Hydrochemical Characterization and Pollution Sensitivity of the Ghiss-Nekor Aquifer (Morocco): Impacts of Agriculture and Seawater Intrusion

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Abstract

The main objective of this study is to examine the evolution and sensitivity of groundwater in the Ghiss-Nekor aquifer, looking at geology, hydrochemistry and water quality. The Ghiss-Nekor aquifer is located in the Rif region, where the geology is made up of limestone, marl and alluvial rocks. The impact of these rocks on groundwater recharge and circulation is significant, such as Mineralization. To achieve our objectives in this study, we began with determining the chemical composition of the groundwater through an in-depth analysis of hydrochemical parameters. The main ions analyzed are cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-). These analyzes enable us to determine the origin of the water and, through various statistical tests such as K-means, PCA, HAC, and Piper's facies diagram we obtain two facies' groups and two factors influencing the nature and quality of the groundwater, we can identify the origin and quality of the groundwater in this aquifer. The groundwater quality was evaluated in compliance with national and international standards. Test results highlighted significant differences in ion concentrations, particularly elevated levels concentration of chloride 828,16 mg/L and sulfate 814,101 mg/L , as well as certain pollutants like nitrate concentration 498,044 mg/L. There is also evidence of contamination from marine intrusion. The sources of pollutants include agricultural activities due to the excessive use of fertilizers and pesticides, industrial and domestic emissions, and the infiltration of untreated wastewater. These sources contribute to the degradation of groundwater quality. To protect the aquifer, various solutions have been proposed to combat pollution and preserve groundwater quality, including the implementation of sustainable agricultural practices and regular monitoring of water quality.

Keywords: saltwater intrusion, groundwater, hydrochemical, quality, facies, statistics, anthropogenic pollution

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1 Introduction

In Morocco, the priority is to develop the water sector, because aquifers contain about 18% of the mobilizable potential of water resources. These reservoirs play a vital role in exploiting water for human use and meeting agricultural and industrial needs. This area, which plays an essential role in economic and social development, faces two major challenges: The Ghiss-Nekor aquifer faces two interrelated challenges: (1) declining water levels due to overexploitation (domestic, agricultural and industrial) is leading to increased pressure on available resources and projections indicate a trend towards absolute water scarcity by 2025 [1] requiring urgent measures to effectively manage this precious resource. and (2) quality deterioration from agricultural nitrate leaching and seawater intrusion.

The Ghiss-Nekor groundwater, located in the Al Hoceima region of Morocco and one of the main alluvial aquifers in the northeastern part of the ABHL zone [2], constitutes an essential resource for the local population, agriculture, and industrial activities. This aquifer represents the main source of fresh water in a region where surface water resources are limited and often insufficient to meet growing needs. The strategic importance of the Ghiss-Nekor aquifer lies in its ability to provide drinking water and support agricultural irrigation, which is crucial for the economic and social development of the region [1].

However, this groundwater is facing several major challenges that threaten its sustainability and quality. Overexploitation of the aquifer, due to increasing water demand, has led to a significant lowering of the piezometric level. This situation has led to the infiltration of seawater into coastal regions, increasing the salinity of groundwater and compromising its potability and use for irrigation: Similar coastal aquifers in Spain [3] or Tunisia [4] show comparable salinization trends.

In addition, intensive human activities, such as agriculture and industry, contribute to the degradation of the quality and quantity of the waters of this aquifer. The excessive use of fertilizers and pesticides causes pollution by nitrates and other chemicals, exacerbating the salinization and contamination of groundwater. The geological nature of the lands crossed by the aquifer, characterized by layers of silt and clay, and the dissolution of evaporites add to the high ionic concentrations, thus increasing the natural mineralization of the waters [5].

To address these challenges, sustainable and integrated water resource management is imperative. Morocco has taken steps to mitigate these problems, including the establishment of seawater desalination centers, such as the one in Ajdir. It is also crucial to establish systems to monitor the quality and quantity of extracted groundwater, protect aquifer recharge areas, prevent pollution through restrictions on the use of chemicals near infiltration areas, and limit water extraction to over exploitation.

The Ghiss-Nekor aquifer plays a crucial role in the economic and social development of the Al Hoceima region. However, it is seriously threatened by overexploitation and pollution. Rigorous management and appropriate protection measures are essential to ensure the sustainability of this groundwater resource, thus ensuring a reliable and good quality supply for generations to come.

