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RESEARCH ARTICLE

Deciphering groundwater pollution in the Lower Anayari Catchment: insights from using δ^2H, δ^{18}O, PMF, and APCS-MLR receptor model

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Abstract

This research provides a comprehensive analysis of groundwater pollution in the Lower Anayari Catchment (LAC) through δ^2H and δ^{18}O isotopic analysis, along with positive matrix factorization (PMF) and PCS-MLR receptor models. Forty groundwater samples were collected from hand-dug wells and equipped boreholes across the LAC. Flame photometry for Na^+ and K^+, complexometric titration for Ca^{2+}, ion chromatography for Cl^-, F^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}, and atomic absorption spectrometry for Mg^{2+}, Fe, Pb, Cd, As, and Ni were analytical techniques/instruments employed. In regard to cations, Na^+ has the highest average concentration of 63.0 mg/L, while Mg^{2+} has the lowest at 2.58 mg/L. Concerning the anions and nutrients, Cl^- has the highest mean concentration of 18.7 mg/L, and Fl^- has the lowest at 0.50 mg/L. Metalloids were detected in trace amount with Fe displaying the highest mean concentration of 0.077 mg/L whereas Cd and As recorded lowest (0.001 mg/L). The average values for groundwater δ^{18}O and δ^2H were − 3.64‰ and − 20.7‰, respectively; the average values for rainwater isotopic composition were − 3.41‰ for δ^{18}O and − 17.4‰ for δ^2H. It is believed that natural geological features, particularly biotite granitoid and volcanic flow/subvolcanic rocks from the Birimian Supergroup, significantly influence groundwater mineralisation. Additionally, the impact of anthropogenic activities on water quality, with urban development and agricultural practices, may be attributed to increasing levels of certain contaminants such as Fe, Ni, NO_3^-, and PO_4^{3-}. This research contributes to the broader field of hydrological study and provides practical implications for managing and conserving water resources in similar contexts. The innovative combination of isotopic and statistical analyses sets a new standard for future studies in groundwater quality assessment, emphasising the need for comprehensive approaches that consider both geological characteristics and human impacts for sustainable water resource management.

Keywords Stable isotope (δ^2H and δ^{18}O) · Hydrological research · Environmental geochemistry · Birimian Supergroup · Natural geological processes · Water resource management

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Introduction

Groundwater, as a critical source of fresh water, is indispensable for human survival, economic development, and ecosystem sustainability (Gao et al. 2021). Globally, it provides about 50% of the potable water supply, 40% of the industrial water needs, and over 20% of the water used for irrigation, making its quality paramount (UNESCO 2021). However, the purity of this vital resource is increasingly threatened by a myriad of contaminants ranging from agricultural runoff and industrial discharges to improper waste disposal (Li et al. 2023b). Pollution of groundwater is a growing concern, affecting the quantity and quality of available water (Asare et al. 2022). Groundwater pollution can occur naturally through geochemical processes or exacerbated by human activities such as over-extraction and land-use changes. Groundwater pollution poses severe risks to public health and compromises ecological integrity and economic growth (C. Li et al. 2020). For instance, in Bangladesh and West Bengal, groundwater pollution with naturally occurring arsenic has led to one of the largest mass poisonings in human history, affecting millions of people (Nickson et al. 1998).

Nitrate contamination in groundwater has emerged as a global concern, impacting millions worldwide. Its primary sources include excessive fertiliser application in agriculture, leaky septic systems, and industrial waste (Ward et al. 2018). This widespread pollution poses significant threats to human health, causing adverse effects like methemoglobinemia in infants and potentially increasing cancer risk (Verma et al. 2023; Ward et al. 2018). Research efforts across continents have employed diverse methods to assess nitrate levels (Sullivan et al. 2019), understand transport mechanisms (Kwon et al. 2021; Wang et al. 2022), biogeochemical processes (Wang et al. 2024), and develop mitigation strategies (Bishayee et al. 2022; Kazakis et al. 2020).

Recent advancements in methodology have significantly enhanced our understanding of groundwater pollution. Stable isotopes, particularly δ^2H and $\delta^{18}O$, have emerged as crucial tools in tracing water sources and pollution pathways (Sankoh et al. 2021). These isotopes, by reflecting the unique signatures of different water sources, aid in distinguishing between natural and anthropogenic influences on groundwater (Weitzman et al. 2021). Additionally, sophisticated statistical techniques like positive matrix factorization (PMF) and principal component analysis coupled with multiple linear regression (PCA-MLR) have been increasingly applied (Salim et al. 2019; Zanotti et al. 2019). These methods excel in deciphering complex environmental datasets, allowing for the identification of pollution sources and their contributions. Their application has provided deeper insights into groundwater pollution dynamics across various landscape (Chen et al. 2022; Jin et al. 2022; Meng et al. 2018; Xie et al. 2023). PMF allows for the dissection of complex environmental datasets, as evidenced in the analysis of polybrominated diphenyl ethers (PBDEs) in the San Francisco Estuary, where it helped reveal the processes affecting PBDE congener patterns in sediments (Rodenburg et al. 2014). This method's ability to handle incomplete data makes it particularly useful in environmental contexts where data uncertainty is common. The APCS-MLR model is effective in identifying and quantifying the sources of pollutants in environmental studies. It is particularly useful because it combines the strengths of each method: PCA for dimensionality reduction and identifying patterns, APCS for source contribution assessment, and MLR for quantifying relationships between sources and pollutants. This integrated approach provides a more comprehensive understanding of environmental data, especially in complex scenarios like air quality assessment where multiple sources contribute to pollution (Zhang et al. 2020). PMF and APCS-MLR have been used complementarily in groundwater studies to enhance the reliability of source identification and apportionment. Zhang et al. (2020) study in Southwest China applied both models to assess groundwater pollution sources, finding that while they identified similar pollution sources, PMF provided a more physically plausible source apportionment with higher *R*-squared values and lower unexplained variability than APCS-MLR. This complementarity suggests that using multiple receptor models can provide a more comprehensive understanding of groundwater pollution sources.

The Lower Anayari Catchment (LAC), a semi-arid region in Ghana covering approximately 253 km^2, has been the subject of various hydrogeochemical studies (Abdul-Wahab et al. 2021, 2022; Zakaria et al. 2021). This catchment is predominantly an agricultural area, with groundwater as the primary water source for domestic and farming purposes. In the Anayari catchment, essential research has been conducted to assess the quality and processes impacting groundwater chemistry, given the region's significant contribution to socioeconomic development and its intense farming activities. This research is particularly focused on nitrate (NO_3^-) contamination, which poses a threat to groundwater quality in many agricultural areas and can have adverse human health implications if consumed excessively. The study by Zakaria et al. (2023) analysed the characteristics of NO^{3-} in groundwater using hydrogeochemical and stable isotope data δ^2H, $\delta^{18}O$, $\delta^{15}N$–NO_3^-, and $\delta^{18}O$–NO_3^-. The study found that NO_3^- levels were mostly lower than the WHO guideline limit and that the primary source of NO_3^- was livestock and septic waste. The contribution of NO_3^- from potential sources was found to be in the order of sewage/manure > soil nitrogen > chemical fertilisers > precipitation. Denitrification was found to influence the NO_3^- concentration in some of the groundwater sources. Also, the use of Bayesian mixing model was applied to estimate the proportional contributions of NO_3^- load in boreholes and hand-dug wells in the catchment. The model demonstrated that soil nitrogen and sewage/manure were the major NO_3^- contributors to boreholes and hand-dug wells, respectively. These studies in LAC provide a crucial context for understanding the dynamics of groundwater quality and the factors influencing it in agriculturally intensive regions. The insights gained from these studies serve as a foundation for applying advanced statistical methods like positive matrix factorization (PMF), principal component analysis (PCA), absolute principal component scores (APCS), and multiple linear regression (MLR), which can further enhance the understanding of source apportionment and pollution dynamics.

This study uses the application of δ^2H and δ^{18}O isotopic analysis, complemented by positive matrix factorization (PMF) and principal component analysis-absolute principal component scores-multiple linear regression (APCS-MLR) models, to provide a nuanced understanding of groundwater pollution processes, which has been a gap in existing research. This study aims to (i) employ δ^2H and δ^{18}O isotopic analysis for tracing the sources of groundwater pollution in the Lower Anayari Catchment; (ii) utilise PMF and APCS-MLR models for quantifying the contribution of various factors to groundwater pollution; and (iii) integrate these methods for a comprehensive assessment of groundwater quality, thereby informing effective management and conservation strategies. This integrated approach is expected to yield insights crucial for the sustainable management of groundwater resources.

