It is suggested that the water is appropriate for agricultural usage because the MAR is less than 50. The region's soluble sodium percentage (SSP), which ranges from 66.09 to 80.03, indicates that all of the samples are quite suitable for irrigation. The water's RSBC in this area ranges from -18.60 to -9.86. This further confirmed that every sample is appropriate for use in agriculture. The area's water KR ranges from 0.68 to 1.46. KR revealed that while 76% of the samples are just marginally appropriate for irrigation, 24% of the samples are suitable for use in agriculture.

Table 7: Summary of irrigation indices calculated for groundwater of the area

Parameters	**Range**	**Irrigation Class**	**Samples (n=29)**	
			In (number)	**In (%)**
SAR (Herman 1978)	<6 6-9 >9	No Problem Increasing Problem Severe Problem	29	100
PI (Doneen, 1964)	<60 >60	Suitable Unsuitable	29	100
MAR (Paliwal, 1972)	<50 >50	Suitable Unsuitable	29	100
SSP (Tood, 1980)	<20 20-40 40-80 >80	Excellent Good Fair Unsuitable	29	100
RSBC (Naseem *et al.* 2010)	<2.5 >2.5	Suitable Unsuitable	29	100
KR (Kelly, 1946)	<1 1-2 >2	Suitable Marginal Unsuitable	07 22	24 76

3.10 Ecological risk

Table 8 presents the ecological risk assessment for heavy metals in the area's surface water. According to the data, the area's surface water has an ER for Cu ranging from 5.35 to 9.75 and an ER for Zn ranging from 0.89 to 1.44. The area's groundwater has an ER for Cd ranging from 30 to 600 and an ER for Cr ranging from 2.24 to 4.78. Moreover, the ER ranges from 4.75 to 9.65 for Ni and from 0.5 to 45 for Pb. The range of the overall risk index (RI) is 55.75 to 620.11. Cu, Zn, Cr, and Pb were shown to have little ecological harm. 4% of the samples each had a modest to significant ecological risk associated with Cd. Furthermore, in 54% and 38% of the area's surface water, respectively, cadmium poses a high and extremely high danger. The study also showed that there are few ecological concerns associated with Cr, Ni, and Pb in the local surface water. According to the overall risk assessment, 44% and 48% of the sample locations are exposed to moderate and significant ecological hazards, respectively, while 4% of the sampling locations are susceptible to low and high ecological risks. Cu ecological risk ranges from 4.75 to 6.33 for groundwater, whereas Zn ecological risk ranges from 1.00 to 1.38. For Cd, the ER ranges from 30 to 1500, but for Cr, it ranges from 2 to 3.33. The ER ranges from 3.33 to 6.52 for Ni and from 5 to 200 for Pb, respectively. Groundwater RI ranges from 48 to 1713.13. This shows that, whereas 33% and 77% of the samples were subjected to low and considerably ecological hazards owing to Cd in the area's groundwater, the area's groundwater is prone to low ecological risks from Cu, Zn, Cr, and Ni. Additionally, 33% of the samples that were gathered were exposed to Pb at low, substantial, and very high risks. According to the overall risk assessment, 83% and 17% of the samples, respectively, are vulnerable to low and severe ecological threats.

Table 8: Ecological Risks of Heavy Metals in water

Water Type		**ER Cu**	**ER Zn**	**ER Cd**	**ER Cr**	**ER Ni**	**ER Pb**	**RI**
Surfacewater	**Minimum**	5.35	0.89	30	2.24	4.75	0.5	55.75
	Maximum	9.75	1.44	600	4.78	9.65	45	620.11
	Average	7.36	1.15	295	3.31	6.33	13.26	326.57
Groundwater	**Minimum**	4.75	1	30	2	3.33	5	48
	Maximum	6.33	1.38	1500	3.33	6.52	200	1713.13
	Average	5.66	1.12	865.71	2.73	5.13	102.14	982.49

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3.11 Human health risk assessment of heavy metals in surface and groundwater

Tables 9 and 10 summarise the health risks—both cancerous and non-cancerous associated with oral consumption and skin contact with certain heavy metals found in the area's surface and groundwater for both adults and children. The following is the descending order of average non-carcinogenic risk (HQ) of heavy metals for both adults and children who eat surfacewater orally: Fe > Cd > Cr > As > Pb > Cu > Zn > Ni; for groundwater, the descending order is Fe > Cd > Cr > Zn > Cu > As > Pb > Ni.

