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Evaluating Groundwater Potability and Health Risks from Nitrates in the Semi-Arid Region of Algeria

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ABSTRACT

In the semi-arid region of Ain Ouassera, Algeria, groundwater from the lower cretaceous aquifer (LC) serves as an essential resource for drinking and various other requirements. This study focuses on evaluating the suitability of water for domestic use and examining the non-carcinogenic health risks associated with consuming water containing high levels of nitrates. To explore these dimensions, the research utilizes the water quality index (WQI) method and the health risk assessment (HRA) model as formulated by the USEPA. The findings categorized the groundwater quality predominantly as "poor" for consumption purposes, with nitrate concentrations ranging from 14 to 112 mg/L, where 40% of the samples exceeded the World Health Organization's (WHO) permissible limit (> 50 mg/L). Furthermore, the health risk analysis indicated that 76.67% of the samples for children and 70% for adults surpass the safety thresholds (QH > 1), signifying a significant risk to the local population. The study also uncovered that the hydrochemical characteristics of the groundwater reflect a mixed composition (CaMgCl) and that mineralization is mainly attributed to the dissolution of carbonates, sulfates, and halite, alongside inverse ion exchange processes and anthropogenic influences. These findings underscore the urgent need for improved groundwater management measures and risk mitigation strategies in the Ain Ouassera region.

Keywords: ain ouassera, health risk assessment, nitrate, water quality index, hierarchical cluster.

INTRODUCTION

In arid and semi-arid regions, such as those covering a large part of Algeria, limited access to surface water resources has historically forced populations to rely heavily on underground aquifers to meet their water needs. This increasing dependence is exacerbated by the overexploitation of aquifers, their gradual depletion, and contamination from anthropogenic activities, threatening the sustainability of these vital water resources. Among the contaminants, nitrates emerge as a major concern, with their presence in groundwater often attributed to intensive agricultural practices and inadequate urban wastewater management (Bouselsal and Saibi, 2022; Ouarekh et al., 2022; Arfa et al., 2022). Ain Ouassera, located in the steppe region of central-northern Algeria, heavily depends on its underground aquifers for a variety of needs, including industrial, agricultural, and residential purposes. The Lower Cretaceous aquifer stands out for its significant hydraulic potential and accessibility (ANRH, 2014; Azlaoui et al., 2021), playing a crucial role in the region's water supply. However, the increasing water demand, coupled with challenges posed by climate change, has led to a decrease in aquifer piezometric levels and a significant deterioration in water quality, notably due to excessive mineralization and notable nitrate pollution. This is primarily attributed to the infiltration of untreated urban wastewater and agricultural drainage waters enriched with fertilizers. Although the scientific literature widely acknowledges the dangers posed by nitrate contamination to water quality and public health, including risks such as methemoglobinemia in infants and increased risks of thyroid diseases and certain long-term cancers (Kumar et al., 2019; Adimalla, 2021; Kharroubi et al., 2024), Ain Ouassera has benefited from only a few studies exploring its water resources (ANRH, 2014) and the hydrochemical characterization of its groundwater (Azlaoui et al., 2017; Azlaoui et al., 2021). These studies have highlighted major challenges related to water quality but have left a significant gap in research on the specific health risks posed by nitrate exposure in this particular region. Despite the recognition of these issues, studies dedicated to evaluating the health risks associated with consuming water contaminated with nitrates in specifically arid and semi-arid contexts, such as Ain Ouassera, remain scarce. This deficiency underscores the urgency and importance of conducting in-depth research to understand and mitigate the impacts of nitrate pollution on public health in this critical area. Addressing this gap, the present study aims to make a significant contribution to understanding the dynamics of groundwater quality in the Ain Ouassera region, with a particular focus on nitrate contamination. Our objectives are twofold: firstly, to assess the water quality of the Lower Cretaceous aquifer in terms of potability and safety for human consumption; and secondly, to quantify the health risks associated with the presence of nitrates for different age groups of the local population. By employing rigorous analytical methods, including statistical analysis, water quality indices, and health risk assessments in accordance with USEPA models, this research aims to provide a solid foundation for water management policies and risk mitigation strategies in the region. In addressing these objectives, our work not only seeks to fill a critical gap in the existing literature but also to raise awareness of public health issues related to water quality in semi-arid regions. Furthermore, it aims to offer concrete recommendations to policymakers for the development of sustainable water resource management strategies, essential for the health of local ecosystems and the well-being of dependent communities.