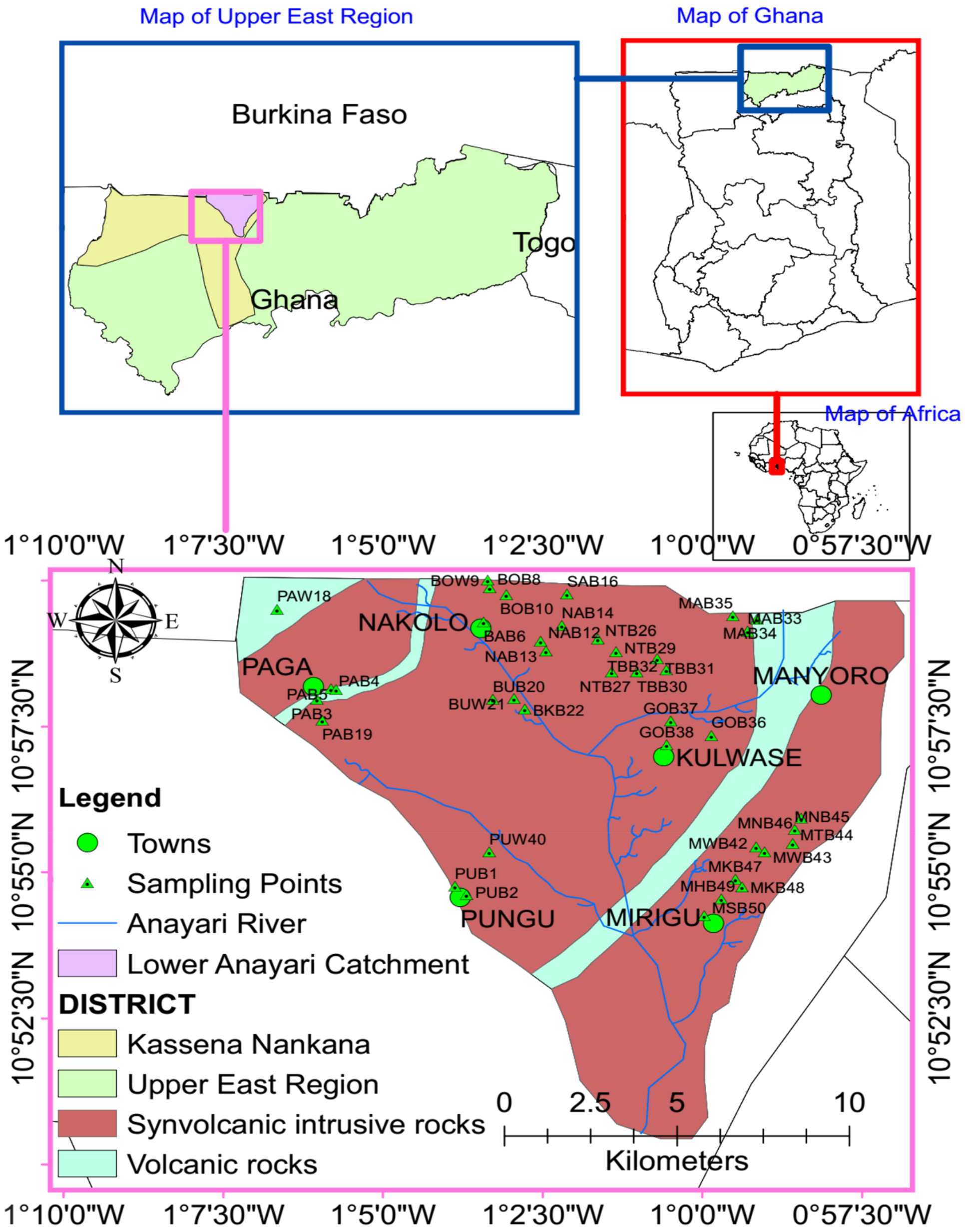


Fig. 1 Map illustrating the geospatial distribution of groundwater sampling locations in the Lower Anayari Catchment

Materials and methods

Study area description

The Lower Anayari Catchment (LAC) is situated within the Upper East Region of Ghana (Fig. 1). It forms a part of the White Volta basin, representing approximately 40% of the overall Anayari catchment. The catchment extends over an area of about 253km^2. The remaining 60% of the Anayari catchment lies across the border in Burkina Faso (Ofosu 2011). Geographically, the LAC overlaps the Kassena-Nankana East Municipal and Kassena-Nankana West District. It is positioned between the town of Navrongo, which serves as the capital of the Kassena-Nankana Municipal, and Sumbrugu, located about 11 km from Bolgatanga, the capital town of the Upper East Region. The precise coordinates for the catchment fall between latitudes 10° 50′ 0″ N to 11° 0′ 0″ N and longitudes 1° 7′ 30″ W to 0° 57′ 30″ W. Within this area, there are six principal communities, each comprising several smaller communities (Abdul-Wahab 2016). The Lower Anayari Catchment experiences a semi-arid climate with a mono-modal rainfall pattern, beginning in early May and ending in late October. The average annual rainfall is about 993 mm. The area sees its highest temperatures in early March, with the lowest temperatures occurring in December and January, influenced by the harmattan winds. The rainy season sees relative humidity around 65%, which drops sharply to below 10% post-rainy season (Martin 2006).

Geology

The Anayari catchment geology is underscored by two predominant rock types (Fig. 1): volcanic rocks and synvolcanic intrusive rocks (Ghana Geological Survey 2009). The oldest geological formations within the catchment are the volcanic rocks, dating back approximately 2196 ± 1 million years. These rocks encompass volcanic flows and subvolcanic rocks, along with minor interbedded volcaniclastics. The expansive coverage of these rocks suggests that the region experienced significant volcanic activity in its ancient past. The volcanic rocks are undifferentiated, indicating a complex mixture of materials without clear distinctions in rock type. Common minerals associated with these volcanic rocks include feldspars, both plagioclase and alkali types, which are ubiquitous in such environments. The synvolcanic intrusive rocks, predominantly biotite granitoid and mostly granodioritic in composition, are slightly younger, estimated at around 2156 ± 1 million years old (Ghana Geological Survey 2009). These intrusive rocks formed during the same volcanic events that produced the volcanic rocks, but they solidified beneath the surface, resulting in a coarse-grained texture indicative of slower cooling rates. Their granodioritic composition implies an intermediate silica content. Quartz and feldspars are the primary minerals in these granitoid rocks, with quartz providing a hard, crystalline structure, and feldspars offering a range of colours from white to pink (Ghana Geological Survey 2009). Biotite mica is a defining mineral in these rocks, giving them a dark hue and reflecting their formation in an iron and magnesium-rich environment.

Hydrogeology

The Lower Anayari Catchment is underlain predominantly by Precambrian basement (PCB) rocks. These ancient rocks are known for their low primary porosity and permeability, characteristics that typically limit the storage and movement of groundwater. Groundwater occurrence within these PCB rocks, however, is largely facilitated by secondary porosity created through chemical weathering, faulting, and fracturing. This secondary porosity, resulting from tectonic activities and isostatic uplift, significantly influences groundwater flow within the basement rocks. Literature indicates that the Birimian Supergroup, a part of the PCB rocks, experiences deeper weathering profiles, averaging about 23 m deep. Furthermore, the presence of significant sub-vertical fractures or fault zones extending to great depths often exceed 150 m, which can serve as major pathways for groundwater movement. The hydrogeological framework within the catchment includes a primary aquifer system that consists of both regolith aquifer, composed of weathered material atop the basement rocks, and the deep fractured rock aquifer as the main hydrogeological units. The regolith and fractured bedrock aquifers are integrated, with the regolith aquifer often displaying higher transmissivity due to its generally greater saturated thickness (Martin 2006). In terms of transmissivity, the PCB rocks exhibit a wide range, from 0.1 to 143.3 m^2/day, with an average transmissivity of 16.6 m^2/day. The specific capacity, which is a measure of the productivity of the aquifer, averages at 9.4 L/min/m.

Sampling, methodology, and analysis

For the study, 40 groundwater samples were collected between September and October 2022 from hand-dug wells and equipped boreholes across the LAC. A global positioning system (GPS) device accurately documented the sampling locations (Fig. 1). Most of the samples were collected from the eastern and northern part of the study area due larger number of boreholes as compared with the southern, western, and central parts which had fewer ones or none. Standard borehole purging and sample collection procedures were adhered to ensure the samples' quality (IAEA 2010; Sundaram et al. 2009). Hand-dug wells in use were also included in the sampling process. In situ filtration was performed using a 0.45-µm cellulose filter and a hand-operated vacuum pump. Cation analysis samples were preserved with nitric acid (HNO_3) to prevent alterations in chemical composition.

All collected groundwater samples were maintained at a temperature of ≤ 4°C during transportation to the analytical laboratory. In the field, parameters such as alkalinity, pH, electrical conductivity (EC), total dissolved solids (TDS), and carbonate $\left(HCO_3^-\right)$ were measured using appropriate equipment. The chemical analysis of each groundwater sample was conducted at the Nuclear Chemistry and Environmental Research Centre, National Nuclear Research Institute (NNRI), Ghana Atomic Energy Commission (GAEC), Accra. The analytical techniques included flame photometry for sodium $\left(Na^+\right)$ and potassium $\left(K^+\right)$, complexometric titration for calcium $\left(Ca^{2+}\right)$, ion chromatography for chloride (Cl^-), fluoride (F^-), nitrate $\left(NO_3^-\right)$, sulphate $\left(SO_4^{2-}\right)$, and phosphate $\left(PO_4^{3-}\right)$, and atomic absorption spectrometry for magnesium $\left(Mg^{2+}\right)$, iron (Fe), lead (Pb), cadmium (Cd), arsenic (As), and nickel (Ni).

Quality assurance and quality control (QA/QC) protocols were rigorously followed to ensure data integrity in assessing groundwater quality. Glassware and containers were acid-soaked and rinsed for decontamination. Boreholes were purged, and well activity confirmed to avoid sampling stagnant water. Additional samples were taken for analytical precision, with necessary preservation for transport. Reagents of analytical grade and calibrated instruments with validated reference materials ensured method accuracy. Charge-balance error (CBE) calculations within ±5% verified analytical quality. The samples were reported only if the charge balance error was within ±5% (3σ).

For isotopic data analysis, water samples were collected in airtight glass vials at each site to prevent any isotopic fractionation due to evaporation. The samples were taken directly from the source to minimise contact with air and potential pollution. Immediately after collection, the samples were sealed and labelled with detailed information, including the date, time, and exact collection location. The samples were then transported to the laboratory under controlled conditions, maintaining a temperature of around 4°C to preserve their isotopic integrity. Samples for rainwater isotopic composition were collected from Navrongo Meteorological station which is near study area between 2014 and 2016. The isotopic analysis of δ^2H and $\delta^{18}O$ was conducted using laser absorption spectroscopy. To ensure the reliability of the results, quality control measures such as the use of international standards and repeated measurements were implemented.