2 Description of the study area

The plain of Ghiss-Nekor Located southeast of the Moroccan Mediterranean city of Al Hoceima, the Ghiss-Nekor plain lies between 35°5' north latitude and 3°45' west longitude figure 1. It is bounded to the north by the Mediterranean Sea, to the south by the Mohammed Ben Abdelkarim El Khattabi Dam (MBAK), to the east by the Temsamane and Ait Touzine mountains, and to the west by National Road No. 2, which crosses the main urban municipalities of Al Hoceima province. In Al Hoceima province, the plain rises on average about 1% from south to north, has a coastline of nearly 14 km, and has an area of about 100 km2 spread between the municipalities of Ait Youssef Ou Ali, Imzouren, and Béni Bouayach, and Trougout and Ijermaouas in Driouch province [6].

The study area has a roughly triangular shape and is crossed by two main rivers. The first is the Ghiss River which crosses the area to the northwest, while the second is the Nekor River which crosses the area at the Arbiaa Taourirte, Bouaarma and Tazouraght mountains.

The plain has a subsoil composed of the Ghiss-Nekor aquifer, the most important in the Moroccan Mediterranean region. The Mediterranean alluvial aquifers of Morocco are the largest, with an area of 90 km2. Les alluvions ont une épaisseur moyenne supérieure a` 200 mètres et atteignent un maximum de 450 mètres dans une dépression observée près de Souani et dans une autre dépression située a` environ un kilomètre a` l'est d'Imzouren, ou` l'on trouve des dépôts importants d'alluvions grossières s'étendant sur environ 5,5 km2. Rainwater, irrigation water from the BMBAK and infiltration from the Ghiss and Nekor rivers, as well as other surrounding watercourses, provide their recharge. The Nekor River is a 5th order classified watercourse which is part of a watershed of 905 km2 and its length is 76 km [6, 7].

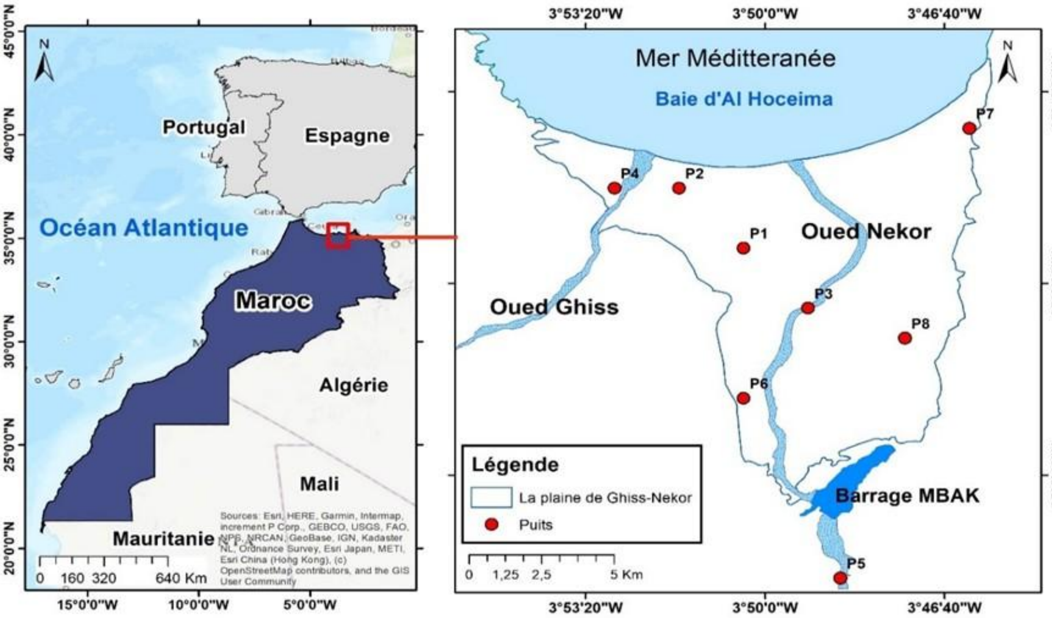


Figure 1: Geographical location of the Ghiss-Nekor plain and location map of the sample collection points (GIS).

