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HYDROGEOLOGY

Statistical approaches for the identification of the origin mineralization groundwaters: case of the Naama Region, Far West-Algeria

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ABSTRACT

Understanding the processes controlling groundwater mineralization is critical for preserving its quality and ensuring sustainable resource management, especially in regions like Naama, Algeria, which rely exclusively on groundwater. This resource faces severe overexploitation and high salinity due to climatic factors and increasing industrial, agricultural, and domestic demands, posing significant challenges to its long-term usability. Hydrochemical analyses, including graphical methods and multivariate statistical tools, were employed to investigate the groundwater chemistry and mechanisms influencing mineralization in the Naama region. The results revealed a relatively homogeneous distribution of groundwater samples, categorized into three hydrochemical groups. These groups are primarily dominated by calcium and magnesium chloride and sulfate waters, influenced by the geological characteristics of the region, such as gypsum-saline formations of the Upper Cretaceous and Triassic clay-gypsum-saline diapirs, and further impacted by inverse ion exchange processes. Group 1 is characterized by higher proportions of calcium and magnesium bicarbonate waters due to the dominance of carbonate formations from the Early Jurassic or Miocene, benefiting from more dynamic recharge zones. Groups 2 and 3 exhibit similar chemical compositions, but Group 3 is distinct for its restricted recharge zones and carbonate formations, leading to the emergence of calcium and magnesium bicarbonate waters. Recharge areas associated with carbonate formations were also vulnerable to anthropogenic pollution. These findings highlight the importance of implementing strict protection measures for sensitive recharge zones to ensure the preservation of this vital resource in the face of increasing environmental and human pressures.

Keywords: Naama aquifers; Mineralization; Multivariate statistical analysis; Hydrochemistry; Pollution.

Enfoques estadísticos para la identificación del origen de las aguas subterráneas de mineralización: caso de la región Naama, extremo oeste de Argelia

RESUMEN

Comprender los procesos que controlan la mineralización de las aguas subterráneas es crucial para preservar su calidad y garantizar una gestión sostenible del recurso, especialmente en regiones como Naama, Argelia, que dependen exclusivamente de este recurso. Las aguas subterráneas en esta región enfrentan una grave sobreexplotación y alta salinidad debido a factores climáticos y al aumento de la demanda industrial, agrícola y doméstica, lo que plantea importantes desafíos para su uso a largo plazo. En este trabajo se realizaron análisis hidroquímicos, incluidos métodos gráficos y herramientas estadísticas multivariantes, para investigar la química de las aguas subterráneas y los mecanismos que influyen en su mineralización en la región de Naama. Los resultados revelaron una distribución relativamente homogénea de las muestras, clasificadas en tres grupos hidroquímicos. Estos grupos están dominados principalmente por aguas de cloruros y sulfatos de calcio y magnesio, influenciadas por las características geológicas de la región, como las formaciones gipso-salinas del Cretácico Superior y los diapiros arcillo-gipso-salinos del Triásico, y afectadas además por procesos de intercambio iónico inverso. El Grupo 1 se caracteriza por una mayor proporción de aguas bicarbonatadas de calcio y magnesio debido al predominio de formaciones carbonatadas del Jurásico Temprano o del Mioceno, que se benefician de zonas de recarga más dinámicas. Los Grupos 2 y 3 muestran composiciones químicas similares, pero el Grupo 3 se distingue por sus zonas de recarga más restringidas y las formaciones carbonatadas, lo que conduce a la aparición de aguas bicarbonatadas de calcio y magnesio. También se encontró que las áreas de recarga asociadas con formaciones carbonatadas son vulnerables a la contaminación antropogénica. Estos hallazgos resaltan la importancia de implementar estrictas medidas de protección para las zonas de recarga sensibles, con el fin de garantizar la preservación de este recurso vital frente a las crecientes presiones ambientales y humanas.

Palabras claves: Acuíferos de Naama; Mineralización; Análisis estadístico multivariante; Hidroquímica; Contaminación

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1. Introduction

Water has always been considered a renewable and inexhaustible source. Nowadays, several countries are affected by the depletion of their water resources due to climatic conditions and increased demand, an inevitable result of population growth and socio-economic development (Hosni et al., 2024; Milano et al., 2013). With an arid climate and the absence of surface water mobilization works, the region of Naama is mainly supplied with available groundwater by the region's multilayer aquifer system (Derdour, Jodar-Abellan, Pardo, Ghoneim, & Hussein, 2022). This resource is in high demand to meet the growing need for water. Indeed, overexploitation and the high salinity rate in these waters pose various quantitative and qualitative problems, which could make the reserves progressively unexploitable. Effective and sustainable management of water resources requires an excellent knowledge of their availability, quality and spatial variability.

The physico-chemical parameters contained in groundwater offer the possibility of identifying the origin of the mineralization of the different aquifers and the origin and degree of pollution. This has prompted several researchers (Liu, Sun, Xu, & Xu, 2018; Shi, Xie, Bu, Li, & Zhou, 2018; Wang, Shi, Wang, & Liu, 2020; Wu et al., 2019) to develop statistical methods aimed at identifying various types of water-rock interactions, quantifying their contributions to the chemical composition of groundwater, and creating models for accurately determining water sources.

Various studies have assessed the groundwater quality in the Wilaya of Naama, Algeria, using different methodologies and parameters. For instance, Lachache et al. (2023) investigated the hydrogeochemical processes of groundwater in the Naama watershed, identifying three major hydrochemical types and their spatial distribution. Another study by Ali and Mountassir (2018) utilized GIS and the Water Quality Index (WQI) to evaluate groundwater quality, finding that 40% of the samples were excellent quality, while 60% were good. Additionally, Derdour, Jodar-Abellan, et al. (2022) proposed using machine learning algorithms to predict Water Quality Indexes at the regional scale, demonstrating high accuracy with models such as Support Vector Machine (SVM) and Ensemble Trees (ET). Furthermore, Derdour, Belam, and Chebab (2022) explored traditional irrigation systems and water harvesting methods in the oasis of Sfissifa, Ksour Mountains, highlighting the effectiveness of ancestral agricultural systems like "Tissfalt" for sustainable water management. Moreover, Hussein et al. (2024) conducted a comprehensive groundwater quality assessment and used machine learning algorithms to predict the Irrigation Water Quality Index in the Wilaya of Naama. Their study, demonstrated the efficacy of models like Support Vector Machine (SVM) and Ensemble Trees (ET) in accurately predicting water quality indexes, emphasizing the potential of advanced computational techniques in groundwater quality management. These studies highlight the importance of sustainable management and regular monitoring of groundwater resources in the region to ensure safe and reliable water supply for domestic, agricultural, and industrial purposes.