MATERIALS AND METHODS

The study area

Ain Oussera is situated in the steppe region in the central-northern part of Algeria (Fig. 1), flanked to the north by the Tell Atlas and to the south by the Saharan Atlas. This area lies roughly 200 km away from the capital of Algeria. The geographic extent of Ain Oussera spans about 100 km from northeast to southwest and 38 km from east to west, encompassing an overall area of roughly 3800 km^2 as of 2012 (Azlaoui et al., 2017). The terrain in Ain Ouassera features elevations varying between 635 meters and 1200 meters. Characterized by a semi-arid climate, it receives scant and erratic annual rainfall, averaging around 250 mm, while annual evapotranspiration amounts to 686 mm. This surpasses the rainfall levels, signifying a deficit in water availability. The geological mapping of Ain Ouassera unveils a prominent anticlinorium with a Cretaceous core, further complicated by a series of anticlines on its southern and northern flanks. These structures extend along an axis that passes through Bou Cedraïa, as indicated by drilling data (Fig. 2) (Azlaoui et al., 2021). This data highlights the dominance of Cretaceous formations, particularly outcropping in the southern part of the studied area, primarily consisting of fine sandy clays, sandy limestones, and coarse sandstones, interspersed with limestone and marl layers. From a hydrogeological perspective, the study area hosts three aquifers with distinct hydraulic potentials (ANRH, 2013; Azlaoui et al., 2021): (i) the Plio-Quaternary aquifer horizon, characterized by highly permeable conglomerates extensively distributed across the plain; (ii); the Turonian aquifer, mainly comprised of dolomitic limestone with limited hydraulic potential; and (iii); the lower Cretaceous (LC) aquifer, identified as Ain Ouassera principal water source. This aquifer exhibits notable characteristics due to its shallow depth and significant thickness, ranging between 85 and 225 meters for the Albian and exceeding 500 meters for the Barremian. The general flow direction of this aquifer is from south to north, thus following the geological gradient (Azlaoui et al., 2017; ANRH, 2014). Water drilling within this zone has yielded flow rates between 25 and 70 l/s. The variability in transmissivity values, from 10^{-3} and 10^{-5} m^2/s, underscores its crucial role in the region's water supply, affirming its central importance in the hydrological management of Ain Ouassera.

Sample collection and laboratory analysis

In the study region, groundwater samples were collected from 30 wells tapping into the

