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Research Paper

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Characterization of the mineralization of groundwater in F'kirina Plain's (North-East Algeria) by hydrochemical methods

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Abstract: The linking between the geological, hydroclimatic, and hydrochemical tools in the study of the effects of the central gas turbine of F'kirina on groundwater has allowed us to determine the origins and evolution of pollutants. The analysis of the physico-chemical quality has focused on 14 samples of drilling and wells in the coring exploited in the region, used for human consumption. The study on groundwater quality shows that the majority of tested physicochemical parameters show high concentrations according to potability standards eligible by the WHO. This might be because of three types of water pollution: natural, caused by the dissolution of evaporated formations and carbonate, which results in high concentrations of Cl^- , Na^+ , SO_4^{2-} , Ca^{2+} , and HCO_3^- ; agricultural, caused by the heavy use of chemical fertilizers; and industrial, caused by the operation of the local gas turbine plant that produces electricity. To this effect, the continuous assessment of the quality of the water is considered a treatment to reduce the deterioration of the quality of the water and eliminate health problems.

Keywords: pollution, water, groundwater, physico-chemical quality, F'kirina.

Introduction

The Earth is generally called the “Blue Planet” because about 71% of its surface is covered by water; however, only 3% is available as freshwater (Kherifi and Bekiri, 2017; Musie and Gonfa, 2023). Furthermore, groundwater represents about 98% of the global freshwater

reserves (Velis et al., 2017). Water is one of the most vital natural resources. It is a key factor for the survival of all living things, as well as essential for industrial and domestic input, tourism, agriculture, and the sustaining of various global ecosystems (Khezzani and Bouchemal, 2018a). Water resources are a pivotal element in the economic development of countries, which has made their availability a prerequisite for realizing the priority objectives for development, especially in the agriculture field (Khezzani and Bouchemal, 2018a; Zhang et al. 2020). Schwarzenbach et al. (2010) reported that problems related to water quality and/or water quantity are going to be more aggravated in the future due to climate change.

At the global level, about 1.8 billion people will live in regions with complete water scarcity by 2025 (Naimi Ait-Aoudia and Berezowska-Azzag, 2016). Furthermore, the Food and Agriculture Organization (FAO) projects that by 2025, almost 480 million people in Africa will be living in areas with high water scarcity (Khezzani and Bouchemal, 2018a; Omotobora et al., 2014), where precipitation and surface water are limited (Li et al., 2021). In arid and semiarid areas, including North Africa and the Middle East, groundwater is the main source of supply for domestic and agricultural activities (El Mahdy, 2020; Khezzani and Bouchemal, 2018b).

Generally, groundwater is less accessible to pollution than surface water due to the fact that it is not easy to be directly exploited by the population (Carrard et al., 2019); however, groundwater can be contaminated by various pollutants in some conditions (Saraswat et al., 2023; Talabi and Kayode, 2019). The natural decontamination processes for polluted groundwater might take decades or even hundreds of years, even if the source of pollution is stopped (Tatti et al., 2019).

In the last few decades, water pollution has been the subject of many academic investigations worldwide (Evans et al., 2019; Zainurin et al., 2022). Furthermore, water pollution has become a hotspot of discussion in many international forums, where much scientific research and government reports have reported that there has been increasing global concern due to the increasing burden of water pollution (Singh et al., 2022). According to some modeling studies, up to 5.5 billion individuals around the world might come into contact with contaminated water by the year 2100 (Tozer, 2023).

The scope of water use is determined according to its physical, chemical, and biological properties (Kafle, 2020). Further, these characteristics should be compared with regulatory national or/and international standards (Bozorg-Haddad et al., 2021). Scientific research has identified many compounds that can pollute the water. For example, toxic metals, trace organic contaminants, pesticides, nanoparticles, microplastics, hydrocarbons (Li et al., 2021), and

various types of microbial pathogens (Kafle, 2020).

Algeria is one of the countries where water availability is limited while needs continue to increase (Bouzid-Lagha and Djelita, 2012). In addition, the country was subject to frequent periods of intense and persistent drought (Schilling et al., 2012). In the northern part of the country, the exploited quantity of groundwater resources is estimated at 1.8 billion m³, which is almost fully used nowadays (Barkat et al., 2021).

Oum El-Bouaghi province (North-East Algeria) is an example of high plain region where agricultural activities that rely principally on groundwater play an important role in the local and national economies. In the F'kirina plain, the National Electricity and Gas Company established a power plant for electricity production (292 MW) works by natural gas. So, there is concern about the probable harmful effects of this energy plant on the surrounding environment. This study aims to monitor groundwater quality in the F'kirina plain by studying its physicochemical characteristics.

Materials and methods

Description Of the Study Area

Administratively, the F'kirina municipality belongs to Oum El Bouaghi province (North-East of Algeria). The plain of F'kirina represents a part of the high plains of Constantine, the mountains of Mellegue, the mountains of Harectas, and those of Nememchas; at 900 m of altitude, it extends on a surface of 650 km². It belongs to the sub-catchment area of Garaet Tarf, which has an area of 2430 km².