The aim of this study is to conduct a comprehensive assessment of water quality across the entire Wilaya of Naama. Utilizing a significant number of samples (123 in total), we employed both graphical tests and multivariate statistical analysis to carry out chemical analyses. Our objectives were to characterize the water quality and identify the sources of mineralization and other influencing factors. Additionally, Geographic Information System (GIS) tools were integrated to provide a critical spatial dimension, complementing the statistical techniques utilized. By combining spatial analysis with statistical methods, GIS enhanced our ability to identify and visualize patterns, relationships, and trends in groundwater quality data, offering a more comprehensive understanding of the underlying processes. This study underscores the importance of sustainable management and regular monitoring of groundwater resources in the region to ensure a safe and reliable water supply for domestic, agricultural, and industrial purposes.

2. Study Area

The wilaya of Naama is part of the southern high plains of Oran. It is situated between the UTM coordinates X: 794,969 m, Y: 3,605,533 m and X: 954,930 m, Y: 3,874,723 m in UTM Zone 30N, placing it in a transitional climate zone between the Tellien Atlas in the northern section and the Saharan Atlas in its western part. This diverse topography influences climate, hydrology, and groundwater recharge patterns (Fig.1). The climate in the region is predominantly semi-arid, characterized by mild, wet winters and hot, dry summers (Bouarfa et al., 2022). Average annual precipitation ranges between 200 mm and 400 mm, depending on altitude and proximity to the mountain ranges, with significant variations due to orographic effects caused by the surrounding hills and mountains (Moussaoui, Derdour, Benaradj, & Hosni, 2024; Moussaoui et al., 2023). These climatic patterns, coupled with the local terrain, influence water infiltration and runoff, directly impacting groundwater quality and recharge (Derdour et al., 2022).

Naama is home to a vast multilayer aquifer system, which is a critical water resource for the region's agricultural and domestic use. The combination of this complex climate, diverse geography, and aquifer system highlights the importance of sustainable water management strategies in the region. With challenges such as climate variability, desertification, and urban expansion, the Wilaya of Naama emphasizes the need to maintain groundwater recharge rates and protect water quality for sustainable use in agriculture, drinking, and ecosystem support.

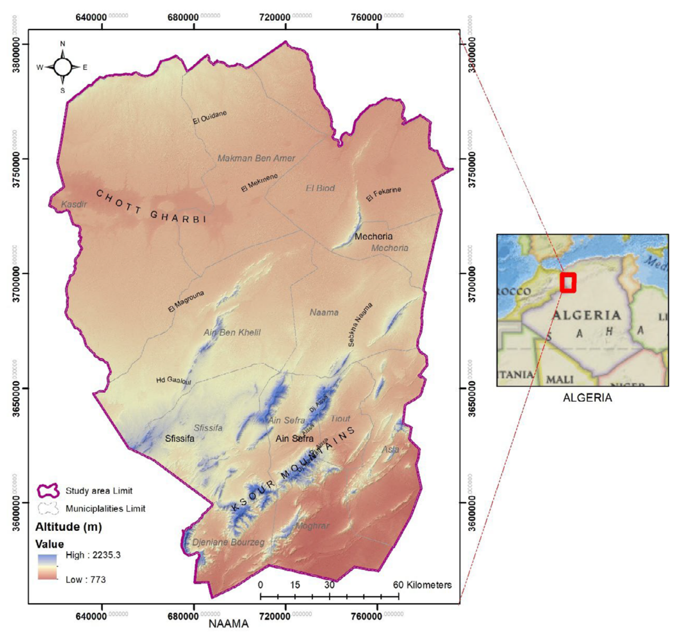

Figure 1. Study area

2.1. Geological and Hydrogeological Setting.

The geological and hydrogeological settings of the Naama region reveal a complex and dynamic history influenced by geological events and processes. According to Meddah, Bertrand, Seddiki, and Tabeliouna (2017), Benyoucef et al. (2017), Mekki et al. (2023), and Benadla, Marok, Soulimane, and Reolid (2023), the region's litho-stratigraphy includes prominent Triassic outcrops associated with diapirs and Upper Triassic tholeiitic volcanism, Lower Jurassic marine carbonates transitioning to marl, and the Ksour deltaic complex formations from the Middle and Upper Jurassic periods (Fig.2). The Lower Cretaceous consists of extensive fluvial deposits, while the Upper Cretaceous features gypsum clays, marls, limestones, and marl limestones from the Cenomano-Turonian age. Post-Turonian deposits and Mio-Pliocene clayey breccias with calcareous elements, marl, and marl-limestone formations further shape the region's geological framework. Quaternary materials, mainly alluvial deposits and sands forming dunes, highlight recent geological activity.

Regarding groundwater resources, Rahmani, Bouanani, Kacemi, and Hamed (2017) identified two potential aquifer systems through geophysical investigations: the Upper Jurassic sandstones and the massive Lower Cretaceous sandstones. The Upper Jurassic sandstones are typically exposed at the foothills of Djebels Aissa, Mekter, Hirech, and Morhad. The Lower Cretaceous sandstones, comprising the Tiloula Formation with clayey intercalations and the massive Tiout Formation with interstitial and fracture porosity, are semi-confined due to interbedded reddish clay layers. The primary recharge of these aquifers is influenced by drainage mechanisms, emphasizing the need for understanding hydrogeological dynamics for sustainable water resource management. The spatial distribution of geological formations varies across the region, with the Lower Jurassic being the most extensive, followed by the Lower Cretaceous, Quaternary deposits, and other formations covering smaller areas. This detailed geological and hydrogeological framework underscores the significance of tectonic shifts, sedimentation, and climatic changes in shaping the Naama region, highlighting the crucial interplay between geological formations and recharge mechanisms in managing groundwater resources sustainably.