The following is a list of average non-carcinogenic risk (HQ) values for children exposed to surfacewater through cutaneous contact with heavy metals: In contrast, for groundwater, the sequence is Fe > Cr > Cd > Pb > Cu > Zn > Ni > As. Cr > Fe > Cd > Pb > Cu > Ni > Zn > As. The following is a list of average non-carcinogenic risk (HQ) values for individuals from surfacewater exposure by dermal contact: Zn > Ni > Cr > Fe > Cd > Pb > Cu > Zn > For groundwater, the sequence is as follows: Fe > Cr > Cd > Pb > Cu > Zn > Ni > As.

The following is a list of the average levels of carcinogenic risk (HQ) for metals in surfacewater and groundwater for both adults and children: Ni > Cd > Cr > As > Pb. Adewumi and Laniyan (2020) state that when a metal's HQ value is more than 1, the heavy metal pollutant may provide possible health risks. The present investigation reveals that the HQ values of Cu, Ni, As, Pb, and Zn are less than 1, signifying that the metals did not individually represent a health risk to children consuming surfacewater orally in Owo metropolis (Table 9). On the other hand, children who consumed surfacewater orally had HQ values for Cd, Cr, and Fe greater than 1. This suggests that children's oral consumption of Cd, Cr, and Fe may have had a negative impact on their health. Through the oral ingestion channel, the HQ for every metal under study was less than 1. This demonstrated that drinking the local groundwater cannot harm children's health in any way due to the presence of particular metals. In both surfacewater and groundwater, children's HQ for heavy metals by cutaneous exposure was less than 1 for younger residents. In comparison to surfacewater and groundwater through oral consumption and cutaneous contact routes, the HQ for all investigated elements in adults was lower (Table 10).

For surfacewater (children: 6.204; adults: 2.659) and groundwater (children: 2.317; adults: 1.478) oral ingestion pathways, the chosen heavy metals' hazard index (HI) was more than 1 for both categories. Therefore, by direct intake of surfacewater and groundwater in the area, the examined metals have a cumulative potential to cause unfavourable health problems to children and adults in the area. This also showed that children in this city are more vulnerable than adults to non-carcinogenic health concerns from oral consumption of heavy metals in water. The HI measured by skin contact with surfacewater (children: 0.816; adults: 0.297) and groundwater (children: 0.512; adults: 0.184) were both less than the danger value 1 (Tables 9 and 10).

Using oral consumption of Cr, Pb, Ni, Cd, and As, the study's calculations for children's lifetime cancer risks were: 1.15×10^{-4}, 3.67×10^{-5}, 3.33×10^{-4}, 4.85×10^{-6}, and 1.21×10^{-7} in groundwater and 3.44×10^{-4}, 1.39×10^{-4}, 6.75×10^{-4}, 2.76×10^{-5}, and 4.79×10^{-7} in surfacewater, respectively (Table 9). The study determined the lifetime cancer risks of grown-ups who consumed Cr, Pb, Ni, Cd, and As by mouth. The results showed that the risks were 7.50×10^{-4}, 3.40×10^{-4}, 1.45×10^{-3}, 5.87×10^{-5}, 1.03×10^{-6} in surfacewater and 2.50×10^{-4}, 7.86×10^{-5}, 7.08×10^{-4}, 1.04×10^{-5}, 2.60×10^{-7} in groundwater, respectively. The total cancer risk associated with the metals under study is 1.21×10^{-3} for surface water and 1.85×10^{-3} for groundwater, respectively, for children, and 2.59×10^{-3} for surface water and 1.05×10^{-3} for groundwater, respectively, for adults.