3 Climatology

The climate in this region is semi-arid Mediterranean, with two distinct seasons: mild, rainy winters and hot, dry summers. The rainy season runs from October to April, while the hot, dry season extends from May to September. Precipitation is intensive, with a maximum of 450 mm recorded in the rainy year 2020/2021 (Figure 2). The average annual temperature in the study area is 16°C. The region's climate is characterized by wide seasonal and interannual variation, as well as geographical dispersion [8].

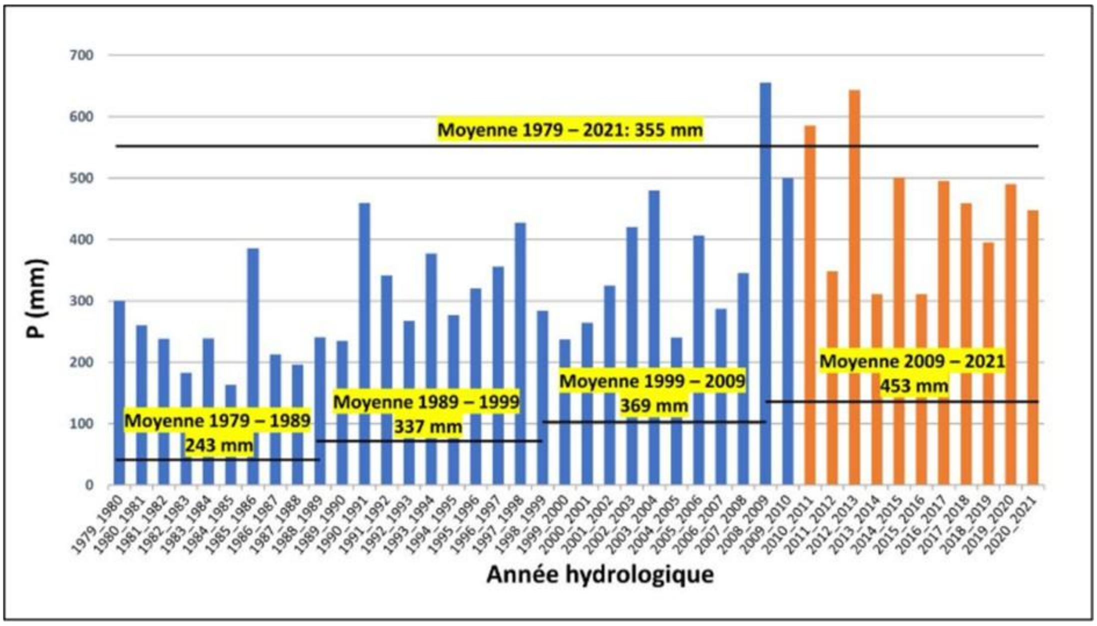


Figure 2: Variation in precipitation for the year 1979 -2021 Al Hociema province.

4 Géology

The Ghis-Nekor plain is a valley between the mountains, filled with a varied alluvial deposit comprising sands, gravels and conglomerates dating from the Plio-Quaternary to the present day. This depression, which covers around a hundred square kilometers, is generally surrounded by schistosandstone flysch, which is completely impermeable. To the northwest, it is bordered by the carbonate formations of the limestone Dorsale of the Bokoya massif and to the northeast by the plio-quaternary vulcanites of Ras Tarf. The eastern edge is characterized by a piedmont formed by a series of depositional cones, the most significant of which lies to the southeast. The Ghis-Nekor plain is composed of a varied alluvial deposit extending from the Pliocene to the present day. Plio-Villafranchian conglomerates, sandstones and silts from the Oued Ghis and Imzouren plateaus can be found to the west of the plain. The Villafranchian-finished alluvial surfaces of the Oued Ghis high plateaux lie to the west of the town of Imzouren, in the A¨ıt Amar or Bouker region [5].

5 Materials and methods

The physicochemical parameters of groundwater samples were analyzed using standardized laboratory protocols. The techniques and instruments used for each parameter are summarized in table 1. All analyses were performed in accordance with standard analytical methods [9].