Naturally, the watersheds formed by the Jebel El Galaa Kebira (1246 m), the Jebel Ammamrat El Kebira (1203 m), and the Jebel El Forne (1184 m) border the study area from the north and the Djebel Boutakhma (1291 m), the Djebel Fedj Amer (1259 m), and the Djebel Bou Tebina (1226 m) from the south. The Jebel El Medjifla (1174 m), the Jebel Fedjijet (1291 m), and the Kef El Assa (1117 m) form a watershed that limits it in the east. In the west, a sizable flat area borders the high plains of Constantine and the Garaet Tarf (Rahal et al., 2021).

The climate of the study region is continental and characterized by two contrasting seasons: one dry and hot in summer and the other rather wet and cold in winter, with short periods in spring and autumn (Ouanes et al., 2017). The annual average evapotranspiration is about 904 mm, significantly higher than the rainfall average estimated at 373 mm. The yearly average

temperature is about 15.7°C. Thus, there is a theoretically quasi-permanent water deficit, and the water is fed laterally either by neighboring basins or by drainage.

The F'kirina area is drained by two important wadis in the southeast, which are Oued Isfert and Oued Oulmen. The geological structure is characterized by limestone mountains whose tectonic movements are extreme. Generally, the quaternary formation covers the F'kirina plain (Ouanes et al., 2017).

Sampling And Analytical Methods

To study the quality of the groundwater of the Quaternary aquifer in the plain of F'kirina, we first conducted reconnaissance trips of the site, during which we selected the boreholes and wells to study physicochemical measurements. The sampling involved 14 wells uniformly distributed over the plain in winter (January 2023) (figure 1).

The water points were located by their geographical coordinates, determined by a GPS-type Garmin. The analyses of chemical elements (major ions in the water: HCO_3^- , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} , and Na^+) were carried out in the chemistry laboratory at the Department of Earth Sciences (University of Constantine, Algeria) using a spectrophotometer type DR2000 in the visible range (325 to 900 nm). The physical parameters pH and electrical conductivity (EC) were measured *in situ* immediately after the sample collection by ourselves, using a multi-parameter HANNA HI9025.

The maps were created using the ArcGIS 10.8 software ARCGIS® (ESRI), and the thermodynamic modeling was done with the Diagram software (version 6.77), while the calculation of the saturation indexes SI was done with the software PHREEQC (version 3.7).

The descriptive statistics were done with XLSTAT 2015 software, and hydrochemical data processing was done using Matlab. For any geochemical study, the separate study of each variable is an important phase when analyzing the chemical behavior, but it is often insufficient.

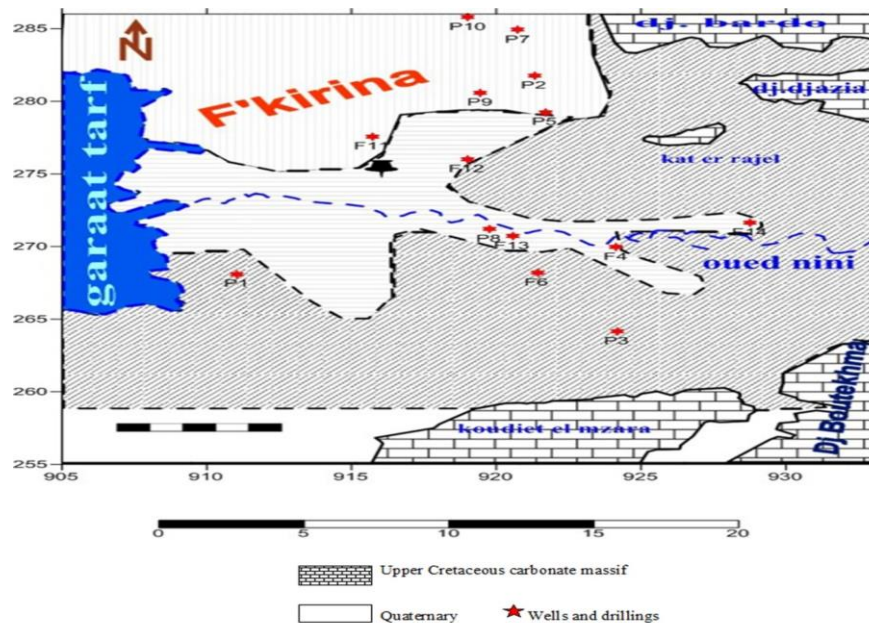


Figure 1. Geological situation of the study area and sampling point inventory map

Therefore, the data must be analyzed, considering their multidimensional nature (Hamzaoui-Azaza et al., 2011). Two statistical methods were used to investigate the sources of water salinization: principal component analysis (PCA) and hierarchical cluster analysis (HCA).