This suggested that consuming surface water increases the risk of cancer in adults compared to children, whereas drinking groundwater increases the risk of cancer in children compared to adults (Tables 9 and 10). The current study's evaluation of cancer risk value was determined to be over the permitted range of 1.00×10^{-6} and 1.00×10^{-4} for cancer health risk. In comparison to the risk range mentioned above, the results of this study suggest that lifetime exposure to current heavy metal concentrations poses cancer risks for both adults and children. Pawelczyk () reported that a risk of 1.00×10^{-3} indicated the risk will definitely require protective measures. Grade-I for Pb, grade-III for As, grade-V for Cd and Cr, and grade-VI for Ni are the risk grades of the metals investigated in surfacewater for children, whereas grade-I for Pb, grade-II for As, grade-III for Cr, and grade-V for Cd and Ni are the risk grades for the metals researched in groundwater. When it comes to surfacewater, the metals under study have risk grades of I for Pb, III for As, IV for Cr, V for Cd, and VI for Ni; when it comes to groundwater, the metals have risk grades of I for Pb, III for As, V for Cr, and VI for Ni. However, for both the adult and kid, the cumulative cancer risk for both water types was VII. This demonstrated that the locals' cumulative risk of developing cancer is quite high due to the heavy metals in the area. As a result, the problem's solution must be found immediately.

Table 9: Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk (CR) of heavy metals for children in surfacewater and groundwater in Owo area

					ADD$_{ingestion}$		**Non-Carcinogenic**				
Metals	**Water Type**	**RfD$_{ingestion}$ (mg/kg/day)**	**RfD$_{dermal}$ (mg/kg/day)**	**CSF$_{ing}$ (mg/kg/day)**	**Non-Cancer**	**Cancer**	**ADD$_{dermal}$**	**HQ$_{ing}$**	**HQ$_{derm}$**	**Cancer Risk Assessment**	**Risk Grades**
Cu	**SW**	4.00×10^{-2}	6.00×10^{-3}		1.25×10^{-2}	1.07×10^{-3}	4.96×10^{-5}	3.11×10^{-1}	8.23×10^{-3}		
	GW				6.07×10^{-3}	5.21×10^{-4}	2.41×10^{-5}	1.52×10^{-1}	4.01×10^{-3}		
Cd	**SW**	5.00×10^{-4}	2.50×10^{-5}	6.00	6.70×10^{-4}	5.74×10^{-5}	2.65×10^{-6}	1.34×10^{0}	5.30×10^{-2}	3.44×10^{-4}	Grade V
	GW				2.23×10^{-4}	1.91×10^{-5}	8.86×10^{-7}	4.47×10^{-1}	1.77×10^{-2}	1.15×10^{-4}	Grade V
Cr	**SW**	3.00×10^{-3}	7.50×10^{-5}	0.50	3.70×10^{-3}	3.18×10^{-4}	2.93×10^{-5}	1.23×10^{0}	3.91×10^{-1}	1.59×10^{-4}	Grade V
	GW				8.56×10^{-4}	7.33×10^{-5}	6.78×10^{-6}	2.85×10^{-1}	9.03×10^{-2}	3.67×10^{-5}	Grade III
Fe	**SW**	7.00×10^{-3}	1.40×10^{-3}		1.17×10^{-2}	1.01×10^{-3}	4.65×10^{-4}	1.68×10^{0}	3.31×10^{-1}		
	GW				6.13×10^{-3}	5.26×10^{-4}	2.43×10^{-4}	8.76×10^{-1}	1.74×10^{-1}		
Ni	**SW**	2.00×10^{-2}	5.40×10^{-3}	1.70	4.63×10^{-3}	3.97×10^{-4}	1.83×10^{-5}	2.31×10^{-1}	3.39×10^{-3}	6.75×10^{-4}	Grade VI
	GW				2.27×10^{-3}	1.94×10^{-4}	8.98×10^{-6}	1.13×10^{-1}	1.67×10^{-3}	3.33×10^{-4}	Grade V
As	**SW**	3.00×10^{-4}	2.85×10^{-4}	1.50	2.13×10^{-4}	1.83×10^{-5}	8.45×10^{-7}	7.11×10^{-1}	2.96×10^{-3}	2.76×10^{-5}	Grade III
	GW				3.78×10^{-5}	3.24×10^{-6}	1.50×10^{-7}	1.26×10^{-1}	5.25×10^{-4}	4.85×10^{-6}	Grade II
Pb	**SW**	1.40×10^{-3}	4.20×10^{-4}	0.009	6.21×10^{-4}	5.33×10^{-5}	9.84×10^{-6}	4.44×10^{-1}	2.34×10^{-2}	4.79×10^{-7}	Grade I
	GW				1.58×10^{-4}	1.35×10^{-5}	2.50×10^{-6}	1.25×10^{-1}	5.95×10^{-3}	1.21×10^{-7}	Grade I
Zn	**SW**	3.00×10^{-1}	6.00×10^{-2}		7.00×10^{-2}	6.60×10^{-3}	1.83×10^{-4}	2.57×10^{-1}	3.05×10^{-3}		
	GW				5.78×10^{-2}	4.96×10^{-3}	1.37×10^{-4}	1.93×10^{-1}	2.29×10^{-3}		
	SW							HI=6.204	HI=0.816	$\sum CR=1.21\times10^{-3}$	Grade VII
	GW							HI=2.317	HI=0.297	$\sum CR=1.85\times10^{-3}$	Grade VII