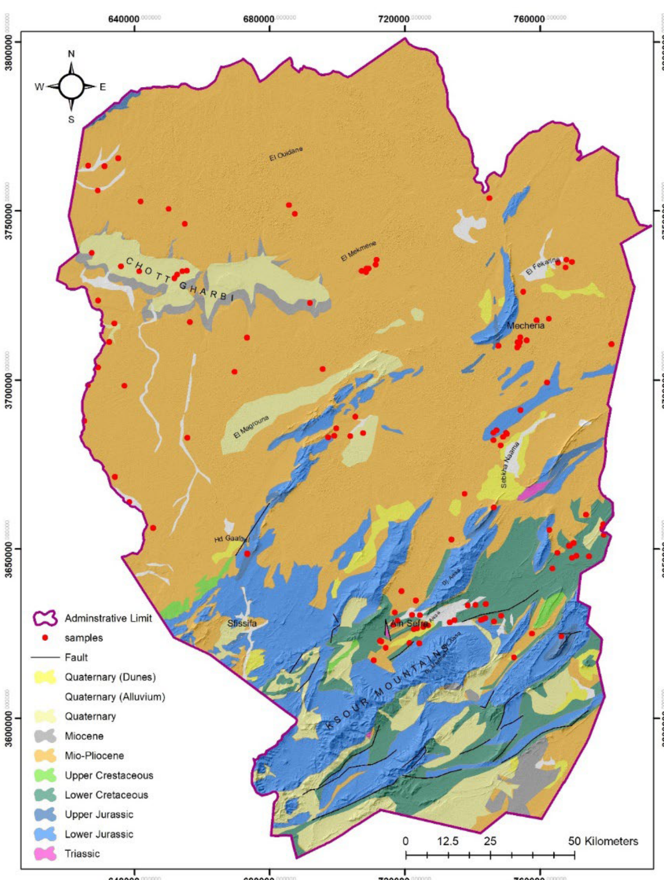

Figure 2. Geological Map of the Study Area with Water Sampling Locations

2.2. Land Cover Land Use Setting.

Land use and land cover significantly influence groundwater recharge and quality via runoff, infiltration, and the interplay between natural and artificial environmental processes (Fig.3). The distribution of various land cover types in the Wilaya of Naama greatly affects groundwater quality. Degraded steppes, covering 13,425.52 km² or 44.83% of the total area, can adversely affect groundwater quality through soil erosion, diminished infiltration, and sediment transport into aquifers, resulting in contamination hazards. Likewise, significantly degraded steppes (11,715.16 km², or 39.12%) might interfere with natural water cycles, diminish recharge rates, and facilitate the infiltration of contaminants into groundwater sources. Dunes (1,699 km², 5.67%) and halophytes (82 km², 0.27%) can enhance localized groundwater recharge by improving infiltration in their areas; nevertheless, an overabundance of salt-tolerant species in halophytes may influence groundwater salinity. Stipa Tenasissima (2,910.76 km², 9.72%) and Psammphytes (513.08 km², 1.71%) are Indigenous vegetation types that enhance soil structure, water retention and minimize runoff, hence facilitating natural recharge processes and enhancing the quality of infiltrated water. Forests (1,385.48 km², 4.63%) function as natural water filtration systems, diminishing impurities that reach aquifers by capturing silt and eliminating pollutants via vegetative mechanisms. These wooded regions are essential for sustaining the natural equilibrium of groundwater replenishment and safeguarding water quality. Nonetheless, agricultural development, urbanization, and deforestation will diminish these natural recharge zones, exacerbating the quality of accessible groundwater due to heightened pollution threats. The correlation between these LULC patterns and groundwater quality underscores the necessity for sustainable management measures to mitigate degradation, enhance natural infiltration processes, and safeguard vegetative buffers that facilitate clean and sustainable groundwater recharge.

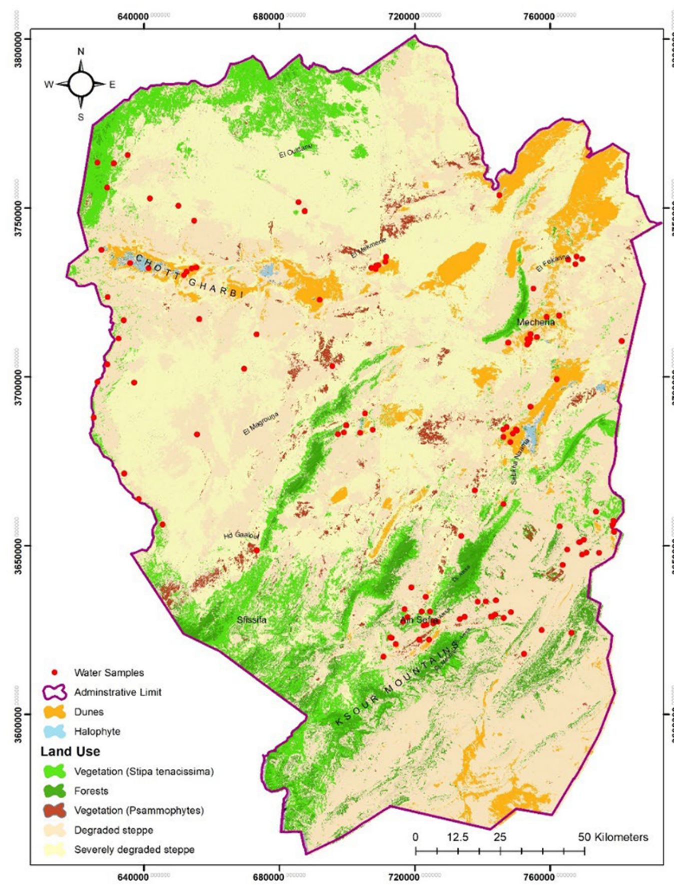

Figure 3. Land Use and Land Cover (LULC) Map of the Study Area with Water Sampling Locations

3. Materials and methods

3.1. Sampling and analysis.

One hundred and twenty-three (123) groundwater samples were obtained from the Directorate of Water Resources of the Wilaya of Naama. The concentrations of eight major ion types (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^- -Cl^-, SO_4^{2-} NO_3^-) were analyzed. All sample collection, preservation, and transportation were executed by certified National Water Resources Agency hydrogeologists, adhering to strict quality assurance and quality control (QA/QC) procedures. Chemical analyses were exclusively conducted in the fully accredited laboratories of this Agency, which is the sole authorized and licensed entity for conducting groundwater quality assessments in agricultural regions, as mandated by state regulatory policies.