Principal component analysis

Principal component analysis (PCA) is a mathematical, multidimensional statistical technique that is essentially descriptive. This allows the deduction of a complex correlation system in smaller dimensions (Gaagai, 2009). Also, it allows for the extraction and presentation of the maximum amount of information contained in a database (Hamzaoui-Azaza et al., 2011).

Hierarchical classification analysis

This method consists of a criterion of aggregation of classes that can be defined by the measure of the degree of similarity or dissimilarity that would exist between the samples. There are several measures to assess the distance or degree of similarity between samples. The Euclidean distance remains the most widely used similarity measure (Hamzaoui-Azaza et al., 2011) the result of the algorithm is a tree of classes, called the dendrogram, which shows how the classes are related (Kamagate et al., 2010) in a form of graphical representations or simplified indices, allowing their interpretation, such as the highlighting of relationships and similarities between variables and/or opposition between observations and to identify the most

correlated variables between them (Gaagai, 2009).

Results and discussion

Several physical and chemical parameters characterize groundwater quality; however, water intended for human consumption must comply with strict parameters that define its potability (Spellman, 2017). The physicochemical analyses of the groundwater of the F'kirina plain showed a significant variation in the concentrations of chemical elements. These exceed the standards of potability at some points of measurement.

Highlighting of the mineralization of the groundwater

The obtained results indicate the presence of several minerals, particularly anhydrite, Gypsum, Aragonite, Calcite, and Dolomite, whose saturation indices vary in a small range.

The groundwaters of the study area are undersaturated with respect to evaporite elements. Concerning Halite and Anhydrite, undersaturation increases the mineralization of the waters, while in Gypsum, this is explained by a dissolution that enriches the waters in Ca^{+2} and SO_4^{2-} . Knowing that Anhydrite, and Gypsum are indexes accelerating the salinity process, this increase is done by dilution. So, these waters are still able to dissolve these minerals. The waters of the study area are oversaturated with respect to Calcite (for points 1, 2, 5, 6, 7, 8, 9, 10, 12), this is due to a precipitation of Calcite, hence a possible enrichment of the waters in calcium bicarbonate; on the other hand, they are undersaturated with respect to Dolomite (with the exception of three points (1,6, and 12), and to Aragonite (except point 12 which is oversaturated). Chlorides are the main elements conditioning the mineralization of water, the variations of the indices of saturation of these different minerals according to chlorides (Figure 2).

The saturation index shows an oversaturation with respect to the indices, highlighting the influence of carbonate formations characterized by Calcite and dolomite. In contrast, we note all points of oversaturation with respect to the indices accelerating the process of salinity, which are Anhydrite, and Gypsum. This increase in salinity is done by dilution.