Table 1: Analytical Techniques and Instruments Used for Water Quality Parameters

Parameter(s)	**Analytical Technique**	**Instrument / Equipment**
pH, EC, TDS, SAL, RES, O_2, ORP	Multiparameter probe	**Consort C3210**, 2-channel analyzer
Temperature (T, °C)	Thermometry	**JEULIN 251028** thermometer
Na^+, K^+	Flame photometry	**ELICO CL 378** (accuracy ± 0.5 ppm)
Cl^-	Argentometric titration	Titration with **$Hg(NO_3)_2$ (0.01 N)**
Ca^{2+}, Mg^{2+}	Complexometric titration	Titration with **EDTA (0.02 M)**
HCO_3^-	Acid-base titration	Titration with **HCl (0.1 M)**
Oxidizable substances	Hot permanganate titration	**$KMnO_4$** method
NO_3^-, SO_4^{2-}	Colorimetric method	**UV-VIS spectrophotometer (LANGE HACH DR-7600, ±1 nm)**
NH_4^+, Mn^{2+}, Al^{3+}, Fe^{2+}	Color indicator tests	Standard **reagent-based kits**

The sampling volume was 1.5 L; 6 wells (P1, P2, P3, P4, P5 and P6) were sampled on March 10, 2024, while the other two wells (P7 and P8) were sampled on March 18, 2024, spread over a coastal area of around 64 km2 (Figure 1). Before starting the sampling campaign, we mapped the sampling sites using Google Earth software to identify areas accessible for representative sampling.

To guarantee methodological consistency and data quality, the groundwater samples in this study were collected, the analytical procedures followed standard methods to ensure reproducibility. Nitrate was determined spectrophotometrically according to ISO 7890-1:1986. Calcium and magnesium concentrations were analyzed using EDTA titration as described in Rodier et al. (2016) [10]. All measurements complied with established protocols and were conducted in triplicate to ensure accuracy., stored, transported and subjected to laboratory analysis in compliance with Jean RODIER standards. The samples were collected in polyethylene bottles and filtered through a 0.45 µm diameter membrane, and reserved at a temperature of 4°C. In this study, the following physico-chemical parameters were measured: pH, temperature (T°C), dissolved oxygen (DO), electrical conductivity (EC), on land and other physicochemical parameters in the laboratory by determining the concentrations of the main cations and anions: : Sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), ammonium (NH_4^+), bicarbonates (HCO_3^-), nitrates (NO_3^-), nitrites (NO_2^-), chlorides (Cl^-), sulfates (SO_4^{2-}), manganese (Mn^{2+}), aluminum (Al^{3+}), iron (Fe^{2+}). (Rodier, J. et coll. (2016)). These analyses are carried out from 2 h after sampling, except for the analyses of: Nitrates (NO_3^-) after 24 h. To gain better insight into the chemical characteristics of the groundwater, we used the 'Diagrammes' software developed by Roland Simler (Hydrogeology Laboratory, University of Avignon, version 2021) to create a Piper diagram. This allowed us to visualize and distinguish different water types based on the proportions of major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (NO_3^- Cl^-, SO_4^{2-}, HCO_3^-). In addition, we carried out statistical analyses using OriginPro (2021) and XLSTAT (v24) to better understand the relationships between samples and detect possible grouping patterns. Specifically, we applied: Hierarchical Cluster Analysis (HCA) to group the samples according to their chemical similarities, K-means clustering to refine and validate these groupings, and Principal Component Analysis (PCA) to identify the main factors influencing groundwater composition while reducing data complexity.

6 Results and discussion

We present the results of hydrochemical analyses of the physicochemical parameters (TAC, TH, Sulfate, Nitrate, TDS, Dissolved oxygen, oxidizability, turbidity, Fe(II), Al(III), Mn(II), NH4.) of groundwater from some sampling points (figure 3).

Figure 3: Physicochemical parameters of groundwater in the Ghiss-Nekor plain (March 2024).

6.1 Physicochemical characteristics of Ghiss-Nekor groundwater

Table 2: Descriptive statistics of measured groundwater parameters in the present study

Descriptive statistics						
Variable	**Units**	**Observe**	**Minimum**	**Maximum**	**Average**	**Standard deviation**
SO_4^{2-}	mg/L	8	501,100	967,670	814,101	159,707
NO_3^-	mg/L	8	12,020	48,860	27,338	13,715
Cl^-	mg/L	8	568,000	1,201,000	828,161	197,883
Ca^{2+}	mg/L	8	170,730	386,350	227,730	71,399
Mg^{2+}	mg/L	8	135,540	297,200	184,955	55,450
NH_4^+	mg/L	8	0.050	0.050	0.050	0.000
Na^+	mg/L	8	254,000	810,020	498,044	164,900
K^+	mg/L	8	2,200	18,020	7,078	5,071
TDS	mg/L	8	2,343,000	3,490,000	2,917,625	387,067
THIS	mg/L	8	2,390,000	5,590,000	3,168,750	1,049,319
pH	—	8	6.650	7.680	7.308	0.336
Dissolved oxygen	mg/L	8	6.480	9.590	8.126	1.083
Oxidizability	mg/L	8	0.621	1.850	1.402	0.431
Turbidity	NTU	8	0.343	3.220	1.535	1.262