Once all ion concentration tests were completed, the AE (analytical errors) were verified by calculating the ionic balance using the Equation 1.

$$IB\,(\%) = \frac{\left[\sum cations - \sum anions\right]}{\sum cations + \sum anions} x\,100 \qquad (1)$$

Where:

- Cations, expressed in milliequivalents per liter (meq/L), include positively charged ions such as calcium, magnesium, sodium, and potassium, contributing to the overall positive charge in water.
- Anions, also expressed in milliequivalents per liter (meq/L), include negatively charged ions like bicarbonate, carbonate, chloride, sulfate, and nitrate, which balance the total ionic charge in the water sample.

An acceptable ionic balance typically falls within ±5% for high-quality analytical data. If the balance exceeds this range, it may indicate errors in sampling, analysis, or calculation (Nordstrom, Ball, Donahoe, & Whittemore, 1989)

3.2. Graphical analytique

Hydrochemical diagrams such as Piper, Gibs, Chadha and the Hierarchical Ascending Classification (HFC) are fundamental tools in hydrogeology to decipher the origin and evolution of groundwater (Arroyo-Figueroa, Chalá, Gutiérrez-Ribon, & Quiñones-Bolaños, 2024). These graphical representations make it possible to transform complex analytical data into intuitive visualizations, revealing essential information on mineralization processes, the geochemical origin of water, water-rock interactions, and the mechanisms of recharge and evolution of aquifers. Note that the CAH diagram offers a statistical classification of samples, the Piper diagram allows to characterize the overall chemical composition, the Gibbs diagram analyzes the control mechanisms of the chemistry, while the Chadha diagram provides a detailed representation of the hydrochemical facies.

3.2.1. Hierarchical ascending classification (CAH)

Hierarchical Ascending Classification (HFC) is an effective statistical technique for the multidimensional analysis of hydrochemical data, grounded in the core principles of hierarchical clustering (Lis-Gutiérrez, Reyna-Niño, Gaitán-Angulo, Viloria, & Enrique Santander Abril, 2018). It facilitates the categorisation of water samples with analogous chemical properties by converting intricate data into a tree structure known as a dendrogram. The primary aims encompass the identification of homogeneous water families, the elucidation of similarities and differences among samples, the simplification of hydrochemical data, and the identification of common sources or processes of mineralisation. The procedure adheres to specific methodological steps: data normalisation, distance calculation between samples, hierarchical cluster creation, and graphical display. CAH provides quick processing of several variables, clear visualisation of correlations among samples, and independence from the variable count. The dendrogram's interpretation relies on the idea that each branch signifies a sample group, with the link height reflecting the degree of similarity, hence facilitating comprehension of groundwater's genesis and evolution (Bouteraa, Mebarki, Bouaicha, Nouaceur, & Laignel, 2019; Zhang et al., 2019).

3.2.2. The Piper diagram

The Piper diagram, developed by Piper (1944) is a graphical representation used to illustrate the main chemical elements and different groundwater facies. It enables the visualization of water evolution, transitioning from one facies to another through either time-spaced analyses or analyses of samples taken from various locations. This diagram proves invaluable in representing diverse analysis groups. It consists of two triangles and a diamond. The two triangles: one for cations and the other for anions are first filled, followed by the diamond. The values used are expressed in % meq/L.

3.2.3. Chadha Diagram

The Chadha Diagram, introduced by Chadha (1999), is a valuable tool for hydrochemical analysis. By plotting the sample groups on this diagram, we can describe various types of water and trace the evolution of hydrochemical processes. This diagram allows us to understand the factors that control groundwater chemistry in the study area. It provides a clear visual representation of the interactions between different chemical elements in the water. This detailed understanding helps in identifying changes over time and variations across different locations, thereby offering insights into the underlying processes affecting groundwater quality.

3.2.4. The Gibbs diagram

The Gibbs diagram, established by Gibbs (1970), has been an essential instrument for elucidating the geochemical mechanisms responsible for groundwater mineralisation. This diagram has been widely utilised in numerous studies to elucidate the determinants affecting groundwater chemistry (Marandi & Shand, 2018; Sunkari, Abu, Zango, & Wani, 2020). The Gibbs diagram is predicated on three fundamental factors: precipitation, evaporation, and water-rock interaction. These parameters are essential in ascertaining the mineralisation process of groundwater.

Gibbs' formulations are crucial for analysing the diagram:

- Gibbs I is defined as $Cl^- / (Cl^- + HCO_3^-)$
- Gibbs II is defined as $(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$ expressed in meq/L. By

examining the positions of water samples on the Gibbs diagram, researchers can deduce the prevailing geochemical processes occurring in a certain study region. This technology offers critical insights into the intricate interactions among diverse chemical constituents in groundwater, aiding in identifying the principal mechanisms influencing its chemical evolution.

3.3. Statistical analyses.

The groundwater study has evolved considerably from conventional graphical techniques to more sophisticated multivariate statistical approaches (Piper, 1944; Schoeller, 1962; Stiff Jr, 1951). These statistical methods offer more in-depth and accurate insights into the chemical composition of groundwater. Correlation analysis helps to evaluate the relationship between variables, identifying similar origins of elements and determining common control processes. Principal Component Analysis (PCA) simplifies and classifies data, identifying the most important variables and following element sources through the use of the correlation matrix and varimax rotation (Abdi & Williams, 2010; Granato, Santos, Escher, Ferreira, & Maggio, 2018; Hasan & Abdulazeez, 2021)

Since the chemical composition of groundwater is also the result of the contribution of multiple factors, the different types of water-rock interactions can be considered as factors. In contrast, the degrees of interaction can be considered as contributions. In addition, the relationship between the individual hydrochemical parameters was determined using Pearson correlation analysis. Spatial associations of groundwater were identified using R-mode factor analysis in SPSS version 24 (Imbrie, 1963). Principal component analysis (PCA) was the primary method for extracting factor analysis in R-mode and data were presented in a rotated matrix using the varimax rotation procedure (Sunkari et al., 2020). Factor analysis was performed by first calculating the correlation coefficient table (correlation matrix) for all hydrochemical parameters using R mode.