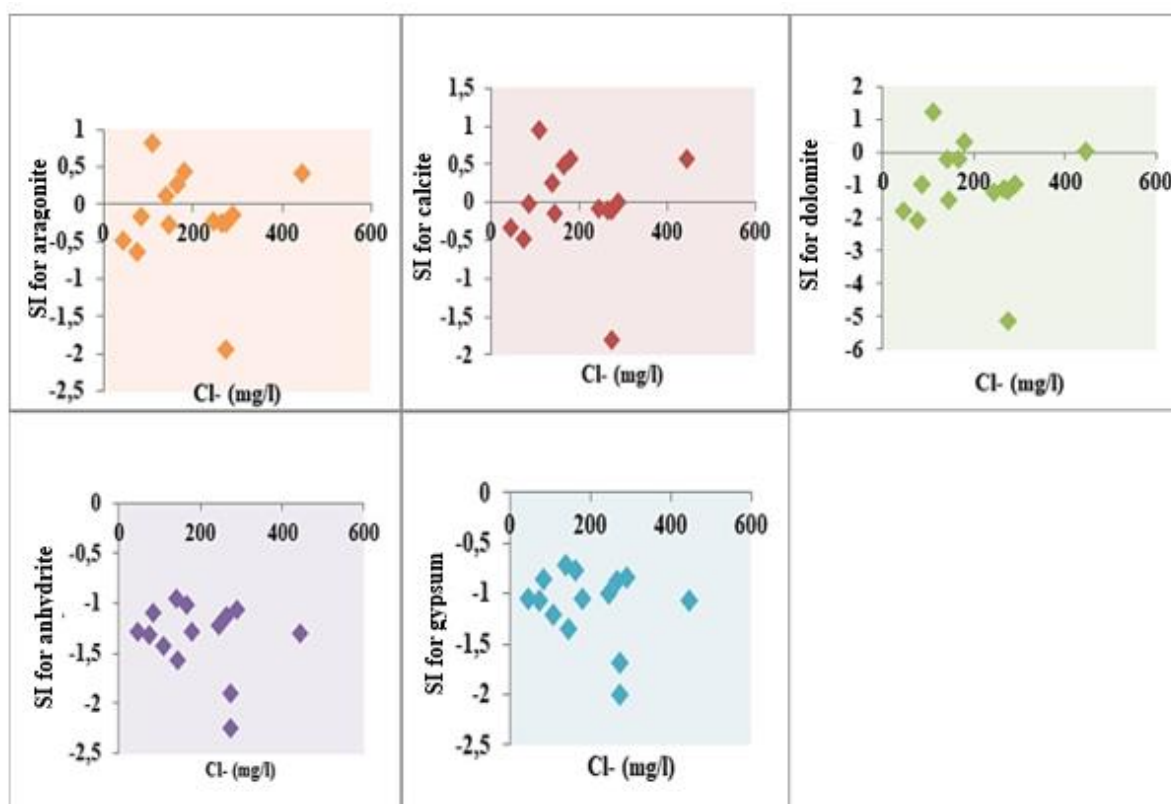


Figure2: Saturation index variation

Study of the physical parameters

Electrical conductivity

The EC provides information about the total amount of dissolved salts in water (Diédhiou et al., 2023). The EC values measured for all the water samples taken in the study area range between 520 $\mu\text{S}/\text{cm}$ and 1930 $\mu\text{S}/\text{cm}$, with an average of 1225 $\mu\text{S}/\text{cm}$. It can be seen that there is an increase in concentration according to the flow direction; therefore, according to this classification, these groundwaters are saline. The majority of the water points in the region have high conductivity, which means a high degree of mineralization. (Figure 3)

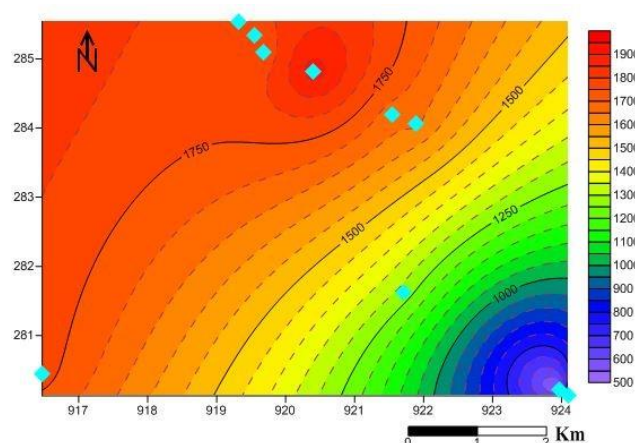


Figure 3. Spatial variation in electrical conductivity of groundwater of the study area

pH

By comparing the results obtained during the analysis of the water samples of the study area with the WHO standards, which are between 6.5 and 8.5 for drinking water, it appears that their pH is normal since it is between 6.6 and 7.5. So, in general, the waters of the study area show similar characteristics to those of alkaline water. According to Aragaw and Gnanachandrasamy (2021) quantity and chemical structure of several inorganic and organic matters dissolved in the groundwater are controlled by pH. However, pH has no direct effect on human health.

Study of chemical parameters

The chemical composition of water must be examined in relation to its impact on land and plants (Belkoun et al., 2024)

Calcium (Ca^{2+}) and Magnesium (Mg^{2+})

The measurement results obtained in the laboratory and the calcium maps for the water studied show that most of the sampling points have high calcium ion contents, with a maximum value of 208.42 mg/L. These concentrations are higher than the standard of potability of water (100 mg/L), except for some points where concentrations are lower (the minimum value is 72.15 mg/L), and exactly the areas adjacent to Garaat Tarf or the flow of groundwater are very low, which indicates that these waters are less influenced by the dissolution of carbonate and gypsum formations (Figure 4a).

The high Ca^{2+} content is related to the presence of a carbonate level due to the dissolution of Companion-Maestrichian formations; due to the impact of sebkha, it is of the origin of agricultural anthropic activity (chemical fertilizers); without forgetting the evaporitic level of triassic formation and the exchange of bases within clay minerals.

The magnesium concentration map shows that the Mg^{2+} content is relatively low in almost the entire study area. It is well below the value recommended by the WHO, which requires a maximum concentration of 50 mg/L (Figure 4b). Sengupta (2013) reported that, over the long term, drinking water hardness can lead to many health problems, such as growth retardation, reproductive failure, and cardiovascular and renal disease.

Sodium (Na^+)

The sodium contents observed for all the water points of the plain vary between 14 mg/L as a minimum value and 276 mg/L as a maximum value, with an average measurement of 145 mg/L (Figure 4c). The high level of this element is attributed to the migration of salt water from the dissolution of evaporite minerals in Sebkha in response to intensive pumping and also from triassic geological formations, as reported by Saraswat et al. (2023).

Chlorides (Cl^-)

Water analysis of the study area revealed normal amounts of chlorides in wells P1, P2, F3, F4, F5, F6, P9, and P10. Ranging from 35.5 to 284 mg/L). The highest concentrations are recorded in wells P7 and P8, with values of 284 and 273.35 mg/L, respectively. It is important to note that the results for this parameter are higher than the WHO's maximum concentration. The variation in content can be linked to the leaching of the triassic formations. For areas near Garaat Et Tarf (Oued-Sebkha), brackish water intrusion areas from the Sebkha occur in response to intensive pumping and migration of salt water. For the points located in the northwest of the plain in this area, the high chloride content can be linked to the pollution of the water table by wastewater from the city of Ain Beida, the use of chemical fertilizers, domestic discharges, and solid discharges from livestock pens (poultry houses).