Statistical analysis

Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) using Ward's method is a widely used statistical technique for grouping data into distinct clusters (Mogaraju 2022). This method is particularly favoured for creating well-defined, compact clusters. Ward's method minimises the total within-cluster variance at each step of the clustering process. The variance measures the Euclidean distance between data points in a multidimensional space.

The process begins by treating each data point as a single cluster. At each step, the pair of clusters that leads to the minimum increase in total within-cluster variance is merged. This increase is calculated using the following Eq. (1):

$$\Delta(\mathrm{SSE}) = \frac{SS(A) + SS(B) - SS(A \cup B)}{2} \tag{1}$$

where Δ(SSE) is the increase in the error sum of squares (SSE), ($SS(A)$), and ($SS(B)$) are the sum of squares within the individual clusters (A) and (B), and ($SS(A \cup B)$) is the sum of squares within the newly formed cluster from the union of (A) and (B).

Hierarchical cluster analysis (HCA) using Ward's method was used to cluster and provide valuable insights into the hydrogeochemical processes based on their electrical conductivity (EC) and $\delta^{18}O$ values.

PMF

PMF, a receptor model developed by the US Environmental Protection Agency, decomposes the data matrix into source profile and contribution matrices (Karakas et al. 2017). The mathematical model for PMF is represented as follows (Eq. 2) (Mu et al. 2023):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} \cdot f_{kj} + e_{ij} \tag{2}$$

Here,(x_{ij}) denotes the concentration of each parameter in each sample, (g_{ik}) represents the concentration of each parameter in each source, (f_{kj}) is the contribution of each source in each sample, (e_{ij}) is the model error, and (p) is the number of factors. The PMF model aims to optimise the (g_{ik}) and (f_{kj}) matrices to best regenerate the (x_{ij}) matrix. The goodness of modelling is evaluated by minimising the objective value(Q), calculated as follows (Eq. 3):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{3}$$

In this equation, (u_{ij}) is the uncertainty matrix, and (n) and (m) are the numbers of samples and parameters, respectively.

Principal component analysis/absolute principal component scores—multiple linear regression

In our study, absolute principal component score multiple linear regression (APCS-MLR) was applied to the factor scores obtained by principal component analysis (PCA) to determine the percentage contribution of each source to groundwater pollution. This approach uses several equations to establish the relationship between water quality variables and their respective sources.

The APCS-MLR model is formulated as follows (Li et al. 2021):

$$C_{ik} = b_{i0} + \sum_{p=1}^{P} b_{ip} \times APCS_{pk} \tag{4}$$

where (i) denotes the count of water quality variables analysed, (k) represents the count of observations, and (p) denotes the factors of the water quality variables. (C_{ik}) is the concentration of the (i) th parameter for sample (k), (b_{i0}) is the MLR constant, (b_{ip}) is the regression coefficient of source (p), and $(APCS_{pk})$ is the absolute principal component.

$$\left(Z_i\right)_j = C_{ij} - \frac{C_j}{\sigma_j} \tag{5}$$

$$\left(Z_o\right)_j = \left(0 - C_j\right)\sigma_j \tag{6}$$

$$\left(A_o\right)_j = \sum_{p=1}^{p} S_{jp} Z_{oj} \tag{7}$$

$$\left(A_z\right)_{ip} = \sum_{p=1}^{p} S_{jp} Z_{ij} \tag{8}$$

$$APCS_{ip} = \left(A_z\right)_{ip} - A_{0j} \tag{9}$$

In these equations, $(\left(Z_k\right)_i)$ is the normalised $(j)th$ variable of the $(i)th$ sample, $(\left(Z_o\right)_j)$ is the normalised absolute zero concentration value of the $(j)th$ variable, $(\overline{C_j})$ and (σ_j) are respectively the mean and standard deviation of the $(i)th$ variable, (S_{jp}) is the score coefficient of the $(p)th$ component for the $(j)th$ variable, $\left(A_z\right)_{ip}$ is the component score for the $(i)th$ sample of the (p) component, $\left(A_o\right)_j$ is the component absolute zero concentration, and $(APCS_{ip})$ is the absolute component score in the APCS-MLR model.

The percentage source contribution (PC_p) is calculated using the absolute value method as follows (Yu et al. 2022):

$$PC_p = \frac{\left|b_{ip} \times \overline{APCS_{pk}}\right|}{b_{i0} + \sum_p \left|b_{ip} \times \overline{APCS_{pk}}\right|} \tag{10}$$

Negative values of $(b_{ij} \times APCS_{pk})$ in this equation indicate a source's negative contribution of over 100%.

$$PC_j = \frac{\left|b_{ip}\right|}{b_{i0} + \sum_p \left|b_{ip} \times \overline{APCS_{pk}}\right|} \tag{11}$$

where $(\overline{APCS_{pk}})$ is the average of the absolute principal component. This equation accounts for the contribution from unidentified sources. The APCS-MLR model offers a comprehensive approach to quantitatively assess the contribution of identified and unidentified sources to groundwater contaminants (Li et al. 2023a; Yu et al. 2022), aiding in a detailed understanding of the groundwater pollution in the Lower Anayari Catchment.

Results

Geochemical and water quality data

The water quality data presents a comprehensive overview of various parameters (Table 1). The pH level, a measure of acidity or alkalinity, averages at 6.89, indicating a slightly acidic environment. This level is moderately stable across samples, as suggested by a standard deviation of 0.24. The temperature of the water samples averages at 32.1°C, with a range from 29.5 to 35°C. The electrical conductivity, a measure of the water's ability to conduct electricity, has a mean value of 429 µS/cm, indicating a significant presence of ions in the groundwater. Total dissolved solids (TDS), which represent the total concentration of dissolved substances in water, average at 215 mg/L. The bicarbonate ion, a significant component of the total alkalinity of water, displays an average concentration of 261 mg/L. Among the cations, sodium has the highest average concentration of 63.0 mg/L, while magnesium has the lowest at 2.58 mg/L. Among the anions and nutrients, chloride has the highest mean concentration of 18.7 mg/L, and fluoride has the lowest at 0.50 mg/L. Heavy metals are present in trace amounts, with iron showing the highest average concentration of 0.077 mg/L and cadmium and arsenic the lowest at 0.001 mg/L. The stable isotopes, $\delta^{18}O$ and $\delta^{2}H$, measured in both groundwater and rainwater, show distinct ranges and mean values, indicative of their respective sources and processes affecting them. The mean values for groundwater $\delta^{18}O$ and $\delta^{2}H$ were − 3.64‰ and − 20.7‰, respectively. The mean values for rainwater isotopic composition were (− 3.41‰ for $\delta^{18}O$ and − 17.4‰ for $\delta^{2}H$).

Table 1 Summary statistics of groundwater quality parameters in the Lower Anayari Catchment

Variable	Unit	Mean	Max	Min	SD	1stQ	3rdQ
pH		6.89	7.40	6.30	0.24	6.70	7.10
Temp	℃	32.1	35.0	29.5	1.12	31.4	32.6
EC	µS/cm	429	734	230	111	345	475
TDS	mg/L	215	368	115	55.6	173	238
HCO_3^-	mg/L	261	512	92.7	85.0	200	284
Na^+	mg/L	63.0	168	18.7	26.3	47.2	67.0
K^+	mg/L	8.97	19.1	1.30	3.96	6.63	10.6
Ca^{2+}	mg/L	35.6	59.2	17.6	9.1	30.4	40.0
Mg^{2+}	mg/L	2.58	5.97	0.72	1.30	1.61	3.53
F^-	mg/L	0.50	2.39	0.001	0.61	0.09	0.68
Cl^-	mg/L	18.8	43.0	0.64	11.8	8.86	28.53
NO_3^-	mg/L	13.8	38.9	0.004	13.2	1.25	26.43
PO_4^{3-}	mg/L	0.39	2.55	0.001	0.60	0.003	0.60
SO_4^{2-}	mg/L	5.81	32.5	0.002	6.62	2.07	6.55
Fe	mg/L	0.077	0.59	0.001	0.17	0.001	0.028
Pb	mg/L	0.003	0.02	0.001	0.005	0.001	0.001
Cd	mg/L	0.001	0.01	0.001	0.001	0.001	0.001
As	mg/L	0.001	0.01	0.001	0.002	0.001	0.001
Ni	mg/L	0.002	0.02	0.001	0.005	0.001	0.001
$\delta^{18}O_{gw}$	‰VSMOW	−3.64	−2.15	−4.35	0.48	−3.96	−3.45
$\delta^{2}H_{gw}$	‰VSMOW	−20.8	−15.2	−25.7	2.38	−22.5	−18.9
$\delta^{18}O_{rain}$	‰VSMOW	−3.41	−0.40	−6.81	1.81	−4.68	−1.98
$\delta^{2}H_{rain}$	‰VSMOW	−17.4	−3.00	−38.4	10.3	−25.5	−10.1

Table 2 Cluster-Based analysis of groundwater variables in the Lower Anayari Catchment

Cluster	Variable	v.test	Mean	Overall mean	SD	Overall SD	*p*-value
1	$\delta^{18}O$	−2.45	−3.85	−3.64	0.26	0.47	0.014
	EC	−4.86	330	429	44.1	110	0.000
2	EC	2.53	474	429	36.7	110	0.011
	$\delta^{18}O$	2.20	−3.47	−3.64	0.55	0.47	0.029
3	EC	4.31	695	429	27.7	110	1.64×10^{-5}

Isotopic data analysis and hierarchical cluster analysis

Table 2 presents a detailed analysis of three clusters (Fig. 2) based on two key groundwater variables: $\delta^{18}O$ and electrical conductivity (EC). For cluster 1 (which includes samples BUB20, MAB33, MAB34, NAB12, and BKB22), $\delta^{18}O$ shows a negative v.test value of −2.45, indicating that its mean value of −3.85 is significantly lower than the overall mean (−3.64). This is accompanied by a standard deviation (SD) of 0.26, compared to the overall SD of 0.47, and a *p*-value of 0.014, suggesting a statistically significant difference from the overall group. EC in cluster 1 also shows a negative v.test value of −4.86, with a mean of 330 µS/cm, notably lower than the overall mean of 429 µS/cm. The SD for EC in this cluster is 44.090 µS/cm, and the *p*-value is extremely low (0.000), highlighting a significant deviation from the overall dataset.