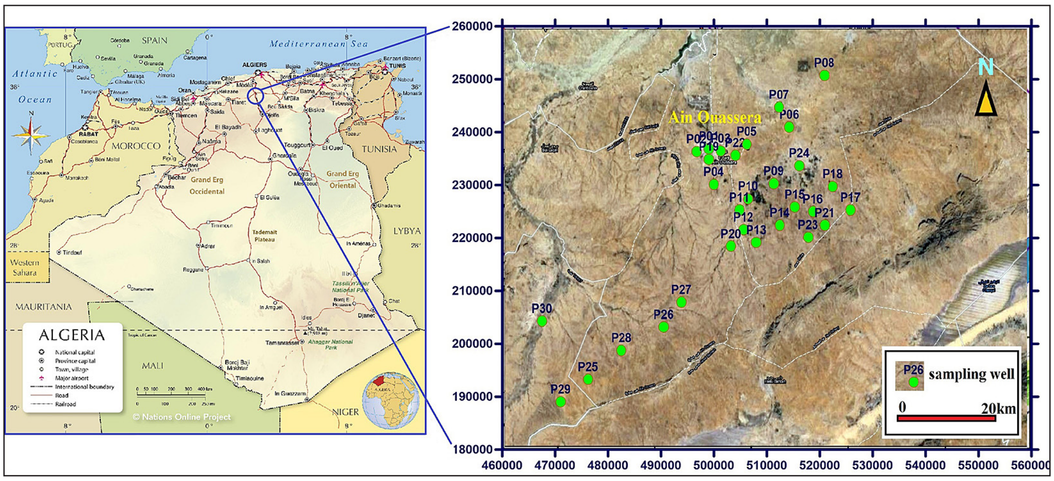

Figure 1. Situation map and inventory of water samples analyzed

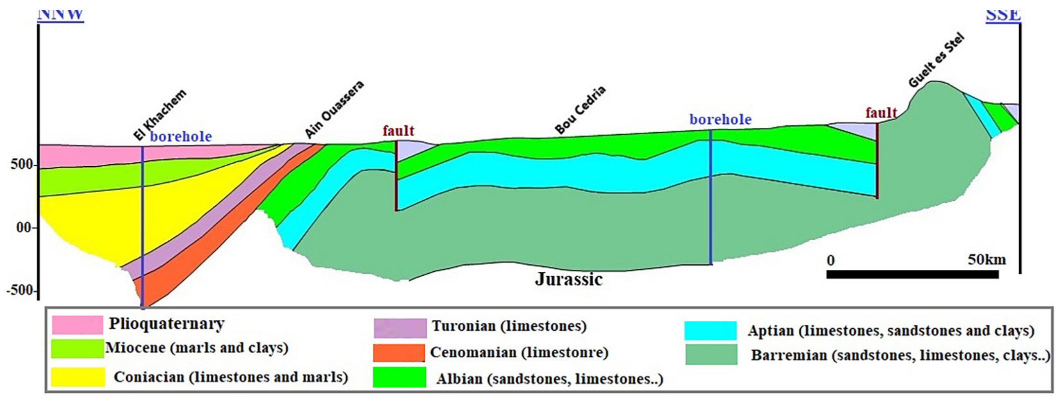

Figure 2. Geological section in the study area

Lower Cretaceous aquifer of Ain Ouassera (Fig. 1). The sampling points were localized using GPS coordinates. Before collection, the wells were subjected to a five-minute pumping procedure, and the sampling bottles were rinsed with the water from the wells being sampled. Two distinct sets of 500 ml plastic bottles; one for cation analysis and the other for anion analysis, were employed for each sampling site. High-purity HNO_3 was added to the samples intended for cation analysis to acidify them to a pH of 2 in the field. Using a portable, waterproof, multiparameter measuring device from Hanna, physicochemical parameters, including total dissolved solids (TDS), pH, and electrical conductivity (EC), were measured immediately after sample collection. A flame photometer was utilized to quantify major cations such as Na^+, Ca^{2+}, and K^+, while an inductively coupled plasma mass spectrometer (ICP-MS) was used for the quantification of the principal ion Mg^{2+}. The argentometric titration method was employed to determine chloride (Cl^-) content. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) concentrations were quantified using standard H_2SO_4 titration. Furthermore, sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations were measured using a UV spectrophotometer.

Water quality index

Horton first presented the water quality index (WQI) approach in 1965. In general, as Abbasnia A al in 2018 noted, the WQI is modified to match certain water utilization scenarios. We focused on WQI as it relates to human consumption in our investigation. Three main processes were involved in calculating our WQI: choosing parameters, identifying sub-indices, and applying a mathematical formula to combine these sub-indices (Boussaada et al., 2023; Tiwari et al., 2017). We used the weighted arithmetic index approach (Hammed et al., 2023; Bouselsal and

Saibi, 2022) to compute the *WQI*. The following equation is used to calculate the values of the water quality index:

$$WQI = \frac{\sum_{n}^{i=1} w_i Qi}{\sum_{n}^{i=1} w_i} \quad (1)$$

For each metric, the recommended standard (Si) was subtracted from the relative weight (*Wi*) (WHO 2017).

$$Wi = k/s \quad (2)$$

And the following formula can be applied to determine the values of *Qi*.

$$Qi = \frac{(\mathrm{Vi}-\mathrm{V0})}{(\mathrm{Si}-\mathrm{V0})} \quad (3)$$

where: Q_i – water quality rating of the n^th^ parameter, W_i – weight of the n^th^ parameter (Table 1), V_i the measured value of the n^th^ parameter, V_o – the ideal value of water quality.

Regular techniques are used to determine the *Wi* unit weight and *Qi* quality rating. For each parameter, the recommended standard (*Si*) is prescribed and its relative weight (*Wi*) is determined.

Human health risk assessment

The health of people may be harmed by consuming water that contains an excessive amount of nitrates. Nitrate concentrations in the CI aquifer's groundwater were compared to allowable limits while accounting for the age and sex of the subjects in order to determine the degree of non-carcinogenic hazard (Adimalla and Qian, 2019). The health risk assessment method was created by the US Environmental Protection Agency (USEPA, 2014; USEPA, 2013; USEPA, 1989) to evaluate and measure detrimental effects on human health (Zhang et al., 2015; Karunanidhi et al., 2020; Kumar et al., 2019). Numerous researchers worldwide have utilized equations (Equation 4) to evaluate health hazards through the calculation of the chronic daily intake (*CDI* (mg/kg/day)). Table 2 offers a thorough summary of the information.

$$CDI = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad (4)$$

In this equation, *C* denotes the concentration of the specific element or pollutant in milligrams per liter (mg/l); *IR* signifies the daily intake rate, which, based on field surveys and climatic studies, is determined to be 3 liters per day for adults (both women and men) and 1.5 liters per day for children; *EF* stands for the frequency of exposure in days per year, consistently set at 365 for both adults and children; *ED* represents the number of years an individual is subjected to the pollutant, calculated as 30 years for adults and 12 years for children; *BW* is the mean body weight, with adults averaging 57.5 kilograms and children 18.7 kilograms; *AT* refers to the total number of days over which exposure is averaged (365 * *ED*).