Table 2 gives an overview of the fundamental data of the physicochemical characteristics of the Ghiss-Nekor groundwater for the sampling points of March 2024. pH values (6.65–7.68) reflect neutral to slightly alkaline conditions, with low variability (SD = 0.33), suggesting homogeneous buffering by carbonate minerals. CE values range from 2390 to 5590 µS/cm with an average of3176.25µS/cm thenexcessive mineralization if $CE > 1500$ ((according to Nalco Water Manual 1983). TDS values range from 2343 to 3490 mg/L with an average of 2917,625 mg/L. Groundwater is generally considered saline if its salt content (TDS) exceeds 1000 mg/l [8, 11]. On the other hand, limnologists consider water to be soft if its TDS level is less than 3000 mg/L.

In this study, we considered water with TDS content up to 3000 mg/L as fresh water. High concentrations were mainly observed on the Mnoud and Souani part of the Ghiss-Nekor plain, with particularly pronounced maximum values in the coastal region (Souai and Rherach). In contrast, $HCO_3^-$is much more concentrated from the point (P1, P2 and P5), reaching a maximum concentration of 439.2 mg/l.

Among the sampled wells, P7, located near the coastline , exhibited the highest values of electrical conductivity and total dissolved solids, reaching over 5500 µS/cm and 3500 mg/L respectively. The elevated levels of chloride and sodium ions further support the hypothesis of seawater intrusion, which is typical in coastal aquifers exposed to marine influence.

The substance is present in high concentrations in the urban area of Imzouren, as NO_3^- well as in rural areas of Mnoud.

The standard deviation of the hydrochemical parameters revealed wide variations in the measured concentrations, particularly for chloride which showed the greatest variation of all the ions examined (SD =221.13 mg/L), and an average of 790.66mg/L [12].

The considerable variations in hydrochemical parameters indicate that salinization could have several different sources in our study area. Marine intrusion could be one of the potential drivers of salinization, which is noticeable in the large variations in EC (SD =1047.4 µS/cm) and TDS (SD =387.07mg/L) [13].

The abundance of cations was discovered in the following order: $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$, while the order of the anions is $NH_4^{+} > SO_4^{2-} > Cl^{-} > NO_3^{-} > PO_4^{3-}$. In research conducted upstream of the Ghiss-Nekor plain, the same order of abundance was obtained [11].

6.2 Piper diagram

The Piper diagram was used to assess the hydrochemical forms of the Ghiss-Nekor coastal aquifer. This diagram is primarily intended to visually distinguish between the various water types, as waters of similar origins are usually grouped together. The diagram consists of a central diamond and two triangles, one for cations (Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+}) and one for anions (Cl^{-}, HCO_3^{-}, CO_3^{2-}, and SO_4^{2-}). Ion concentrations were measured in mg/L to generate the data points in the graph, and then the results for cations and anions were added separately. These sums were then used to determine the percentage contribution of each ion to the total [11, 12].

Points were plotted within the cation and anion triangles and then projected onto the diamond by identifying the intersection of two parallel lines at the ends of the triangle. This is where the hydrochemical forms were established. Once the Piper diagram has been classified, it is possible to divide sample groups based on geography, geological formation, or water source.