The region has a semi-arid climate, so we also link the high concentrations to the leaching of surface saline concentrations in cases of heavy rain and to the contamination of groundwater by the waters of the Sebkha (Garaat Tarf). It would be useful to attribute the high

concentrations also to the pollution of the groundwater by the wastewater from the gas turbine plant (Figure 4d).

Many studies reported that even in the case of excessive amounts in drinking water, chlorides would not have any harmful effects on the health of the consumer, especially in the case of adults of working age (Bashir et al., 2012; Kończak and Janson, 2021). The chloride concentrations in the body are well regulated by a complex system involving both the nervous system and the hormonal system. Even after the intake of large amounts of chloride through food and water, chloride balance is maintained, mainly through the excretion of excess chloride in the urine (Honig et al., 2020). In irrigation water, a high content of chloride can lead to plant toxicity through the reduction of soil permeability (Yıldız and Karakuş, 2020).

Bicarbonate (HCO_3^-)

The examination of the bicarbonate map shows a decrease in content in the direction of flow, with an average of 247 mg/l. The maximum value is 1061 mg/l, and the minimum is 116 mg/l, measured near the carbonate outcrops. The increase in bicarbonate content just at the outlet of the Maestrichtian limestones is attributed to their high solubility. Moving away from the outcrops, the water becomes saturated, the carbonates precipitate, and their content decreases in the water. This is thus controlled by the dissolution of the carbonate minerals in the northeast of the basin. The studied water has a high content of bicarbonates compared to the considered ions. This content confirms its bicarbonate origin (Figure 4e).

The higher content of bicarbonate in the groundwater indicates the predominance of the mineral dissolution process (Aragaw and Gnanachandrasamy, 2021). Although bicarbonate has an important place in human physiology, its high level in drinking water can lead to many health problems, including hypertension, kidney stones, brain dysfunction, and systemic acidosis (Alka and Casey 2014).

Sulfates (SO_4^{2-})

Examination of the map shows that sulfate concentrations are high at wells P1 (350 mg/L), P7 (280 mg/L), and P8 (260 mg/L). This explains the influence of the discharges from the power plant close to these water points. It is inspired by the additional precipitation of sulfides resulting from the activity of the stray electric current, followed by oxidation-reduction

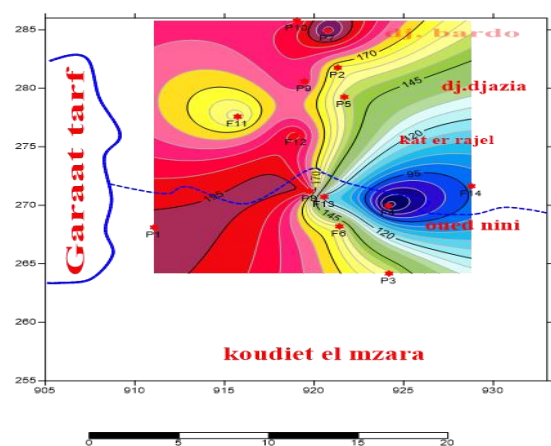
reactions under the effect of rainfall, which will produce an infiltration of sulfate ions into the groundwater, resulting in the bad odor, which is quite noticeable despite the absence of sewage networks in this area. There is a possibility of the dissolution of SO_2^- rich formations such as quaternary clay (Figure 4f).

The presence of gypsiferous inclusions ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and evaporitic saline rocks (Na_2SO_4) would also be responsible for the increase in sulfate content. The sulfate values found at the other sampling points studied are between 30 and 250 mg/L and remain below the maximum permissible concentration decreed by the standard imposed by the WHO (250 mg/L). In humans, the high content of sulfate can cause intestinal problems such as diarrhea (Heizer et al., 1997)

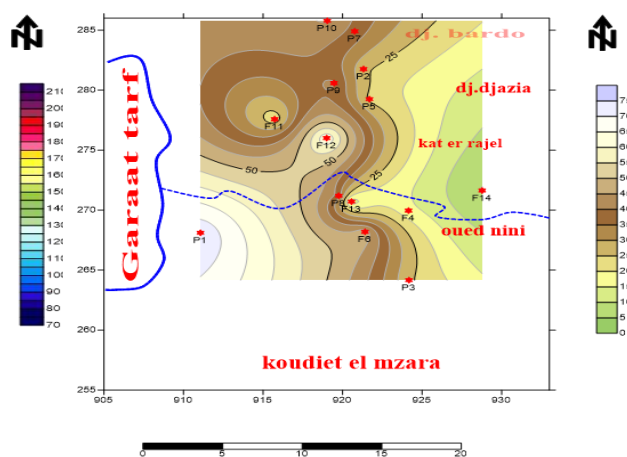
Nitrates (NO_3^-)

The nitrate levels are alarming, as they exceed by far the WHO potability standards, which recommend a maximum limit value of 50 mg/L for natural waters. The contaminated foci are located in the north and northwest of F'kirina town; this is attributed to agricultural pollution caused by using natural and artificial nitrate fertilizers in crops and intensive livestock farming. In the southwest, water contamination is attributed to the domestic wastewater of the agglomeration of F'kirina, which is discharged uncontrolled into Oued Nini (Figure 4g).