The potential non-carcinogenic risk from exposure to a contaminant is quantified through the hazard quotient (*HQ*) (Kharroubi et al., 2024; Kaur et al., 2020; Shaikh et al., 2020), which is derived using the formula outlined in Equation 5. This metric is instrumental in assessing the health risks contaminants in water may pose, serving as an essential evaluation tool within the field of environmental health:

$$HQ = \frac{CDI}{RfD} \quad (5)$$

Table 1. Weight of useful parameters for calculating WQI

Parameter	qi	Si	Wi
pH	4	8.5	0.114285
Electrical conductivity	4	1500	0.114285
Total dissolved solids	5	500	0.114285
Calcium	2	75	0.0571428
Magnesium	1	50	0.0285714
Sodium	2	200	0.0571428
Potassium	2	12	0.0571428
Chloride	3	250	0.085714
Bicarbonate	3	300	0.085714
Sulfate	4	250	0.114285
Nitrate	5	50	0.114285
Total	35	–	1

Table 2. Hydrochemical parameter variation in LC groundwater

Well	WHO Standards 2017	Mean	Min	Max	S–D
pH	6.5–8.5	7.28	6.77	7.72	0.25
TDS (mg/l)	500–1500	1375	1032	1505	133.31
EC (µS/cm)	500–1500	2150	1618	2352	207.62
SO_4^{2-} (mg/l)	250–400	378	249	450	73.54
Cl^- (mg/l)	250–600	381	180	468	101.93
HCO_3^- (mg/l)	300–600	206	163	218	13.43
NO_3^- (mg/l)	50	48	14	112	26.07
Ca^{2+} (mg/l)	75–200	138	100	156	15.21
Mg^{2+} (mg/l)	50–150	68	44	90	15.94
Na^+ (mg/l)	200	203	110	250	39.37
K^+ (mg/l)	12	19	12	28	4.87
TH (mg/l)	100-500	628	480	750	98

Here, the reference dose (*RfD*) for nitrate, a common contaminant, has been established at 1.6 mg per kilogram per day (Adimalla and Qian, 2019). A hazard quotient (*HQ*) exceeding 1 signals an unacceptable contaminant level in drinking water, indicating a potential health hazard. On the other hand, an *HQ* below 1 is deemed to indicate a contaminant level that is generally considered safe for human health (Kaur et al., 2020).

Multivariate statistical analysis

In order to shed light on hydrochemical processes, this work uses three well-known multivariate statistical techniques: principle component analysis (PCA), hierarchical cluster analysis (HCA), and multiple correlation analysis (MCA). The software XLSTAT was used to implement these techniques. To investigate relationships within the dataset, the Pearson correlation coefficient was used in this research. Correlation levels were classified as "very strong" ($\pm 1 < r < \pm 0.8$), "high" ($\pm 0.8 < r < 0.6$), and "low" ($0 < r < \pm 0.6$) according to their coefficient (r) values (Mudgal et al., 2009; Hammad et al., 2023; Bouselsal, 2016). Principal component analysis (PCA) was extensively utilized in this study. PCA, a widely recognized technique in multivariate statistics, is known for its applicability across various scientific disciplines (Kharroubi et al., 2022; Farhat et al., 2019; Mahanty et al., 2023). It focuses on analyzing interrelated dependent variables, representing observed data matrices. In this research, PCA aimed to identify factors influencing water chemistry by interpreting chemical loadings on principal components. Conversely, hierarchical cluster analysis (HCA) is widely utilized in the field of water quality analysis. It offers a structured methodology for categorizing extensive datasets into clusters by aligning them according to their common traits. To quantify the dissimilarities among groups of observations, Euclidean distances are employed. This technique facilitates the arrangement of data into discrete, albeit related, clusters, thereby uncovering inherent trends within water quality research.