Table 10: Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk (CR) of heavy metals for adults in surfacewater and groundwater in Owo area

					$ADD_{ingestion}$		**Non-Carcinogenic**				
Metals	**Water Type**	**$RfD_{ingestion}$ (mg/kg/day)**	**RfD_{dermal} (mg/kg/day)**	**CSF_{ing} (mg/kg/day)**	**Non-Cancer**	**Cancer**	**ADD_{dermal}**	**HQ_{ing}**	**HQ_{derm}**	**Cancer Risk Assessment**	**Risk Grades**
Cu	**SW**	4.00×10^{-2}	6.00×10^{-3}		5.35×10^{-2}	2.29×10^{-3}	2.89×10^{-5}	1.34×10^{-1}	4.81×10^{-3}		
	GW				2.61×10^{-2}	1.11×10^{-3}	1.41×10^{-5}	6.51×10^{-2}	2.34×10^{-3}		
Cd	**SW**	5.00×10^{-4}	2.50×10^{-5}	6.00	2.87×10^{-4}	1.23×10^{-4}	1.55×10^{-6}	5.74×10^{-1}	6.19×10^{-2}	7.50×10^{-4}	Grade VI
	GW				9.51×10^{-5}	4.10×10^{-5}	5.17×10^{-7}	1.91×10^{-1}	2.07×10^{-2}	2.50×10^{-4}	Grade V
Cr	**SW**	3.00×10^{-3}	7.50×10^{-5}	0.50	1.56×10^{-3}	6.80×10^{-4}	1.71×10^{-5}	5.29×10^{-1}	2.28×10^{-1}	3.40×10^{-4}	Grade V
	GW				3.67×10^{-4}	1.57×10^{-4}	3.96×10^{-6}	1.22×10^{-1}	5.28×10^{-2}	7.86×10^{-5}	Grade IV
Fe	**SW**	7.00×10^{-3}	1.40×10^{-3}		5.02×10^{-3}	2.16×10^{-3}	2.71×10^{-4}	7.18×10^{-1}	1.94×10^{-1}		
	GW				2.62×10^{-3}	1.13×10^{-3}	1.42×10^{-4}	3.76×10^{-1}	1.01×10^{-1}		
Ni	**SW**	2.00×10^{-2}	5.40×10^{-3}	1.70	1.98×10^{-3}	8.50×10^{-4}	1.07×10^{-5}	9.91×10^{-2}	1.98×10^{-3}	1.45×10^{-3}	Grade V
	GW				9.76×10^{-4}	4.16×10^{-4}	5.25×10^{-6}	4.86×10^{-2}	9.71×10^{-4}	7.08×10^{-4}	Grade VI
As	**SW**	3.00×10^{-4}	2.85×10^{-4}	1.50	9.14×10^{-5}	3.92×10^{-5}	4.96×10^{-7}	3.05×10^{-1}	1.73×10^{-3}	5.87×10^{-5}	Grade IV
	GW				1.62×10^{-5}	6.94×10^{-6}	8.74×10^{-7}	5.39×10^{-1}	3.07×10^{-4}	1.04×10^{-5}	Grade III
Pb	**SW**	1.40×10^{-3}	4.20×10^{-4}	0.009	2.66×10^{-4}	1.14×10^{-4}	5.75×10^{-6}	1.90×10^{-1}	1.36×10^{-2}	1.03×10^{-6}	Grade II
	GW				6.76×10^{-5}	2.90×10^{-5}	1.46×10^{-6}	5.39×10^{-2}	3.47×10^{-3}	2.61×10^{-7}	Grade I
Zn	**SW**	3.00×10^{-1}	6.00×10^{-2}		3.30×10^{-2}	1.45×10^{-2}	1.78×10^{-4}	1.10×10^{-1}	2.97×10^{-3}		
	GW				2.48×10^{-2}	1.06×10^{-2}	1.34×10^{-4}	8.26×10^{-2}	2.23×10^{-3}		
	SW							HI=2.659	HI=0.512	$\sum CR = 2.59\times10^{-3}$	Grade VII
	GW							HI=1.478	HI=0.184	$\sum CR = 1.05\times10^{-3}$	Grade VII