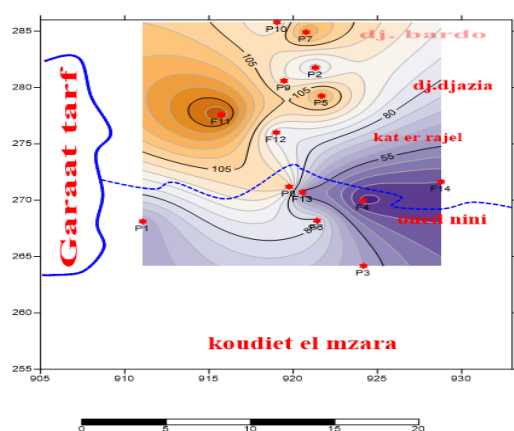
The high nitrate level above the allowed values in drinking water causes considerable health risks for the population (Zendehbad et al., 2022). For example, methemoglobinemia in bottle-fed infants under six months occurs when nitrates (NO_3^-) transform into nitrites (NO_2^-) in the stomach. The oxidation process leads to the transformation of hemoglobin into methemoglobin, which reduces the oxygen transport capacity of the blood (Riaz et al., 2024, Shaban et al., 2023). Also, other studies reported that a high concentration of nitrate can cause stomach cancer (Saraswat et al., 2023).



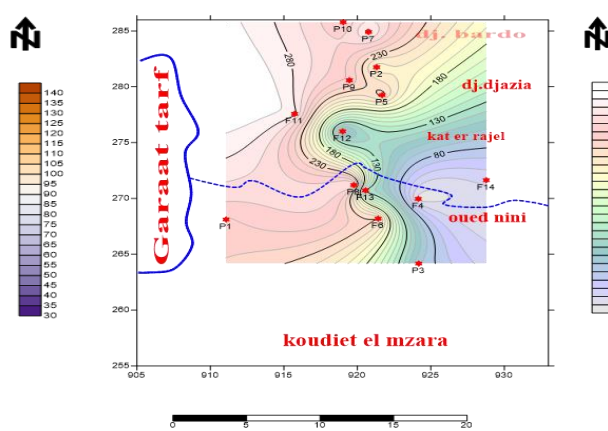
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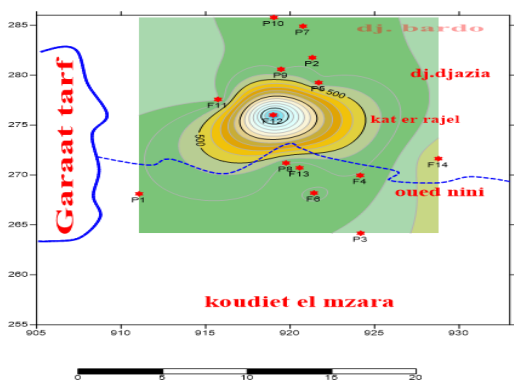
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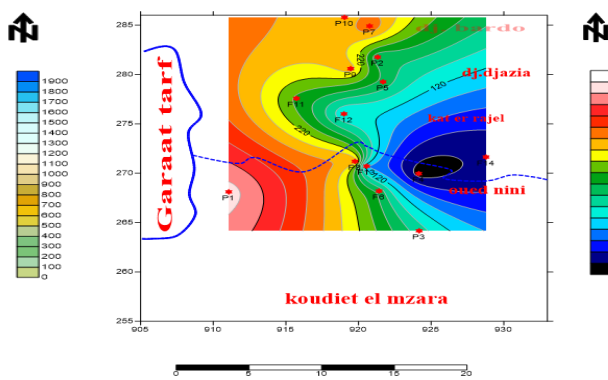
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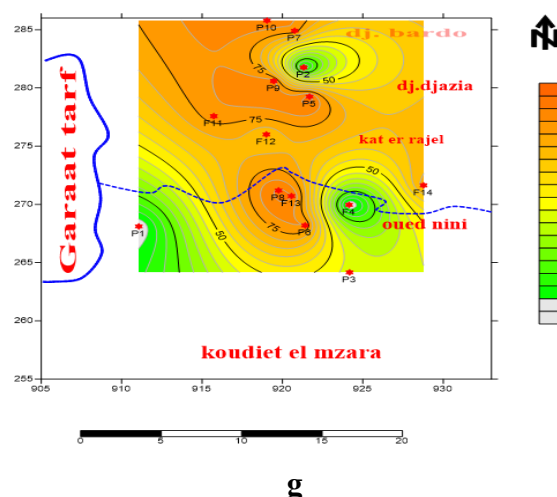