RESULTS AND DISCUSSION

Groundwater hydrochemistry

The EC of the waters in the studied region exhibits a variation range from 1618 to 2352 µS/cm, with a significant average value of 2149 µS/cm. Notably, waters characterized by high conductivity are primarily located within the boreholes of Ain Ouassera city, particularly wells P1 and P2, with respective values of 2352 and 2342 µS/cm. Similarly, the total dissolved solids (TDS) concentration follows this trend, fluctuating between 1032 and 1505 mg/l, to stabilize at an average of 1375 mg/l (Table 2). Regarding pH, it varies from 6.77 to 7.72, averaging at 7.27, indicating a remarkable proximity to neutrality in the analyzed waters. Water hardness (TH), a key indicator of calcium and magnesium levels, reveals that the more these elements are present, the harder the water is considered. In the examined samples, calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations vary respectively between 100 to 156 mg/l and 44 to 90 mg/l. The hardness measured in the waters of this region varies between 480 and 750 mg/l, with an average of 628 mg/l, thus demonstrating that these waters are very hard (Sewyer and McMcartly, 1967; Arfa et al., 2022; Hammad et al., 2023).

Sodium (Na^+) concentrations prove to be high, exceeding the WHO standard of 200 mg/l in 80% of the analyzed wells, with a peak at 250 mg/l in well P21 and a minimum of 110 mg/l in well P30. Moreover, potassium (K^+) levels also exceed the WHO-recommended limit of 12 mg/l, reaching up to 28 mg/l in well P9, while the observed minimum is 12 mg/l in well P29, with an overall average of 19 mg/l. Regarding sulfate ions (SO_4^{2-}), their concentrations, when exceeding the drinking water guideline values, can cause digestive disorders such as diarrhea. 60% of the samples surpass the WHO limit, which is 400 mg/l (Tab. 2), according to the research, with concentrations varying from 249 to 450 mg/l and an average of 378 mg/l. Chloride (Cl^-) levels display variable concentrations, ranging from 180 mg/l in well P30 to 467 mg/l in well P22. Bicarbonate (HCO_3^-) contents lie between 163 and 218 mg/l, with an average of 205 mg/l. Lastly, nitrate (NO_3^-) concentrations range from 14 to 112 mg/l, with an average concentration of 47 mg/l, noting that 40% of the samples surpass the WHO limit. The high nitrate concentrations in arid and semi-arid zones in Algeria are attributed to the infiltration of drainage water from agricultural areas and wastewater from urban zones (Satouh et al., 2021; Bouselsal and Saibi., 2022).

Groundwater quality assessment

WQI simplifies the assessment of water quality by translating complex data into a singular indicator, making the information accessible and understandable to all. The development process of the WQI involves selecting essential parameters, creating sub-indices, assigning weights, and aggregating them (Abbasnia et al., 2018; Tiwari et al., 2014). Vital for assessing water quality for various uses, the WQI informs environmental policies, raises public awareness, and guides improvement actions, highlighting areas needing attention. The Water Quality Index determines water quality based on hydrochemical criteria and classifies it into different categories (Misaghi et al., 2017; Kebili et al., 2021): excellent (< 50), good (50 to 100), poor (100 to 200), very poor (200 to 300), and unsuitable for consumption (> 300). Analyses of groundwater samples from the LC in Ain Ouassera reveal a WQI ranging from 109 to 192, with an average of 159 (Table 4), indicating that this water is of poor quality for consumption.

WQI mapping, shown in Figure 3, reveals that the highest indices are located in Ain Ouassera, with values between 180 and 192, primarily resulting from contamination by infiltration of wastewater and sanitation water. Agricultural regions situated in the eastern and central parts of