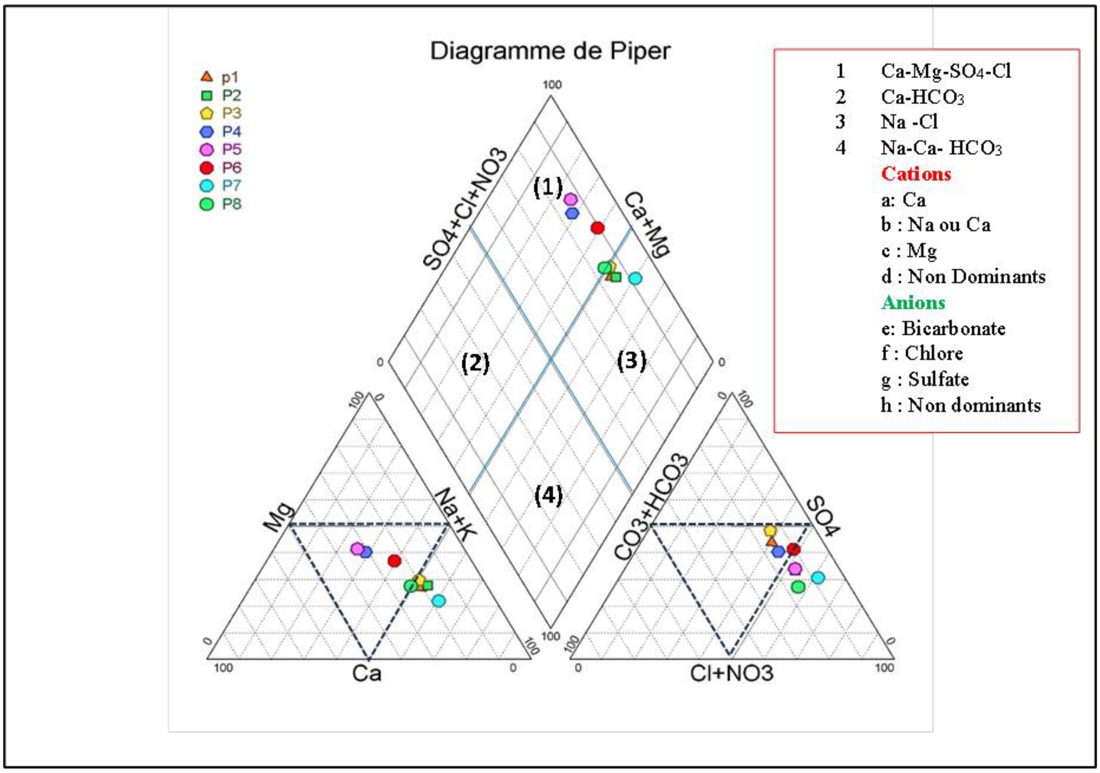


Figure 4: Piper diagram of the facies of the Ghiss-Nekor plain.

The Piper diagram (Figure 4) reveals two dominant facies: (1) Na-Cl type (5 out of 8 samples), indicating saline intrusion in coastal wells (P7, P8), and (2) mixed Ca-Mg-Cl-SO_4 type (3 out of 8 samples), reflecting dissolution of evaporites in upstream areas (P1–P3).

The Na-Cl facies observed in five samples coincides with high chloride concentrations (> 1000 mg/L), particularly in well P7, which is located near the coastline and likely influenced by seawater intrusion. In contrast, elevated Cl^- levels in well P8, situated inland, may reflect other processes such as evaporite dissolution or anthropogenic inputs while the Ca-Mg-Cl-SO_4 samples (P1–P3) correlate with local gypsum dissolution (SO_4^{2-} > 500mg/L)

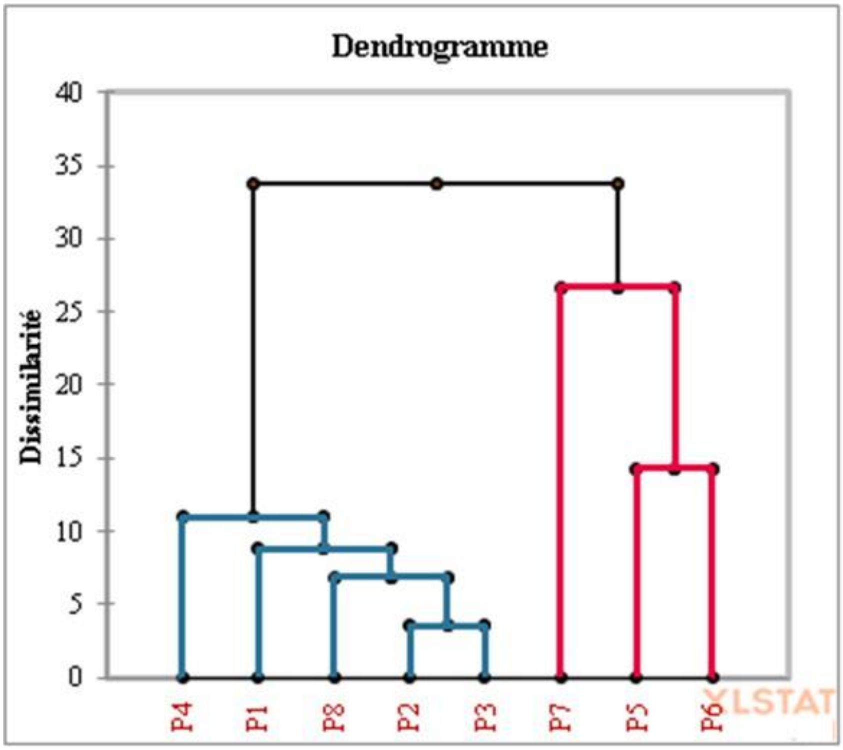
The chemical composition of a water sample depends on its major ionic components. The influence of interactions between water and surrounding minerals has an impact on the particular chemical character of the sample. The cause of this interaction can be various, such as rainfall, dissolution, ion exchange, geological structure and mineralogy of the watershed/aquifer [14].