In contrast, cluster 2, which comprises samples GOB37, PAB19, MNB45, MWB43, and MKB47, exhibits a different pattern. EC has a positive v.test value of 2.53, with its mean (474 µS/cm) being higher than the overall mean and a *p*-value of 0.011, indicating a significant difference. The SD for EC in this cluster is smaller (36.7 µS/cm) compared to the overall SD. For $\delta^{18}O$, the v.test value is 2.18, with a mean of −3.47, slightly higher than the overall mean, and a *p*-value of 0.029, suggesting a notable but less pronounced difference from the overall group.

Cluster 3 (with samples MWB42, PAB3, and MHB49) is characterised by a single variable, EC, which shows a markedly high v.test value of 4.31. The mean EC value in this cluster is 695 µS/cm, significantly higher than the overall

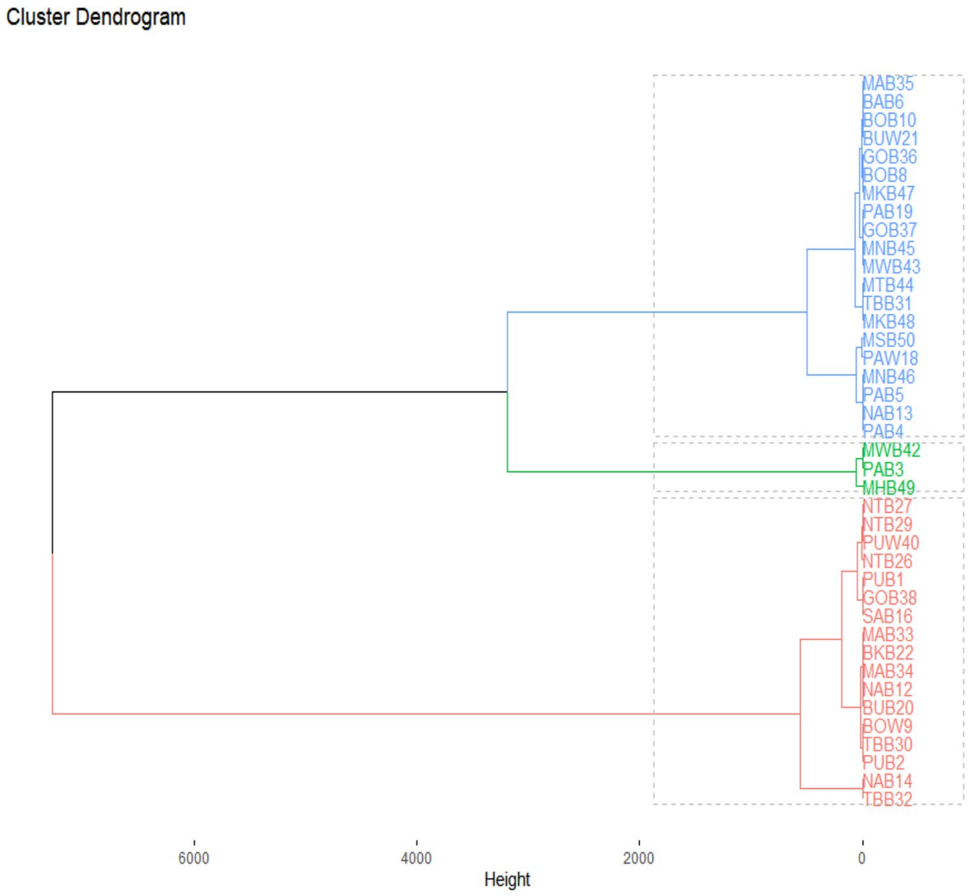


Fig. 2 Hierarchical cluster dendrogram of groundwater samples from Lower Anayari Catchment. Red (cluster 1), blue (cluster 2), and green (cluster 3)

mean, and the SD is 27.7 μS/cm, indicating a more consistent set of readings within this cluster. The *p*-value is extremely low (1.64×10^{-5}), underscoring a strong statistical significance. These clusters reveal distinct geochemical signatures in groundwater samples, with significant variations in EC and $\delta^{18}O$ values, reflecting differences in groundwater sources, mineralisation processes, or hydrogeological conditions.

The isotopic composition data of groundwater in the Lower Anayari Catchment provides critical insights into groundwater pollution in the study area. Cluster analysis reveals significant differences in groundwater mineralisation and potential pollution. Cluster 1 shows lower mineralisation, suggesting fresher water sources, while cluster 2 indicates higher mineralisation and possible evaporation effects. Cluster 3 stands out with markedly high mineralisation (high EC values), pointing to severe pollution, possibly from natural geological processes or anthropogenic activities.

The diagram presented in Fig. 3 is a plot of isotopic composition, specifically showing the relationship between $\delta^{18}O$ and $\delta^{2}H$ values of groundwater and rain samples. In the diagram, three distinct clusters of groundwater samples are plotted against the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL), which serve as references for typical isotopic compositions of precipitation in equilibrium with the atmosphere. These lines are defined by the equations $\delta^{2}H = 8.13\delta^{18}O + 10.13$ for the GMWL (Rozanski et al. 1993) and $\delta^{2}H = 7.22\delta^{18}O + 8.66$ for the LMWL (Gibrilla et al. 2022), with the latter being more specific to local precipitation patterns. Cluster 1 (red) lies closer to the LMWL, indicating that the groundwater samples are more influenced by local precipitation. The proximity to the LMWL suggests less evaporation and potential quick recharge from recent rainfall. Cluster 2 (blue) are also aligned close to the LMWL but are slightly more enriched in heavier isotopes compared to cluster 1, which could imply some evaporation before recharge or longer interaction with the local geology. Cluster 3 (green) are much more enriched in the heavier isotopes, indicating significant evaporation or possibly water–rock interaction processes that have shifted their isotopic composition away from the signature of local rainfall. In the context of groundwater pollution in the Lower Anayari Catchment, this diagram could indicate that clusters 1 and 2, being closer to the LMWL, represent fresher water, possibly less affected by pollution. In contrast, cluster 3, which is more isotopically enriched, might be more subject to processes like evaporation and mineral dissolution that can contribute to pollution. This aligns with the data suggesting that cluster 3 has a higher mean electrical conductivity, a proxy for salinity, supporting the interpretation that these samples have undergone more extensive pollution.

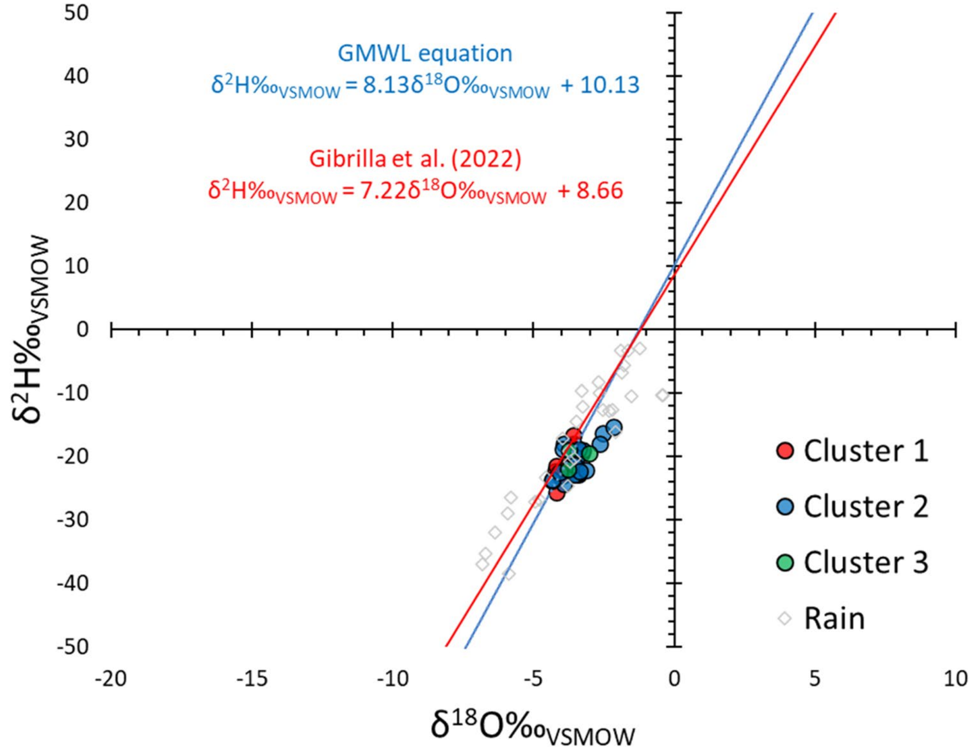


Fig. 3 Plot of $\delta^{18}O$ vs δ^2H values for groundwater clusters and rain samples in the Lower Anayari Catchment area, with reference to the global meteoric water line (GMWL) and local meteoric water line (LMWL) (Gibrilla et al. 2022)