4. Results

4.1. Graphical analytic

4.1.1. Cluster Analysis.

The application of cluster analysis to the sampled water data reveals the presence of three distinct classes (Fig. 4).

- Class 1: Includes ions associated with saline and evaporitic formations, such as Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}.
- Class 2: Characterized by the presence of bicarbonates (HCO_3^-) and nitrates (NO_3^-).

- Class 3: Dominated by K^+ ions, primarily linked to evaporitic and saline formations.

Furthermore, this analysis enabled the classification of water sampling points into three distinct groups

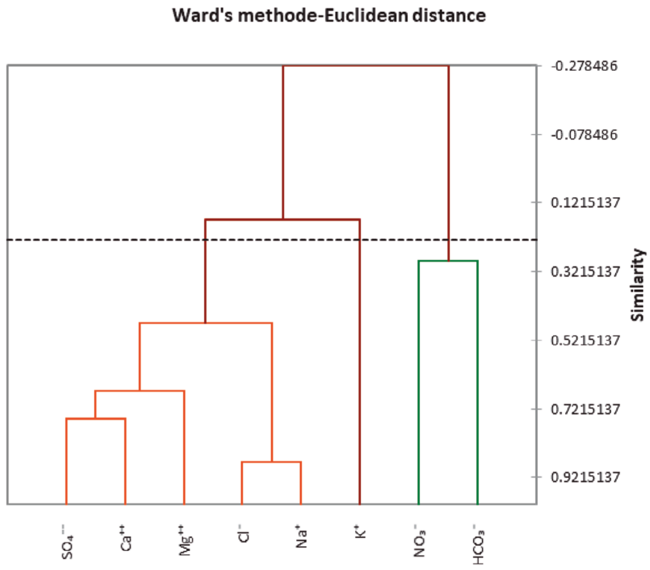

Figure 4. Hierarchical Ascending Classification (HAC) of Physico-Chemical Parameters of Sampled Water

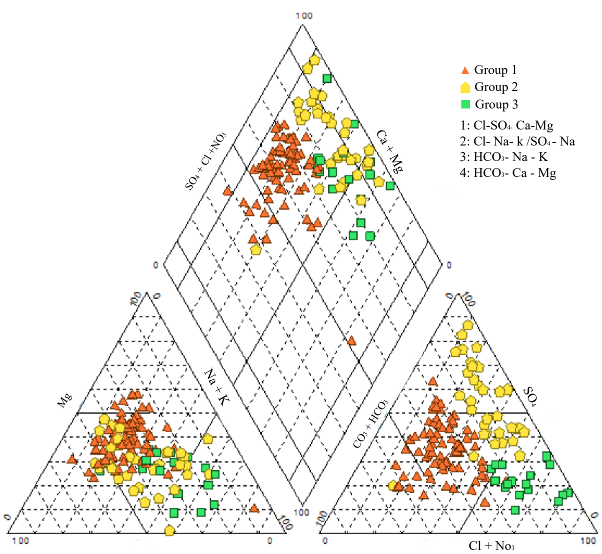

Figure 5. Piper Diagram of Groundwater in the Naama Region

4.1.2. Piper Diagram

The Piper diagram is a commonly employed tool for categorizing and illustrating the chemical composition of water samples according to their predominant ion concentrations (Fig. 5). The analysis indicates that the Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} facies is predominant, constituting 82.93% of the water samples. The groundwater in the research area predominantly contains substantial amounts of calcium, magnesium, chloride, and sulfate ions. This facies generally indicates water sources affected by processes like rock-water interactions, when minerals containing these ions dissolve into the groundwater. The subsequent most common water type, comprising 9.76% of the samples, is the Cl^--Na^++K^+ or SO_4^{2-}-Na^+ facies. This indicates a significant impact of sodium and potassium, in conjunction with chloride and sulfate, which may signify sources affected by evaporitic conditions or human activities like agricultural runoff. Finally, the Ca^{2+}-HCO_3^--Mg^{2+} sample category constitutes 7.31% of the overall total. This facies are frequently linked to groundwater that has seen considerable interaction with carbonate rocks, resulting in the breakdown of calcium and magnesium carbonates. This water typically signifies recharge zones when precipitation permeates the soil and solubilizes carbonate minerals. Plotting these results on the Piper diagram provides critical insights into the prevailing hydrochemical processes and the spatial distribution of various water types within the studied area. The prevalence of the Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} facies underscores the crucial influence of geological formations and mineral dissolution on groundwater chemistry.

4.1.3. Chadha Diagram

The Chadha diagram effectively classifies and visualizes the hydrochemical processes influencing groundwater chemistry. The data plotted on this diagram (Fig. 6) reveals several key insights:

- Field 6 (Inverse Ion Exchange Water Type - Ca-Mg-Cl/SO_4): The majority of the samples (80.48%) fall into this category, indicating that these waters are primarily of the Ca-Mg-Cl type. In this type, alkaline earth metals (Ca^{2+} and Mg^{2+}) dominate over alkali metals (Na^+ and K^+), and strong acids (Cl^- and SO_4^{2-}) outweigh weak acids (HCO_3^-). This dominance suggests significant ion exchange processes where calcium and magnesium replace sodium and potassium on mineral surfaces. The results confirm the findings of the Piper diagram, which also highlighted the prevalence of these chemical constituents.
- Field 7 (Seawater Na-Cl Type): A smaller portion of the samples (11.38%) is located in this field. This indicates that in these water samples, alkali metals (Na^+ and K^+) exceed alkaline earth metals (Ca^{2+} and Mg^{2+}), and strong acids (Cl^-) are more prevalent than weak acids. This type of water is typically influenced by seawater intrusion or evaporitic conditions, contributing to higher salinity.
- Field 5 (Ca-Mg-HCO_3 Recharge Water): The remaining samples (8.13%) are in this field, indicating waters characterized by Ca-Mg-HCO_3 composition. This suggests recharge water, where calcium and magnesium are prevalent alongside bicarbonates, pointing to fresh groundwater that has interacted with carbonate rocks and possibly undergone minimal mineralization.