According to the results obtained, the majority of samples from the upstream of the basin and the samples taken in the middle of the basin have calcium-sulfate (Ca-SO4) or magnesium-sulfate (Mg-SO4) chemical properties.

On the other hand, the samples from downstream are of a sulfate-sodium (Na-SO4) to chloride-sodium (Na-Cl) nature. The geological nature of the aquifers of the Ghiss-Nekor basin is perfectly compatible with the confirmed hydrochemical facies [6, 15].

6.3 Hierarchical Cluster Analysis (HCA)

Identification of Natural Groups: Using HCA, one can identify natural groups in the data, such as water samples with similar chemical composition or contamination profiles. Figure 5 shows 2 groups in the ascending hierarchical classification. The six samples P1, P2, P3, P4 and P8 constitute the first group. The second group is composed of 3 samples P5, P7 and P6.



Class 1	Class 2
P1	P5
P3	P7
P2	P6
P8	

Figure 5: HCA dendrogram of groundwater at the study points

Table 3: Results by class

Class	1	2
Number of objects per class	5	3
Sum of weights	5	3
Intra-class variance	7,54	20,49
Minimum distance to the barycenter	1,63	3,17
Average distance to the barycenter	2,41	3,67
Maximum distance to the barycenter	2,95	4,21

6.4 Principal Component Analysis (PCA) Statistical Test

Principal Component Analysis (PCA) is a statistical technique used primarily to reduce the dimensionality of data sets while retaining as much information as possible.

- Reduce the number of variables by combining the initial variables into a set of new variables called CP.

- Used to analyze and simplify geochemical, hydrological or environmental data of the water table, in order to identify the main factors that influence the sensitivity of groundwater.

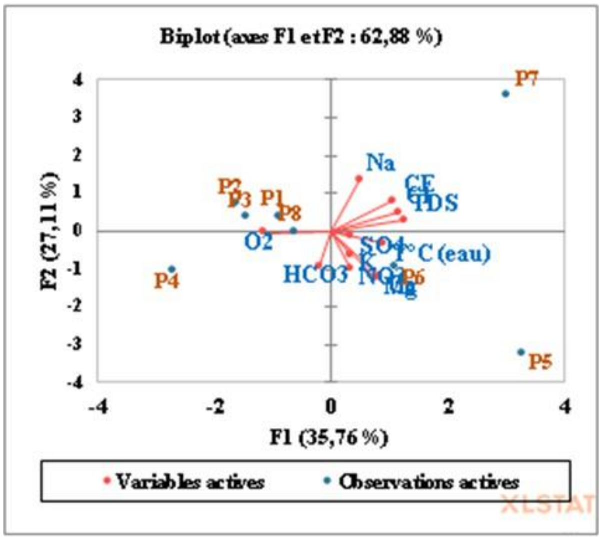
Table 4: Eigenvalues of factors

	F1	F2	F3	F4
Eigenvalue	4,292	3,253	2,001	1,209
Variability (%)	35,764	27,111	16,671	10,076
% cumulative	35,764	62,876	79,547	89,623

F1 explains 35.8% of variance, dominated by Na^{+}-Cl^{-} (Figure 5). This triad These ions may indicate dominant geochemical processes such as mineral dissolution, salinization due to seawater intrusion or intense evaporation in arid areas. Na^{+} Cl^{-}. The (F2) explains 27.111% of the total variance. Together with F1, they explain 62.876% of the variance. F2 related to other important ions such as Mg^{2+}, Ca^{2+} and SO_4^{2-}. These ions suggest secondary processes such as the dissolution of mineral sulfates (such as gypsum), the influence of human activities (such as agriculture), and the degradation of organic matter.