PMF analysis

Factor profiles in the Lower Anayari Catchment

Concentration of species In analysing the concentration of species within the groundwater, distinct patterns emerge across the five factors (Table 3). Factor 1: geological weathering and mineral leaching factor—characterised by high concentrations of electrical Conductivity (EC), bicarbonate (HCO_3), sodium (Na), calcium (Ca), and magnesium (Mg). This indicates a significant influence from natural geological processes (Abdul-Wahab et al. 2021; Zakaria et al. 2021). Factor 2: urbanisation influence factor—this factor exhibits somewhat higher concentrations of chloride (Cl), iron (Fe), and nickel (Ni). These elements could be

Table 3 Distribution of groundwater quality parameters across five factors in PMF Base Run #14. This table outlines the factor profiles for various groundwater quality parameters

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	3.37	6.29×10^{-2}	1.56	4.22×10^{-1}	1.33
EC	2.14×10^{2}	1.86×10^{1}	7.06×10^{1}	2.47×10^{1}	8.46×10^{1}
HCO_3^-	1.43×10^{2}	1.24×10^{1}	3.81×10^{1}	5.09×10	4.48×10^{1}
Na^+	3.39×10^{1}	2.92×10	8.96×10	1.35×10	8.53
K^+	4.47	2.97×10^{-2}	1.75	8.80×10^{-1}	3.13×10^{-11}
Ca^{2+}	1.71×10^{1}	1.34	5.21	1.75	7.91
Mg^{2+}	7.31×10^{-1}	1.38×10^{-1}	3.17×10^{-1}	0.000	7.87×10^{-1}
F^-	1.33×10^{-03}	1.01×10^{-2}	0.000	2.84×10^{-1}	2.07×10^{-3}
Cl^-	3.61×10^{-1}	4.71×10^{-1}	5.62	2.55	1.55
NO_3^-	1.36×10^{-1}	0.000	1.14×10^{-1}	6.02×10^{-1}	7.04
PO_4^{3-}	1.66×10^{-2}	4.74×10^{-3}	2.76×10^{-1}	7.26×10^{-03}	2.21×10^{-7}
SO_4^{2-}	2.96×10^{-2}	5.00×10^{-2}	1.64×10^{-1}	1.86	1.04
Fe	3.22×10^{-03}	7.35×10^{-2}	1.71×10^{-9}	4.16×10^{-4}	2.17×10^{-3}
Pb	2.86×10^{-4}	1.67×10^{-03}	1.09×10^{-4}	4.98×10^{-05}	1.23×10^{-4}
Cd	2.59×10^{-4}	5.19×10^{-4}	1.10×10^{-4}	3.88×10^{-05}	1.05×10^{-4}
As	2.68×10^{-4}	7.37×10^{-4}	1.09×10^{-4}	4.06×10^{-05}	1.08×10^{-4}
Ni	2.81×10^{-4}	1.39×10^{-3}	1.06×10^{-4}	4.44×10^{-5}	1.24×10^{-4}

influenced by urban development. Factor 3: point source fertiliser impact factor—marked by high concentrations of chloride (Cl) and nitrate (NO_3), suggesting an impact from agricultural practices, particularly the use of fertilisers and manure on farmlands (Zakaria et al. 2023). Factor 4: mixed mineralogical and anthropogenic factor—shows higher levels of fluoride (F), chloride (Cl), nitrate (NO_3), and sulphate (SO_4), indicating a mix of natural mineralogical processes and human influences from farming and urbanisation. Factor 5: non-point source agricultural nitrate factor—notable for its high nitrate (NO_3) concentration, pointing to intense agricultural practices, especially the use of nitrogen-based fertilisers (Zakaria et al. 2023).

Percentage contribution of species Table 4 shows that the contributions of different species to these factors vary, highlighting the dominant processes or sources influencing the groundwater chemistry. Factor 1 contributes significantly (51 to 61%) to pH, EC, HCO_3, Na, K, and Ca, underscoring the influence of the area's natural geological composition. Factor 2, despite lower overall contributions, is particularly influential for Fe (92.7%) and Ni (71.3%), suggesting an impact from specific urban sources. Factor 3 is dominant for phosphate (PO_4) at 90.61%, indicating a strong link to agricultural runoff. Factor 4 primarily impacts fluoride (F) at 95.5% and sulphate (SO_4) at 59.2%, reflecting the influence of mineral deposits and possibly certain types of rocks. Factor 5 significantly influences nitrate (NO_3) at 89.2%, aligning with the intensive use of agricultural fertilisers.

Table 4 Relative contribution of groundwater quality parameters across five factors in PMF Base Run #14

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	50.0	0.93	23.1	6.27	19.7
EC	51.9	4.51	17.1	5.95	20.5
HCO_3^-	58.8	5.08	15.6	2.09	18.4
Na^+	60.9	5.25	16.1	2.42	15.3
K^+	62.7	0.42	24.6	12.3	0.00
Ca^{2+}	51.4	4.02	15.6	5.24	23.7
Mg^{2+}	37.0	7.00	16.1	0.00	39.9
F^-	0.45	3.39	0.00	95.5	0.70
Cl^-	3.42	4.47	53.3	24.2	14.7
NO_3^-	1.72	0.00	1.41	7.63	89.2
PO_4^{3-}	5.45	1.56	90.6	2.38	0.00
SO_4^{2-}	0.94	1.60	5.21	59.2	33.1
Fe	4.06	92.7	0.00	0.53	2.73
Pb	12.7	74.5	4.83	2.22	5.75
Cd	25.1	50.3	10.7	3.76	10.2
As	21.2	58.4	8.63	3.22	8.57
Ni	14.5	71.3	5.49	2.29	6.40

Table 5 Proportional contribution of groundwater quality parameters to each factor in PMF Base Run #14

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	0.81	0.17	1.17	1.07	0.84
EC	51.3	51.6	53.2	62.4	53.7
HCO_3^-	34.3	34.3	28.7	12.9	28.5
Na^+	8.11	8.08	6.75	3.42	5.41
K^+	1.07	0.08	1.32	2.24	0
Ca^{2+}	4.10	3.71	3.93	4.44	5.02
Mg^{2+}	0.17	0.38	0.24	0	0.50
F^-	0	0.03	0	0.72	0.001
Cl^-	0.09	1.30	4.24	6.48	0.98
NO_3^-	0.03	0	0.08	1.53	4.47
PO_4^{3-}	0.004	0.01	0.21	0.02	0
SO_4^{2-}	0.007	0.14	0.12	4.72	0.66
Fe	0.0008	0.20	0	0.001	0.001
Pb	0.0001	0.005	0.0001	0.0001	0.0001
Cd	0.0001	0.001	0.0001	0.0001	0.0001
As	0.0001	0.002	0.0001	0.0001	0.0001
Ni	0.0001	0.004	0.0001	0.0001	0.0001

Percentage contribution to factor total Each factor's total contribution is defined by varying levels of specific constituents, highlighting different influences on the water's salinity and quality (Table 5). Factor 1 is characterised by high contributions of EC (51.3%) and HCO_3 (34.3%), indicative of natural mineral dissolution processes. Factor 2 shows similar dominance of EC and HCO_3, suggesting a consistent geological influence. Factor 3 continues to be dominated by EC (53.2%), but with an increased chloride (Cl) contribution (4.24%), possibly indicating varied sources of pollution. Factor 4 is marked by higher concentrations of EC (62.4%) and Cl (6.48%), suggesting stronger pollution influences, possibly from both geological and anthropogenic activities. Factor 5 shows significant EC (53.7%) and HCO_3 (28.5%), with a notable rise in nitrate (NO_3^-) (4.47%), aligning with agricultural impacts. Other constituents like sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and trace elements also contribute across factors, but to a lesser extent compared to the dominant species. pH levels, while consistent, contribute less significantly across all factors, reflecting the influence of both natural and anthropogenic activities on the water chemistry in the Lower Anayari Catchment area.

APCS-MLR receptor

The correlation matrix helps determine the association between variables and help to reveal key observations (Mu et al. 2023; Yu et al. 2022; Li et al. 2021). The result of the Spearman correlation shown in Fig. 4 indicated that pH showed a very low correlation with most of the parameters

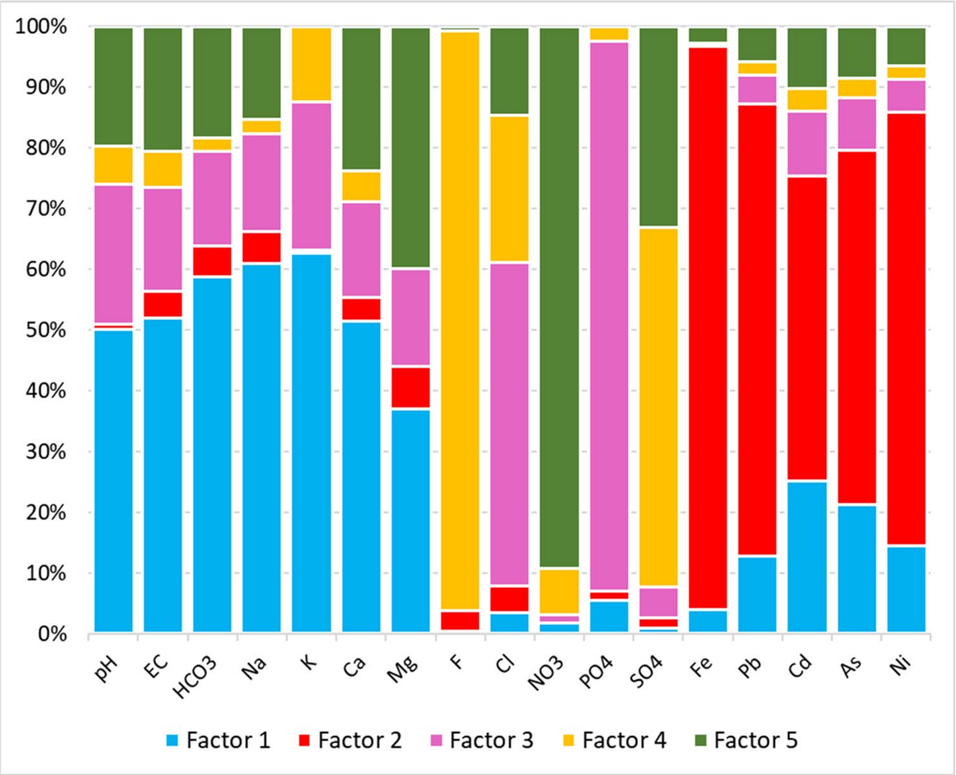


Fig. 4 Correlation matrix heatmap showing the interrelationships between various water quality parameters (pH, EC, ions, and heavy metals) in the Lower Anayari Catchment groundwater samples, with the colour intensity and circle size representing the strength and nature of the correlation (blue for positive and red for negative)