The application of Chadha diagram in our study area, provides a comprehensive view of the hydrochemical processes at play, illustrating the dominance of specific ion exchange reactions and the varying influences of different water sources on the groundwater chemistry in the study area.

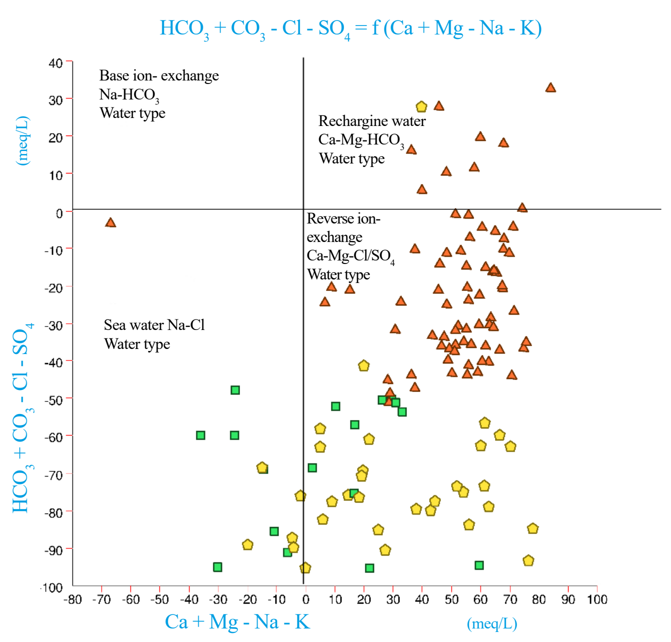

Figure 6. Chadha diagram of the Groundwater samples

4.1.4. Gibbs Diagram Analysis

The Gibbs diagrams (Fig. 7a and 7b) provide valuable insights into the study area's geochemical processes controlling groundwater mineralization. The analysis of water points on these diagrams revealed that the values for Gibbs I range from 0.09 to 0.95, and for Gibbs II, they range from 0.24 to 0.94. These variations indicate that water-rock interactions and evaporation processes primarily influence the mineralization of the region's groundwater. Gibbs I measures the ratio of chloride ions (Cl^-) to the sum of chloride and bicarbonate ions ($Cl^- + HCO_3^-$). At the same time, Gibbs II evaluates the ratio of sodium and potassium ions ($Na^+ + K^+$) to the total of sodium, potassium, and calcium ions ($Na^+ + K^+ + Ca^{2+}$). The results from these diagrams suggest that:

- Water-Rock Interaction: The interaction between water and rock is a dominant process, leading to the dissolution of minerals into the groundwater. This interaction significantly contributes to the overall mineral content of the water.
- Evaporation: Evaporation plays a crucial role, especially in regions where surface water evaporates, leaving behind higher concentrations of dissolved solids. This process further enhances the mineralization of groundwater.

Additionally, it is observed that the Total Dissolved Solids (TDS) content increases with longer contact time between water and rock. This trend indicates that extended interaction periods allow more minerals to dissolve into the groundwater, thereby elevating the TDS levels. The Gibbs diagrams effectively illustrate these processes, offering a clear understanding of the geochemical factors that govern groundwater quality in the region.

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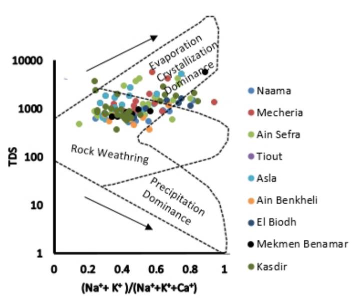

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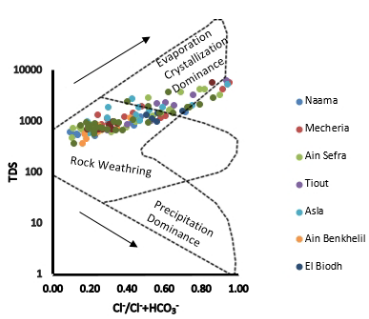

Figure 7. Gibbs diagram showing the mechanism that is most involved in Chemical control of groundwater

4.2. Statistical analysis

Descriptive analysis of the chemical elements in the Naama region highlights significant variability in their spatial distributions. The majority of the coefficients of variation exceed 50% (Table 1), indicating pronounced heterogeneity in the concentration of these elements across the study area. This heterogeneity could be attributed to a combination of geological, hydrological, and anthropogenic factors influencing the chemical composition of the waters. In contrast, bicarbonates exhibit coefficients of variation below 50%, suggesting a relatively homogeneous spatial distribution. This consistency may point to a more uniform source or process governing bicarbonate concentrations, such as carbonate rock dissolution or limited external influences compared to other chemical elements. Such findings emphasize the importance of considering spatial variability when analyzing water chemistry, as it provides insights into the underlying environmental and geochemical processes shaping the study area.