4. CONCLUSIONS

In summary, this study highlights the vital significance of water as a finite natural resource that is necessary for human survival and a variety of activities. Water quality is defined by its chemical, physical, and biological characteristics. It is seen as a critical component that affects both environmental health and human health. The clear connection between human health and water quality emphasises how important it is to have access to clean, safe drinking water, particularly in areas where heavy metal pollution can cause diseases related to contaminated water. The study sought to close a knowledge gap about the quality of surface and groundwater in the research region, highlighting the lack of previous evaluations in this area. The results of the physicochemical examination showed that the concentrations in the water samples were often lower than those recommended by international bodies.

However, differences were noted in comparison to other areas, emphasising the distinctiveness of the local water quality. The effect of human activity on water quality was shown using cluster analysis and correlation studies, where different clusters indicated similar causes of contamination. The correlation coefficients indicated that the hydrochemical parameters were interdependent, suggesting that the dissolution of halite, salt contributions from industrial and domestic wastes, and the dissolution of minerals containing sulphur might be possible sources. Bivariate diagrams, Piper diagrams, Gibbs diagrams, and Durov plots were used in further study. These showed the importance of rock weathering, particularly by basement complex rocks, and revealed the dominance of Ca-Cl water types. Toxic metal buildup in water samples has been attributed mostly to silicate weathering and ion exchange mechanisms.

The evaluation of ecological risk indices revealed that while certain heavy metals presented little ecological concern, others showed moderate to significant dangers. While groundwater quality was mainly impacted by geogenic processes, surface water was typically rated as having extremely low quality by the Water Quality Index (WQI), most likely due to increased human activity. The assessment of the water's appropriateness for agricultural use revealed favourable circumstances, which were corroborated by metrics including the residual sodium bicarbonate (RSBC), permeability index (PI), and sodium adsorption ratio (SAR). But the ecological risk assessment highlighted possible risks and the need for cautious water management.

The necessity for preventative actions was highlighted by the non-carcinogenic and carcinogenic risk evaluations for heavy metals in surfacewater and groundwater. These studies revealed possible health hazards, particularly for youngsters. Concerns over the overall health effects of extended exposure to the heavy metal concentrations in the water were raised by the cumulative cancer risk, especially for adults. In order to protect the environment and the public's health, this thorough study concludes by highlighting how urgent it is to solve water quality concerns in the study region and stressing the necessity of efficient water management plans, pollution control techniques, and ongoing monitoring.

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