except for a moderate negative correlation with calcium (Ca) and a moderate positive correlation with bicarbonate (HCO_3) and magnesium (Mg). Electrical conductivity (EC) had a strong positive correlation with HCO_3, sodium (Na), and especially with magnesium (Mg), indicating that these ions are significant contributors to the conductivity of the groundwater and hence its salinity (Fig. 4). A very high positive correlation was observed between HCO_3 and Na, suggesting a commonality in their source or geochemical processes affecting their concentrations. Potassium (K) showed a moderate correlation with calcium (Ca) and a low to moderate correlation with other ions, suggesting a lesser role in the pollution process or a different source/pathway. Calcium (Ca) exhibited a strong positive correlation with magnesium (Mg), which might indicate the dissolution of minerals such as dolomite or calcite affecting the groundwater composition (Fig. 4). Fluoride (F) showed a moderate positive correlation with chloride (Cl) and nitrate (NO_3), which could imply anthropogenic pollution sources affecting its levels. Chloride (Cl) showed a strong negative correlation with nitrate (NO_3), indicating that their sources or the processes affecting their concentrations will likely differ. Nitrate (NO_3) had a moderate negative correlation with phosphate (PO_4) and sulphate (SO_4), suggesting different sources or processes, such as agricultural runoff versus industrial discharges. The heavy metals, iron (Fe), lead (Pb), cadmium (Cd), arsenic (As), and nickel (Ni) all showed very high positive correlations with one another, which might indicate a common source, potentially from anthropogenic activities or natural mineralisation processes. The correlations of EC with Fe, Pb, Cd, As, and Ni were moderate, suggesting that while these elements contribute to the overall groundwater chemistry, they are not the most dominant factors in the pollution process.

The PCA extracted four principal components (PCs) with eigenvalues greater than 1, explaining a cumulative variance of 73.8% (Table 6). The first principal component (PC1) accounted for 33.3% of the total variance and was strongly influenced by Fe, Pb, Cd, As, Ni, and EC, indicating a significant impact of these parameters on groundwater quality. The second principal component (PC2), explaining 20.5% of the variance, was predominantly influenced by pH, EC, HCO_3, Na, K, and Ca, suggesting a combined effect of these variables on pollution. Notably, PC3, which accounted for 11.9% of the total variance, was characterised mainly by high NO_3, PO_4, and SO_4 loadings. This component's dominance by nutrients and sulphate implies potential anthropogenic sources impacting the groundwater chemistry. The fourth principal component (PC4), contributing to 7.97% of the variance, was significantly associated with PO_4, F, and Cl, indicating additional factors influencing the groundwater salinity.

In Table 7, the pH level, crucial for indicating groundwater's acidic or basic nature, remains largely unaffected by identified factors, with 98.8% of its variance attributed to unidentified sources. This suggests that the pH of groundwater in the LAC is influenced by components or processes not captured within the scope of the current analysis. The EC was found

Table 6 Principal component analysis of groundwater quality variables in the Lower Anayari Catchment

Variables	Principal component			
	1	2	3	4
pH	0.35	0.54	−0.11	0.34
EC	0.65	0.66	0.06	0.00
HCO_3^-	0.60	0.62	−0.20	−0.35
Na^+	0.46	0.56	−0.43	−0.33
K^+	0.14	0.62	−0.08	0.47
Ca^{2+}	0.62	0.54	0.12	−0.02
Mg^{2+}	0.44	0.44	0.15	−0.05
F^-	0.20	0.04	0.42	0.47
Cl^-	0.12	0.16	−0.71	0.36
NO_3^-	0.05	0.22	0.72	0.16
PO_4^{3-}	−0.03	−0.24	−0.42	0.62
SO_4^{2-}	−0.04	0.37	0.60	0.12
Fe	0.89	−0.42	0.02	−0.01
Pb	0.89	−0.42	0.04	0.08
Cd	0.88	−0.43	0.06	0.03
As	0.90	−0.42	0.04	0.04
Ni	0.85	−0.45	0.03	−0.04
Eigenvalue	5.66	3.49	2.03	1.35
% of Variance	33.32	20.53	11.94	7.97
Cumulative %	33.32	53.85	65.79	73.75

to be significantly influenced by factor 2, with a lesser but notable contribution from factor 1. This indicates a substantial anthropogenic influence, possibly from agricultural runoff. Bicarbonate (HCO_3) ions are primarily affected by factor 1. Sodium (Na) and potassium (K) showed diverse influences, with factors 3 and 4 being the most influential, respectively. Calcium (Ca) and magnesium (Mg), with factor 2 having the most considerable impact on Ca and factor 1 on Mg, suggesting a link to geological features and human activities. Fluoride (F) was found to be predominantly influenced by factor 4, hinting at a distinctive geochemical interaction or pollution source. Chloride (Cl) levels show a significant impact from factor 3, while nitrate (NO_3) is highly influenced by factors 2 and 3. Sources of phosphate (PO_4), sulphate (SO4), and the heavy metals—iron (Fe), lead (Pb), cadmium (Cd), arsenic (As), and nickel (Ni) in groundwater—are majorly anthropogenic, as evidenced by the high percentages attributed to factor 1, with Fe and Pb being primarily influenced by it, and Cd displaying a notable 65.8% impact from this factor. This could indicate some human-related contamination events.

Integrated analysis

The comprehensive analysis of isotopic and statistical data in the study of groundwater chemistry reveals a multifaceted narrative (Mu et al. 2023; Asare et al. 2022; Yu et al. 2022). Isotopic data, particularly $\delta^{18}O$, alongside hierarchical cluster analysis, delineates distinct groundwater clusters, each with unique isotopic signatures and electrical conductivity (EC) levels, suggesting variations in groundwater sources and mineralisation processes. The positive matrix factorization (PMF) (Fig. 5) analysis further enhances this understanding by highlighting the influence of both natural geological factors and

Table 7 PCA-APCS-MLR model results for groundwater quality parameters in the Lower Anayari Catchment

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Unidentified sources	Observed mean	Predicted mean	Predicted/observed	R^2	*p-value*
pH	0	0	0.90	0.30	98.8	6.89 ± 0.24	6.89 ± 0.06	0.95	0.05	0.75
EC	3.80	17.3	0.10	1.20	77.5	429 ± 111	429.40 ± 103	0.94	0.85	4.20×10^{-14}
HCO_3^-	9.80	5.50	1.60	4.90	78.2	261 ± 85.0	261.14 ± 80.8	0.93	0.90	$<2.2\times10^{-16}$
Na^+	2.10	2.70	8.00	10.4	76.8	63.0 ± 26.3	63.03 ± 23.9	0.81	0.83	7.12×10^{-13}
K^+	0.20	7.30	3.50	9.60	79.4	9.00 ± 3.96	8.97 ± 3.31	0.89	0.70	1.18×10^{-08}
Ca^{2+}	4.20	14.8	1.20	0.50	79.3	35.6 ± 9.05	35.60 ± 6.99	0.87	0.60	1.51×10^{-06}
Mg^{2+}	11.4	6.30	0.90	6.40	75.1	2.58 ± 1.29	2.58 ± 0.84	0.81	0.42	0.0007
F^-	2.70	0.10	18.1	56.6	22.5	0.50 ± 0.61	0.50 ± 0.40	0.60	0.42	0.0006
Cl^-	0.10	0.60	25.3	5.50	68.5	18.8 ± 11.8	18.77 ± 9.34	0.89	0.63	3.84×10^{-07}
NO_3^-	1.10	40.8	54.5	1.80	1.80	13.8 ± 13.2	13.82 ± 10.0	0.91	0.58	2.76×10^{-06}
PO_4^{3-}	3.30	9.70	4.20	20.5	62.3	0.39 ± 0.60	0.386 ± 0.45	0.56	0.55	9.58×10^{-06}
SO_4^{2-}	3.00	6.50	36.1	30.4	24.1	5.81 ± 6.62	5.81 ± 4.73	0.50	0.51	3.63×10^{-05}
Fe	31.0	30.5	9.70	1.40	27.5	0.077 ± 0.17	0.077 ± 0.17	1.08	0.98	$<2.2\times10^{-16}$
Pb	39.2	36.5	2.10	2.80	19.5	0.003 ± 0.005	0.003 ± 0.005	1.06	0.98	$<2.2\times10^{-16}$
Cd	65.8	8.40	1.30	1.20	23.3	0.001 ± 0.002	0.001 ± 0.001	0.97	0.97	$<2.2\times10^{-16}$
As	38.4	8.20	4.40	6.40	42.6	0.001 ± 0.002	0.001 ± 0.002	0.96	0.99	$<2.2\times10^{-16}$
Ni	26.5	33.3	10.7	4.60	24.9	0.002 ± 0.005	0.002 ± 0.004	0.90	0.92	$<2.2\times10^{-16}$