Table 1. Parameter values of the four principal water groups

Variable	Minimum	Maximum	CV
Ca^{2+}	24,00	122,00	99,42
Mg^{2+}	3,00	452,00	81,96
Na^+	5,00	277,00	126,83
K^+	1,00	261,00	229,28
Cl^-	21,00	819,00	159,64
SO_4^{2-}	53,00	370,00	110,16
HCO_3^-	3,00	529,00	25,86
NO_3^-	1,00	390,00	140,72

4.2.1. Correlation analysis.

The correlation matrix in Table 2 reveals significant relationships between groundwater quality parameters, with strong to very strong correlations observed between Ca^{2+}/Cl^- (0.761), Ca^{2+}/Mg^{2+} (0.67), Ca^{2+}/SO_4^{2-} (0.749), Mg^{2+}/Cl^- (0.693), Mg^{2+}/SO_4^{2-} (0.718), and Na^+/Cl^- (0.875). These correlations suggest that the majority of chlorides originate from the dissolution of NaCl, $CaCl_2$, and $MgCl_2$, while sulfates primarily come from evaporitic minerals like $MgSO_4$. Additionally, the matrix highlights the role of carbonate dissolution/precipitation and ion exchange processes with clay and sulfate minerals, reflected by moderate and non-significant correlations among other parameters. Interestingly, negative correlations are also present, indicating inverse relationships between certain ions. Furthermore, negative correlations between parameters such as Ca^{2+} and HCO_3^- suggest competitive interactions or different sources and processes affecting their concentrations. The correlation matrix provides a comprehensive view of the dominant geochemical processes and interactions influencing groundwater quality in the study area, emphasizing the complex interplay between various chemical constituents.

Table 2. Correlation matrix of the different parameters of groundwater quality. Values in bold indicating correlation coefficients ((Pearson (n)).

Variables	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	SO_4^{--}	HCO_3^-	NO_3^-
Ca^{++}	**1**							
Mg^{++}	**0.67**	**1**						
Na^+	**0.606**	0.597	**1**					
K^+	0.17	**0.622**	**0.518**	**1**				
Cl^-	**0.761**	**0.693**	**0.875**	0.431	**1**			
SO_4^{--}	**0.749**	**0.718**	**0.597**	0.429	0.472	**1**		
HCO_3^-	-0.23	-0.085	-0.113	0.002	-0.13	-0.278	**1**	
NO_3^-	0.051	0.217	-0.027	-0.022	0.021	0.018	0.29	**1**

4.2.2. Principal component analysis (PCA).

The Principal Component Analysis (PCA) performed on 123 water samples in the study area revealed eight variables, with the initial four factors accounting for 88.397% of the total variance, offering a comprehensive understanding of the mineralization processes in the aquifer system (Table 3). Factor 1 (F1), accounting for 50.671% of the variance, is primarily influenced by the chemical elements Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}, indicating the axis of salt and gypsiferous mineralization and highlighting the significant role of these ions in groundwater mineralization. Factor 2 (F2), accounting for 16.708% of the variance, is defined by HCO_3^- and NO_3^-, highlighting the geochemical processes of carbonate dissolution and the penetration of nitrate-rich surface water, which considerably influence the overall water chemistry. Factor 3 (F3) accounts for 11.808% of the variance and is correlated with Ca^{2+}, NO_3^-, and K^+, highlighting the effects of soil leaching and irrigation water infiltration, so reflecting the influence of agricultural practices on groundwater quality. Factor 4 (F4), representing 9.210% of the variation, encompasses Cl^-, SO_4^{2-}, HCO_3^-, Na^+, and K^+, indicating secondary mineralization processes resulting from the dissolution of sulfate and carbonate formations, further diversifying groundwater's chemical composition. The PCA results provide a comprehensive insight into the prevailing geochemical processes and mineralization mechanisms within the aquifer system, highlighting the intricate interactions among different chemical constituents.

Table 3. Eigenvalues and Contributions of variables (%): of the waters of the Naama aquifer.

Eigenvalues				
	F1	F2	F3	F4
Valeur propre	4.054	1.337	0.945	0.737
Variabilité (%)	50.671	16.708	11.808	9.210
% cumulé	50.671	67.379	79.187	**88.397**
Contributions of variables (%)				
	F1	F2	F3	F4
Ca^{++}	**17.107**	0.826	**18.323**	4.066
Mg^{++}	**18.894**	3.622	0.003	7.605
Na^+	**18.158**	0.000	2.996	**13.005**
K^+	9.115	2.427	**46.512**	**16.610**
Cl^-	**18.859**	0.033	0.021	**21.471**
SO_4^{--}	**16.543**	1.026	3.070	**12.085**
HCO_3^-	1.254	**45.955**	5.827	**17.292**
NO_3^-	0.070	**46.110**	**23.248**	7.868

5. Discussion

This study conducted in the Naama region of Algeria provides critical insights into groundwater mineralization processes, which are essential for sustainable water resource management in arid regions. Understanding the processes controlling groundwater mineralization is crucial for preserving its quality and ensuring sustainable resource management, especially in areas like Naama, which rely heavily on groundwater. The findings indicate that groundwater quality is significantly influenced by geological formations and anthropogenic activities, leading to distinct hydrochemical groups characterized by varying mineralization levels. This research enhances our understanding of local hydrogeological dynamics and offers valuable comparisons with similar conditions in other arid regions worldwide. Several parallels emerge when comparing the groundwater mineralization patterns observed in Naama with those in El Bayadh and Bechar. Both regions exhibit similar geological formations that influence groundwater chemistry. For instance, El Bayadh is characterized by a predominance of limestone and gypsum formations, contributing to high mineralization levels. A study by Derdour et al. (2023) has shown that the hydrochemical composition of groundwater in the region of Adrar is primarily influenced by evaporation and ion exchange processes, akin to those observed in Naama. Similarly, Bechar's groundwater is affected by saline deposits and evaporation, leading to increased salinity levels (Mebarki, Kendouci, & Bendida, 2024). In Tunisia, particularly in the Chott Djerad region, groundwater quality is compromised by high salinity due to similar climatic conditions and anthropogenic pressures (Kraiem, Zouari, Chkir, & Agoune, 2014). When examining anthropogenic impacts on groundwater quality, comparing the Naama region with other arid regions such as the Central Valley in California, USA, and the Atacama Desert in Chile (Burow, Jurgens, Belitz, & Dubrovsky, 2013; Herrera et al., 2018). Extensive agricultural practices in California's Central Valley have led to significant groundwater depletion and salinization (Burow et al., 2013). The reliance on irrigation has increased mineralization levels due to the leaching of salts from the soil and applying fertilizers, which can contaminate aquifers. This situation parallels the challenges faced in Naama, where agricultural demands coupled with over-extraction have led to rising salinity levels and concerns about water quality. In the Atacama Desert, mining activities have severely impacted groundwater resources (Herrera et al., 2018). Another comparable region is the Arabian Peninsula, where rapid urbanization and industrialization have led to increased water demand and subsequent over-exploitation of groundwater resources. In Saudi Arabia, for instance, excessive pumping has resulted in declining water tables and deteriorating water quality due to salinization (Al-Naeem, 2014). This mirrors the situation in Naama, where high salinity levels threaten the usability of groundwater for agricultural and domestic purposes.