(F3) explains 16.671% of the total variance. Together with F1 and F2, it explains 79.547% of the variance. F3 captured additional variation related to less abundant but significant ions such as potassium K^{+} and nitrates (NO_3^{-}) These ions are associated with anthropogenic sources such as agricultural fertilizers and wastewater [8].

The fourth PC (F4) explains 10.076% of the total variance, bringing the cumulative total to 89.623%. F4 could capture specific aspects such as seasonal variations, point sources of pollution, or specific geological influences that are not dominant but still significant [16].



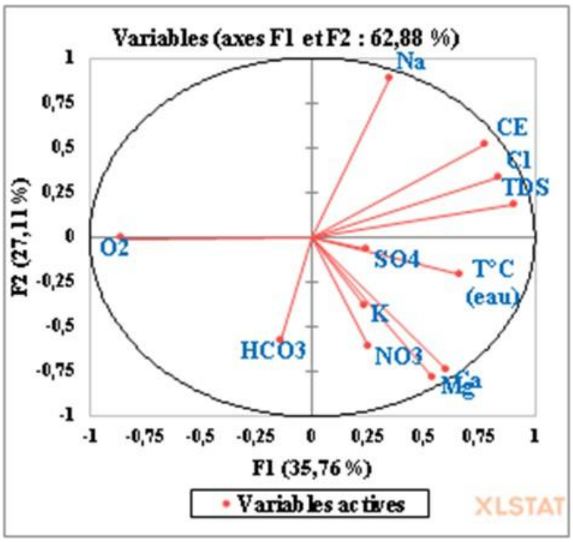


Figure 6: Analysis of water samples and graphical representation in the CP factorial plane.

6.5 means statistical test

Table 5: Group classes by distance

Results by class:	**1**	**2**
Class	P1, P2, P3, P4, P6 and P8	P5 and P7
Number of objects per class	6	2
Sum of weights	6	2
Intra-class variance	116524,910	2098684,810
Minimum distance to the barycenter	195,033	1024,374
Average distance to the barycenter	302,797	1024,374
Maximum distance to the barycenter	389,704	1024,374

Class 1 samples are relatively homogeneous in terms of chemical composition. This indicates that they probably originate from similar sources or from constant geochemical processes in the water table.

Origin of ions: Natural: The composition of Cl^-, K^+, Ca^{2+}, Mg^{2+}, Na^+, and SO_4^{2-} and indicates a natural origin, probably due to the dissolution of minerals present in the aquifer (calcite, dolomite, gypsum, halite, etc.).

Constant geochemical factors: Parameters such as pH, electrical conductivity (EC) and temperature are relatively constant, suggesting a homogeneous geological influence.

Class 2 samples show great heterogeneity. Large distances from the barycenter indicate very varied chemical compositions, suggesting different influences or sources of contamination.

Origin of ions: Potential anthropogenic contamination: High levels of nitrates NO_3^- and chlorides (Cl^-) in P5 and P7 may indicate contamination from agricultural (fertilizers) or industrial sources.

Specific local influences: High values of some ions such as Ca^{2+} and Mg^{2+} may be due to local geological variations, such as intrusions of other types of groundwater or specific human activities.

Unique local processes: Samples P5 and P7 show distinct characteristics that could result from specific local processes or point contamination.

7 Conclusion

The Ghiss-Nekor plain, located in a region with varied geology, is experiencing an increase in the concentrations of chloride (Cl^-) and sulfate (SO_4^{2-}) ions in its groundwater. This evolution is influenced by geological and anthropogenic factors. Geological nature of the Ghiss-Nekor nappe sedimentary rocks contain soluble minerals such as (NaCl) and gypsum $CaSO_4 \cdot 2H_2O$. Evaporite rocks formed by the evaporation of ancient seawater, contribute to the high presence of chloride and sulfate. Chemical weathering releases chloride and sulfate ions into groundwater by dissolving minerals. Sources of Chloride and Sulfate Ions salt water intrusion from proximity to the sea and excessive pumping of coastal groundwater. Agricultural pollution due to the intensive use of fertilizers containing these ions. Industrial activities through discharges of untreated industrial effluents. Domestic waste also contributes to the increase in ions.

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