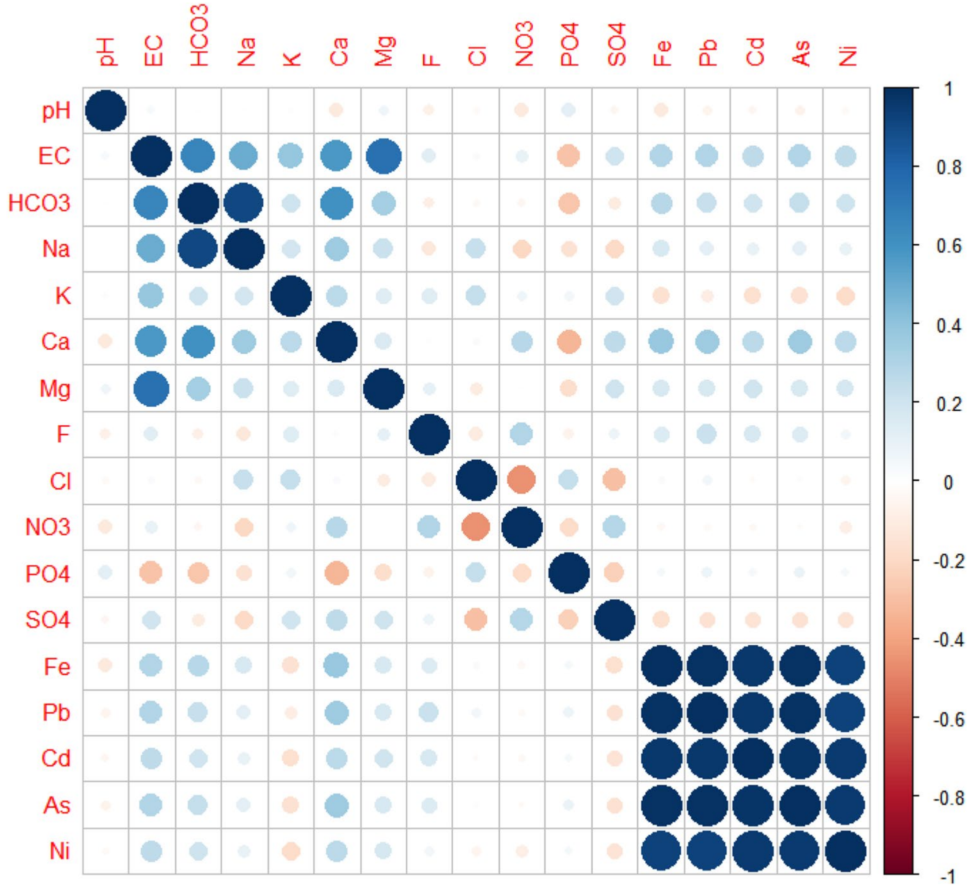


Fig. 5 Stacked bar chart from positive matrix factorization (PMF) analysis depicting the contribution of different factors to the concentration of various physicochemical parameters and heavy metals in the groundwater of the Lower Anayari Catchment

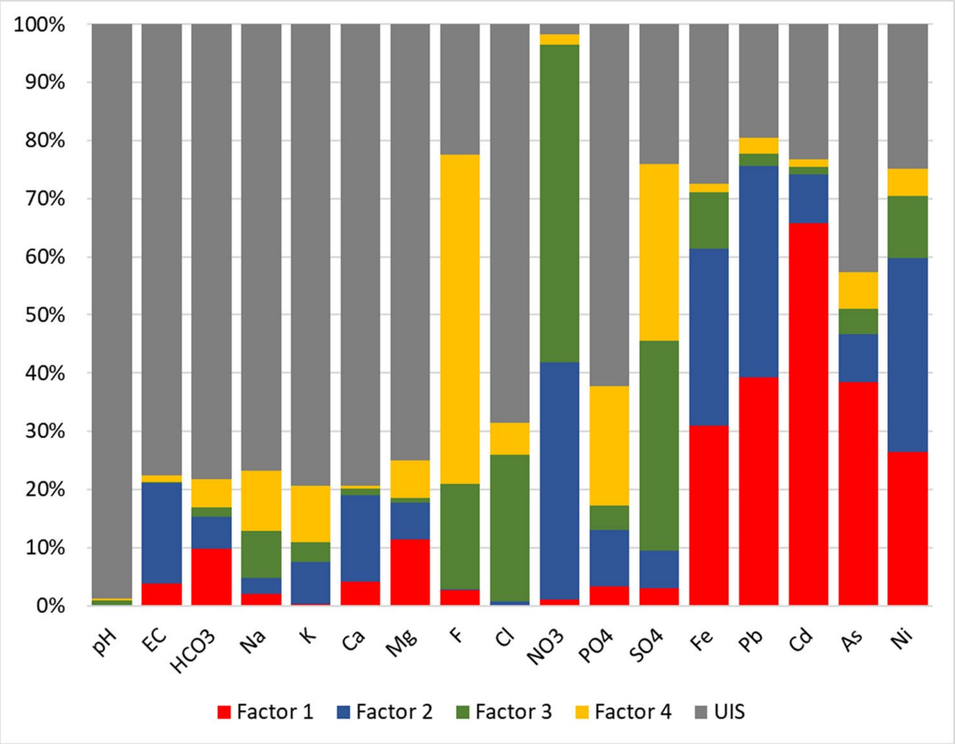
human activities. For instance, certain factors reflect the impact of geological weathering, while others indicate urbanisation and agricultural impacts, marked by specific ion concentrations. The principal component analysis (PCA), complemented by absolute principal component scores (APCS) and multiple linear regression (MLR) shown in Fig. 6, provides deeper insight, uncovering strong correlations between EC and various ions, and identifying principal components that signify the dominance of heavy metals and EC, suggesting anthropogenic influences. Together, these methods integrate to paint a detailed picture of groundwater chemistry, influenced by a complex interplay of natural processes and human interventions, and underscore the dynamic balance between environmental factors and anthropogenic activities in shaping groundwater quality.

Discussion

Groundwater pollution characterisation

The groundwater pollution in the LAC reveals a complex interplay of geochemical processes influenced by the area's geological characteristics, including the presence of biotite granitoid and volcanic flow/subvolcanic rocks. Variations in $\delta^{18}O$ and EC across the clusters indicate distinct groundwater sources and mineralisation mechanisms. These geological formations, through chemical weathering, faulting, and fracturing, appear to influence the geochemical signatures observed. The data suggests a significant impact of natural geological processes, such as interactions with biotite granitoid and volcanic materials, as well as anthropogenic activities on groundwater quality, reflecting the catchment's hydrogeological diversity and the on-going environmental challenges. The findings from the LAC underscore the intricate relationship between groundwater chemistry and the underlying geological framework, particularly the influence of biotite granitoid and volcanic flow/subvolcanic rocks. The distinct $\delta^{18}O$ and EC values observed across the clusters suggest varying degrees of mineralisation. The lower EC and $\delta^{18}O$ values in cluster 1 might reflect a lesser influence of salinisation or anthropogenic activities, while the higher values in clusters 2 and 3 suggest increased mineralisation, potentially due to deeper groundwater interactions with

Fig. 6 Proportional contributions of identified factors from PCA-APCS-MLR analysis to the concentrations of various water quality parameters and contaminants in the Lower Anayari Catchment, with UIS representing the unidentified source information



the biotite granitoid and volcanic rocks. Surface activities such as agriculture, as indicated by nitrate concentrations, could also exacerbate these variations. The impact of the geology, including biotite granitoid and volcanic flow/subvolcanic rocks from the Birimian Supergroup, on groundwater mineralisation is significant. This is evident from factor 1's high concentrations of EC, HCO^{3-}, Na, Ca, and Mg, which reflect the deep weathering processes affecting the groundwater's mineral content. This points to natural geological processes like silicate weathering and dissolution of silicate minerals as key contributors to groundwater salinity (Yidana et al. 2020). Factor 2's influence, characterised by elevated levels of iron (Fe) and nickel (Ni), points towards the significant impact of urbanisation on groundwater chemistry (Ullah et al. 2022), likely stemming contributions from local motorcycle repair shops, which are prevalent in the study area. These shops, through the handling of metal parts and the use of various chemicals for cleaning and maintenance, could be a source of Fe and Ni contamination. Factors 3 and 5, with high concentrations of agricultural markers like NO_3 and PO_4, indicate the profound impact of farming practices, particularly fertiliser and manure use, on groundwater quality (Zakaria et al. 2023). Factor 4, characterised by a mix of F, Cl, NO_3, and SO_4, suggests a combination of natural mineralogical processes and human influences, including agricultural runoff and urban pollution. In the Lower Anayari Catchment, groundwater pollution emerges as a multifaceted phenomenon shaped by the region's geological backdrop and intensified by human activities. The Birimian Supergroup's geological influence is evident in the water's mineral composition, reflecting natural processes like silicate weathering. Concurrently, agricultural practices and urban development imprint their signatures, altering the groundwater's chemical profile.