Figure 4. Spatial Variation of chemical parameters levels in groundwater of the study area; **a:** Calcium, **b:** Magnesium, **c:** Sodium, **d:** Chloride, **e:** Bicarbonate, **f:** Sulfate, **g:** Nitrate

Statistical study

Study of the eigenvalues (Diagonalization)

The analysis used three factors, and the eigenvalues of the factors of each factorial axis are presented in Figure 5. These values are expressed as the percentage of total variance as well as their accumulation. The first axis has an eigenvalue of 4.75, which explains 59.35 % of the total variance. The second axis has an eigenvalue equal to 1.37 (the percentage of variance expressed is 17.1 % for factor 2). The third axis has an eigenvalue of 0.98 or 12.24% of the total variance. The cumulative percentages of F1, F2, and F3 are successively 59.35 %, 76.44 %, and 88.69 %.

The representation using the first two factors gives a satisfactory account for the analysis approach of the variables and individuals and the structure of the scatterplots because they encompass all the information with 76.44 % of the total variance. We can also present the set of axes as a histogram of the information on each axis.

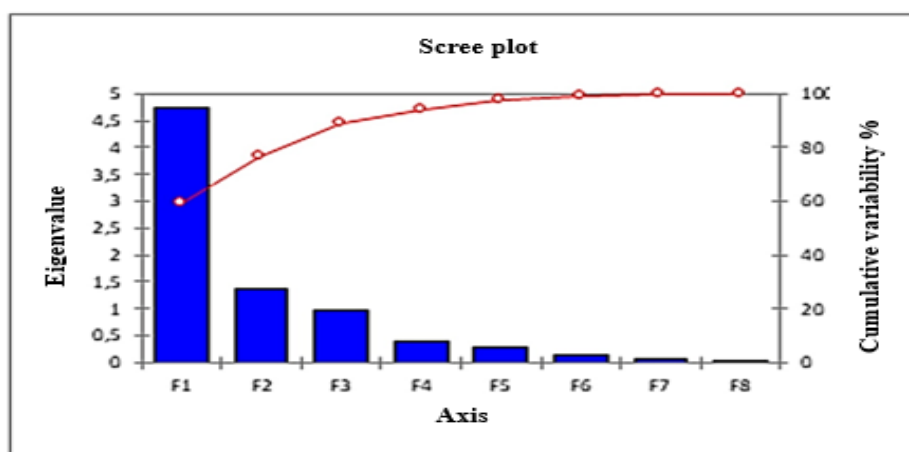


Figure 5. Histogram of eigenvalues

Study of the variables

In our case, the circle of correlations (Figure 6) shows that the elements Mg^{2+} , Na^+ , Ca^{2+} , K^+ , Cl^- , and SO_4^{2-} are significantly positively correlated to the I axis. These elements are also associated with each other; NO_3^- is significantly negatively related to axis II; HCO_3^- is significantly positively correlated to axis II.

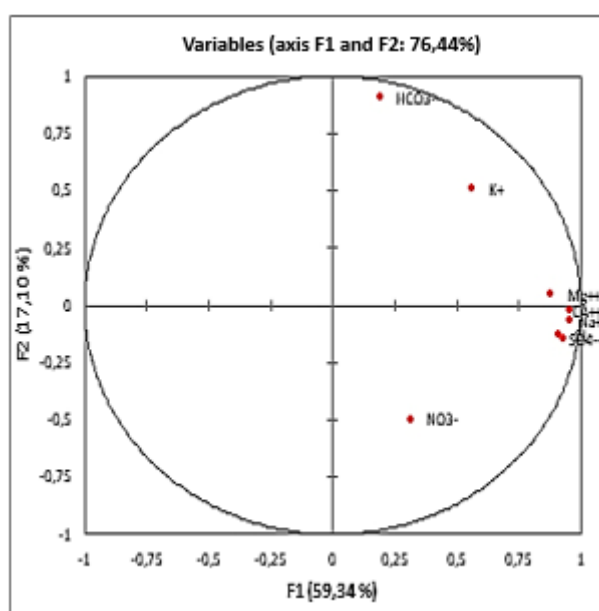


Figure 6. Correlation circle (axes 1 and 2)

The correlation circle is also useful to interpret the significance of the axes. In our case, axis I can be related to magnesium or hardness. Axis II is related to bicarbonate. The data

analysis is performed on 9 variables, and it shows a variance of 76.44 % on the I-II plane. Several relationships between the chemical elements were observed. Axis I (59.34 %) presents the salinity pole with a double hardness relationship and chemical components, indicating two different origins. On the one hand, a proportion with Na^+ and Cl^- indicating a natural origin of salinity (Sebkha), and on the other hand with Ca^{2+} , Mg^{2+} , SO_4^{2-} , Na^+ , and HCO_3^- , indicating a continental origin (Evaporitic salinity).