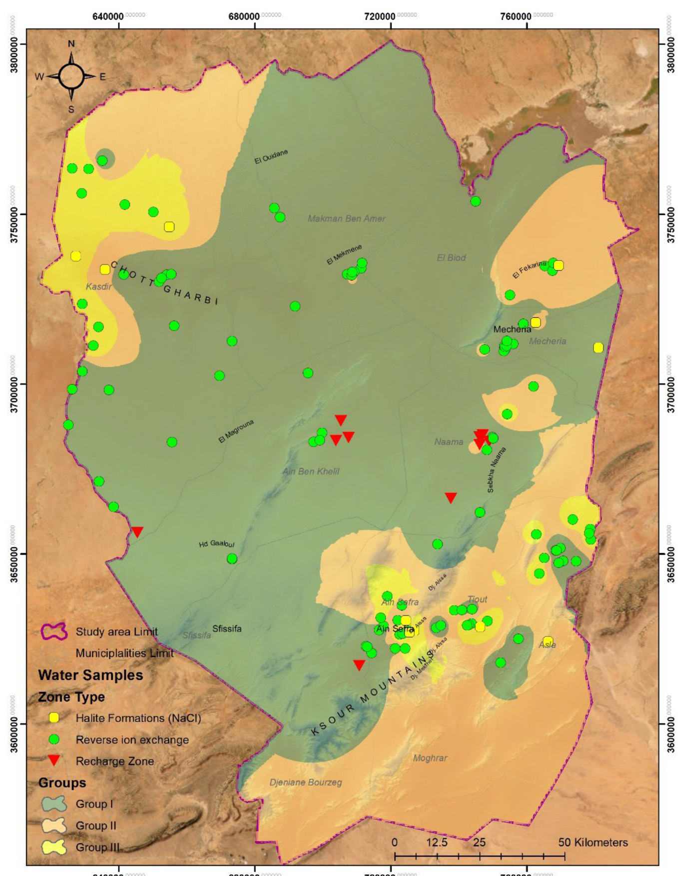

Figure 8. Overview of Groundwater Hydrogeochemistry in the study area

The performance of this study is underscored by its comprehensive approach, utilizing a robust dataset of 123 groundwater samples analyzed through multivariate statistical methods. This methodological rigor not only enhances the reliability of the findings but also sets a precedent for future research in similar contexts. The novelty of this research lies in its detailed examination of groundwater mineralization sources within a specific regional context while highlighting the interplay between natural geological processes and human activities. This study distinguishes itself by employing advanced statistical tools like Piper diagrams, Gibbs plots, Chadha diagrams, Hierarchical Ascending Classification (HAC), and Principal Component Analysis (PCA) to provide a more nuanced understanding of hydrochemical variations compared to traditional methods used in earlier assessments (Derdour, Jodar-Abellan, et al., 2022; Hussein et al., 2024; Lachache et al., 2023). By identifying sensitive recharge zones vulnerable to pollution, this research emphasizes the need for targeted protection measures, an aspect often overlooked in previous regional studies. This research contributes significantly to the existing body of knowledge regarding groundwater management in arid regions. It reinforces the importance of sustainable practices while providing a framework for future studies to mitigate the impacts of climate change and human activity on vital water resources. The findings serve as a reminder that effective management strategies are essential for preserving groundwater quality and ensuring its availability for future generations amidst increasing environmental pressures.

Figure 8 effectively summarizes the study's findings, presenting the results of the Cluster Analysis and the various water types identified through the Chadha diagram. This figure illustrates the spatial distribution of the different water groups, including recharge zones, reverse ion exchange areas, and halite formations, providing a comprehensive overview of the hydrogeochemical processes and groundwater quality variations across the study area.

6. Conclusion

The study on groundwater mineralization in the Naama region of Algeria provides a detailed examination of the hydrochemical characteristics and influencing factors affecting this essential resource. Through graphical tests and multivariate statistical analyses, the research identified a relatively homogeneous distribution of groundwater samples, categorizing them into three primary hydrochemical groups. Calcium and magnesium chloride and sulfate waters predominantly characterize these groups. This composition reflects the geological features of the region, particularly the gypsum-saline formations from the Upper Cretaceous and Triassic periods. The analysis revealed that Group 1 contains a higher concentration of calcium and magnesium bicarbonate waters, linked to carbonate formations from the Lower Jurassic or Miocene. These formations benefit from more active recharge zones than Groups 2 and 3, which exhibit similar chemical properties, although Group 3 is noted for its limited recharge capacity. The findings highlight significant environmental vulnerabilities associated with the recharge areas of carbonate aquifers, which are increasingly exposed to anthropogenic pollution. This underscores the urgent need for implementing strict protection measures, enhancing regulatory frameworks, ensuring continuous monitoring, and raising awareness among local communities about safeguarding this vital resource. The study aims not only to characterize water quality but also to protect an ecosystem crucial for environmental sustainability and human welfare. Despite these contributions, several limitations were encountered during this research. Data collection was affected by geopolitical factors related to the border region, restricting access to certain areas and resulting in incomplete datasets. Additionally, many local farmers were hesitant to allow entry to their farms for data collection purposes. These challenges may limit the findings' comprehensiveness and applicability across the wider Naama region. Nevertheless, this research is a valuable tool for decision-makers in water resource management. The insights gained can inform policies aimed at sustainable groundwater management and protection strategies tailored to address the unique challenges faced by the Naama region. Future studies should aim to overcome existing barriers to data collection through innovative approaches such as remote sensing or community engagement initiatives that promote local cooperation. Additionally, integrating advanced techniques like isotopic analysis could provide a more comprehensive assessment. Longitudinal studies are also recommended to monitor changes over time in response to environmental pressures and human activities.

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