Additionally, the PCA results corroborate these insights. The first principal component (PC1) highlights the combined influence of natural mineralisation and anthropogenic activities (Abdul-Wahab et al. 2022), while the second (PC2) emphasises natural geochemical processes in pollution. Notably, PC3's dominance by nutrients and sulphate points to anthropogenic sources, aligning with the agricultural activities in the catchment. The groundwater pollution in the LAC is significantly impacted by the region's distinctive geological and hydrogeological contexts. The area's geology is characterised by the prevalence of biotite granitoid and volcanic flow/subvolcanic rocks from the Birimian Supergroup, which are associated with profound weathering processes. These geological features, noted for their typically low porosity and permeability, contribute to the unique geochemical composition of the groundwater in LAC. This underpins the specific mineralisation patterns observed in the groundwater, indicative of the underlying geology's influence on water quality. The strong positive correlations of electrical conductivity (EC) with bicarbonate (HCO_3), sodium (Na), and magnesium (Mg) suggest a significant role of mineral dissolution, particularly silicate weathering, in contributing to groundwater salinity. The moderate positive correlation between fluoride (F) and chloride (Cl) with nitrate (NO_3) indicates anthropogenic influences, potentially from agricultural practices like fertiliser use, echoing the region's reliance on agriculture, while the presence of volcanic rocks and the deep weathering characteristic of the Birimian Supergroup play a crucial role in mineral dissolution, contributing to the salinity. This natural process is compounded by anthropogenic influences, notably from agriculture, as evidenced by the correlations and PCA results.

Comparison with previous studies

The investigation into the groundwater pollution in the LAC offers insights that both align with and expand upon existing literature in the field of hydrogeology and environmental science. A pivotal aspect of the LAC findings is the influence of geological features on groundwater chemistry. This aligns with the established understanding in the field, as evidenced by studies such as Yidana et al. (2020), which highlighted the role of regional geology, particularly volcanic and sedimentary rocks, in shaping groundwater ion concentrations. The LAC's geological setting, dominated by the Birimian Supergroup, contributes significantly to the mineralisation of its groundwater. This is reminiscent of findings from similar geological settings, such as those reported by Maria et al. (2022) in volcanic regions of Indonesia, where rock-water interactions markedly influenced groundwater chemistry.

The impact of urbanisation on groundwater quality, particularly through elevated levels of heavy metals, is another point of convergence between the LAC findings and existing literature. The detection of increased Fe and Ni levels in the LAC, attributed to urban activities such as motorcycle repair shops, mirrors broader trends noted in global studies like those by Widyarsana et al. (2022), which documented automotive hazardous waste management in automotive shops of Indonesia's Metropolitan City. However, the LAC study offers a more localised perspective, highlighting specific urban activities as contamination sources, a detail often overlooked in broader studies.

Agricultural activities' impact on groundwater quality, especially concerning nitrate pollution, is a well-established narrative in environmental research. The LAC study's identification of agricultural influences on nitrate and phosphate levels is consistent with findings from global agricultural regions, as outlined in the seminal work by Gomes et al. (2023). Their study emphasised the direct link between fertiliser use and elevated nitrate levels in groundwater, a pattern also evident in the LAC. Finally, the LAC study distinguishes between natural and anthropogenic sources of groundwater pollution. This nuanced understanding echoes the findings of Sheikhy Narany et al. (2014), who explored the dual sources of pollution in groundwater. The LAC's differentiation between natural geochemical processes (factor 1) and mixed anthropogenic influences (factor 4) in pollution adds depth to the existing discourse, underscoring the complex interplay of these sources in regional contexts. The LAC study not only corroborates established findings in groundwater science but also enhances the understanding of localised impacts, such as those from specific urban activities. It reinforces the need to consider both broad global trends and region-specific factors in environmental and hydrogeological research.

Implications for groundwater management

The comprehensive study of groundwater pollution in the Lower Anayari Catchment (LAC) provides pivotal insights for groundwater management strategies, both within the catchment and in regions with similar environmental contexts. The findings emphasise the significant role of geological features, particularly the Birimian Supergroup, in influencing groundwater chemistry. This aspect aligns with the broader understanding in hydrogeology that regional geology, including volcanic and sedimentary rocks, shapes groundwater ion concentrations (Zakaria et al. 2021; Zango et al. 2021). Such knowledge is crucial for groundwater management, as it necessitates an understanding of the natural geological setting to determine the baseline quality and mineral content of groundwater. In areas with similar geological formations, this approach can predict and manage groundwater quality effectively.

Also, the study's revelation of elevated levels of heavy metals in the LAC, attributed to urban activities like motorcycle repair shops, underscores the impact of urbanisation on groundwater quality (Egbi et al. 2017). This necessitates the implementation of groundwater management strategies that focus on monitoring urban industrial runoff and waste disposal. In urban areas, it is essential to regularly monitor for heavy metals and other urban-related contaminants. Furthermore, urban planning and environmental regulations need to integrate controls on activities that potentially contaminate groundwater, ensuring proper waste disposal mechanisms and treatment facilities for industrial effluents (Egbi et al. 2017).

Furthermore, the impact of agricultural activities on groundwater quality, particularly concerning nitrate pollution, is a well-established narrative in environmental research (Bishayee et al. 2022; Li et al. 2023b; Verma et al. 2023). The LAC study's identification of agricultural influences on nitrate and phosphate levels is consistent with global trends. Groundwater management in agricultural areas should thus include strategies for sustainable farming practices. These practices might encompass the judicious use of fertilisers and the adoption of best irrigation practices to reduce runoff. Moreover, educating farmers about the implications of fertiliser use and promoting sustainable practices are vital in mitigating the impact on groundwater quality.

A critical aspect of the study is the differentiation between natural geochemical processes and anthropogenic influences on pollution. This nuanced understanding is essential for formulating effective groundwater management strategies that address both natural and human-induced factors. Such a dual approach ensures a comprehensive understanding and response, encompassing remediation techniques for anthropogenic pollution and adaptation strategies for natural geochemical influences (Zhang et al. 2020).

The LAC study's focus on the localised impacts of specific urban activities on groundwater contamination highlights the importance of region-specific assessments. Groundwater management strategies should be tailored to local conditions and activities to ensure relevance and efficacy in addressing unique regional challenges. This approach underlines the significance of understanding localised environmental impacts for effective groundwater management. Finally, the LAC study reinforces the need for an integrated approach that considers both global trends and local factors in groundwater management. This requires collaboration across various disciplines, including hydrogeologists, urban planners, agricultural experts, local communities, and policymakers. Such a comprehensive approach ensures that groundwater management strategies are well-informed, context-specific, and effective in addressing the multifaceted nature of groundwater quality issues (Jakeman et al. 2016).

Limitations and future research

The Lower Anayari Catchment (LAC) study, while providing valuable insights into groundwater pollution, exhibits certain limitations that open up areas for future research. Firstly, the study's spatial and temporal scope may limit the applicability of its findings over broader regions or longer periods, given the dynamic nature of groundwater systems. Moreover, the specific focus on the Birimian Supergroup's geological influence may not directly translate to regions with differing geological contexts. Additionally, while the study identifies key anthropogenic factors affecting groundwater, a more nuanced exploration of diverse human activities and their cumulative impacts would be beneficial.

Future research should therefore aim for extended monitoring programmes to understand the temporal and spatial dynamics of groundwater. Comparative studies across varied geological settings would elucidate broader applicability of the findings. There is also a need for in-depth analysis of the specific mechanisms through which urbanisation and agriculture affect groundwater, potentially utilising advanced analytical techniques. Moreover, understanding the implications of climate change on groundwater systems, as well as the socio-economic factors influencing groundwater use and management, would provide a more holistic perspective. Finally, exploring the effectiveness of current policies and governance structures in groundwater management could lead to more effective strategies for sustainable water use. Addressing these areas will enhance our understanding and management of groundwater resources in diverse contexts.

Conclusion

This study conducted a detailed analysis to delineate groundwater pollution in the Lower Anayari Catchment by employing δ^2H, δ^{18}O, PMF, and APCS-MLR Receptor Model. The evaluation focused on the source of groundwater pollution and ecological environment protection, resulting in the development of a comprehensive and easily explicable set of appraisal indicators. Findings from this study revealed that the highest concentration of cations detected is Na^+ (63.0 mg/L) whereas Mg^{2+} content is lowest (2.58 mg/L). For the anions and nutrients, Fl^- has the lowest concentration of 0.50 mg/L and Cl^- with highest concentration (18.7 mg/L). In regard to metalloids, Cd and As recorded lowest (0.001 mg/L) whiles Fe exhibited the highest mean concentration (0.077 mg/L). Respectively, the average values for groundwater δ^{18}O and δ^2H were − 3.64‰ and − 20.7‰ while the average values for rainwater isotopic composition were − 3.41‰ for δ^{18}O and − 17.4‰ for δ^2H. The study revealed that the groundwater quality in LAC is intricately influenced by both natural geological features and anthropogenic activities. It is also believed that the major contributor to the mineralisation of groundwater in the study area is due to the presence of synvolcanic intrusives like biotite granitoid and volcanic rocks from the Birimian Supergroup, undergoing deep weathering processes. Local motorcycle repair shops may be the primary source contributing to elevated levels of iron (Fe) and nickel (Ni) discharging into groundwater in the area. Moreover, the influence of agricultural practices, especially the use of fertilisers and manure, is evident from the high concentrations of nitrate (NO_3) and phosphate (PO_4), which align with global findings on agricultural impacts on groundwater. By understanding groundwater pollution in the study area, it will aid in decision-makers in formulating rational development and utilisation policies, enhancing the quality and efficiency use of groundwater resources. Furthermore, it eases the identification of geological environmental risks, thereby enhancing environmental protection competences.

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Author contribution Dickson Abdul-Wahab and Ebenezer Aquisman Asare conceived the study and carried out the design of the experiment. Dickson Abdul-Wahab carried out the sample preparation and analysis. Dickson Abdul-Wahab and Ebenezer Aquisman Asare assessed the data, and Dickson Abdul-Wahab, Ebenezer Aquisman Asare, Rafeah Wahi, Zainab Ngaini, Nana Ama Browne Klutse, and Anita Asamoah helped to draft and edited the manuscript. The author(s) read and approved the final manuscript.

Data availability All data generated or analysed during this study are included in this paper.

Declarations

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