Axis II (17.10%) indicates both the redox pole by an inverse relationship between bicarbonates HCO_3^- , and nitrates (NO_3^-) with the boreholes. To confirm the fact that a variable is strongly related to a factor, The higher the cosine (in absolute value), the more the variable is related to the axis. The closer the cosine is to zero, the less the variable is associated with the axis.

The results summarized in Table 1 indicates that the elements Mg^{2+} , Na^+ , Ca^{2+} , and SO_4^{2-} contribute to forming the I axis. Mg is strongly linked to axis I, and HCO_3^- is strongly linked to axis II, so we conclude that the principal component analysis shows that chlorides, sulfates, and sodium present significant concentrations, reflecting the salinity of the wells in the east and center of the plain. The leaching of salts and evaporation can explain this. The bicarbonates present important contents, showing the effect of the contributions made by the limestone edges. The important presence of nutrients can be linked to agricultural activities and the shallow depth of the works.

Table 1. Eigenvectors

Variables	F1	F2	F3
HCO_3^-	0.0882	0.7744	0.1154
SO_4^{2-}	0.4264	-0.1237	-0.1798
Cl^-	0.4195	-0.1131	-0.0739
NO_3^-	0.1439	-0.4246	0.7754
Ca^{2+}	0.4386	-0.0213	-0.0142
Mg^{2+}	0.4034	0.0397	-0.2998
Na^+	0.4390	-0.0563	-0.0387
K^+	0.2568	0.4321	0.5061

Result for the hierarchical ascending classification in the study area

The hierarchical ascending classification of Ward (1963) was then used to group the cells

into sample groups. The number of classes is then determined according to the chosen Euclidean distance. Thus, a distance of 0.6 results in the distribution of 6 classes, a distance of 0.8 results in 4 classes, and a distance of 1 distinguishes 3 classes of stations.

The choice of the number of classes resulting from this classification is left to the user; it must, therefore, be determined according to the objectives of the application and the appreciation of the analysis. In the context of this work, we have chosen to distinguish four (4) classes of parameters with a cutoff at the Euclidean distance of 0.8 because it is a good compromise between a limited number of classes and a good representation of the differences in properties. The four classes thus obtained are represented in Figure 7.

Similar to most studies focusing on pollution, the electricity power plant showed indicators of groundwater pollution in the F'kirina Plain. In fact, the results were expected because, rarely, humans practice industrial activities that do not contribute to environmental pollution. The danger will remain unless local authorities take preventive and remedial solutions in the short and long term. Risk can be reduced by implementing a mitigation strategy with best management practice.

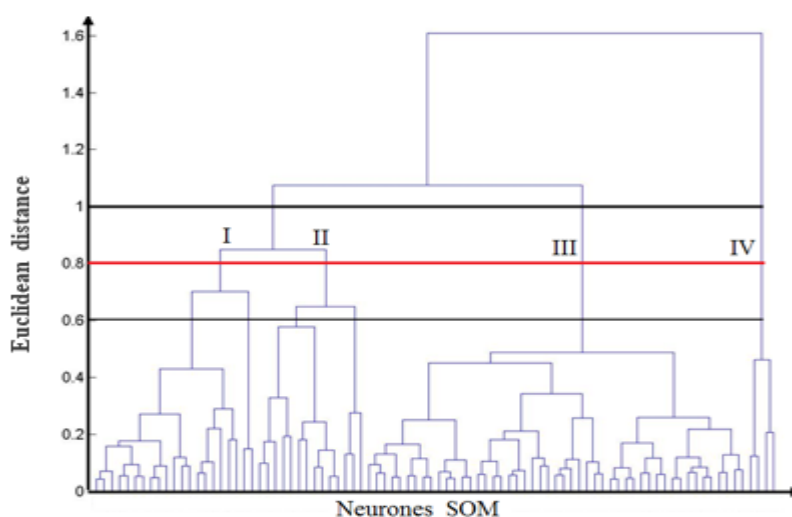


Figure 7. Classification tree of the physico-chemical parameters of the groundwater of the F'kirina plain with the method of topological maps (SOM)

Conclusion

The results of the physicochemical analyses allowed us to evaluate the impact of industry and agriculture activities, as well as anarchic urbanization related to demographic growth, on the

groundwater of F'kirina Plain. The available geological studies show that the F'kirina plain is a meo-plio-quaternary formation, while the local hydro-climatic conditions show that the plain of F'kirina is located in a semi-arid bioclimatic stage. Also, interpretation of results allowed us to characterize the quality of this water resource and its spatial and temporal evolution, which reported being highly exposed to pollution originating from domestic discharges, discharges from the local electricity power plant, and fertilizer used in agriculture. This worrying situation affects environmental and public health and it is important to take some urgent preventive and curative measures, such as ensuring the continuous work of the existing purification station within the gas turbine plant, building a wastewater treatment plant appropriate to the surrounding agglomerations of population in the F'kirina Plain, and rationalizing the use of chemical fertilizers in agriculture. However, continuous and periodic monitoring of the groundwater quality is mandatory to avoid various health and environmental disasters.

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