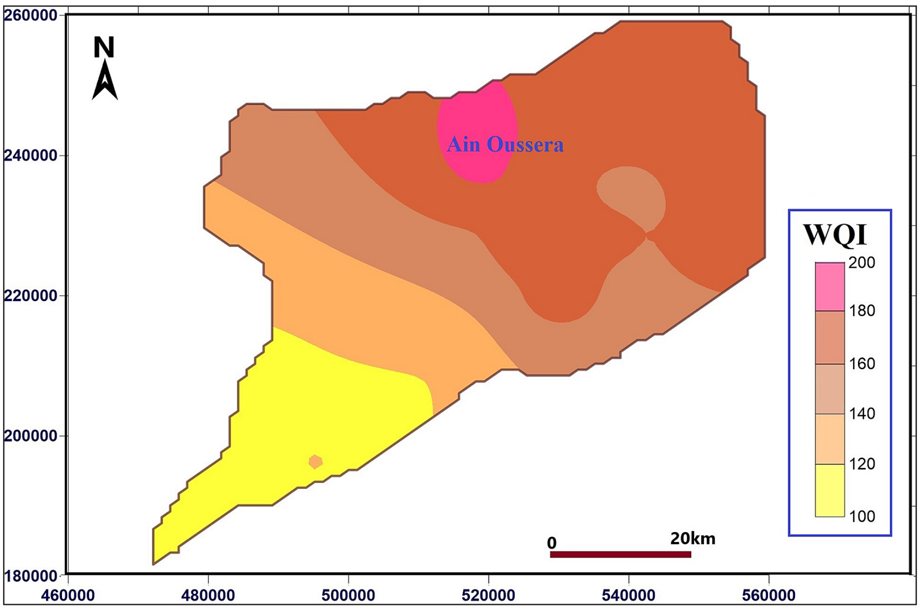

Figure 3. Water quality map of LC groundwater in Ain Ouassera

the study region display WQIs of 140 to 180, influenced by fertilizer use, drainage processes, and salt accumulation due to evaporation. In contrast, the southern part of the region, less affected by anthropogenic activities, exhibits the lowest WQI indices in the study area (less than 140).

Health risk assessment

Prolonged exposure to groundwater with high nitrate levels can have adverse health effects, including but not limited to premature births, birth defects related to the nervous system, low birth weight, thyroid disorders, multiple sclerosis, and diabetes (WHO, 2017; Adimalla, 2021; Azhdarpoor et al., 2019). Children are particularly susceptible to the harmful effects of nitrate-rich water consumption, presenting a higher non-carcinogenic health risk than adults. The detection of elevated nitrate levels in the region's aquifers raises concerns about the future exacerbation of this situation. According to the data from this region's study, presented in Table 2, 40% of groundwater samples exhibited nitrate levels exceeding the World Health Organization's recommended threshold (50 mg/L). It is therefore imperative to assess the long-term health hazards posed by these nitrates, especially since the local population largely relies on these resources for their drinking water supply. Young individuals appear to be the most affected by high nitrate concentrations in water, although evaluations have also been conducted among adults for a comprehensive understanding of health risks. Analyzes of chronic health risks associated with nitrate contamination of groundwater have been shown in Table 3. Chronic health risk indices (HQ) ranged from 0.21 to 5.61 for children and from 0.13 to 3.65 for adults, with respective averages of 2.30 and 1.50. These results reveal that 76.67% of samples in children and 70% in adults exceeded the safety threshold of 1.0, highlighting a significantly higher risk in young individuals compared to adults, 1.50 times greater (Das et al., 2023).

The distribution of HQ indices for childrens and adults, as illustrated by Figures 4 and 5, shows a prevalence of risk in Ain Ouassera city and the bordering agricultural areas, surpassing the safety threshold. In contrast, the southern sectors of the study indicate acceptable risk levels, underscoring the absence of harm in consuming groundwater in these areas. To address this situation, it is crucial for local water sector authorities to implement measures aimed at improving water quality for consumption. This includes establishing effective sanitation systems, reducing the use of chemical fertilizers in agriculture to decrease harmful infiltrations, and investing in advanced water treatment technologies, such as reverse osmosis and ion exchange, to reduce nitrate concentration in groundwater.

Multivariate analysis

Correlation matrix

The correlation matrix allows for the detection of existing links between different variables, whether positive or negative. It aggregates

Table 3. Variation of water quality and HQ for adults and children

Well	WQI	HQ-adult	HQ-children
P01	192	3.65	5.61
P02	183	3.00	4.61
P03	186	3.36	5.16
P19	181	2.48	3.81
P22	168	1.60	2.46
P05	174	1.83	2.81
P06	172	1.89	2.91
P07	168	1.37	2.11
P08	172	1.53	2.36
P09	177	2.05	3.16
P10	180	2.41	3.71
P11	174	1.57	2.41
P12	171	1.50	2.31
P13	179	2.35	3.61
P14	173	2.02	3.11
P15	170	1.83	2.81
P16	165	1.34	2.06
P17	170	1.70	2.61
P18	157	1.14	1.75
P04	163	1.34	2.06
P20	154	0.82	1.25
P21	149	0.62	0.95
P23	152	0.46	0.70
P24	153	0.88	1.35
P25	121	1.01	1.55
P26	119	0.36	0.56
P27	122	0.38	0.58
P28	116	0.19	0.30
P29	112	0.14	0.21
P30	109	0.13	0.21

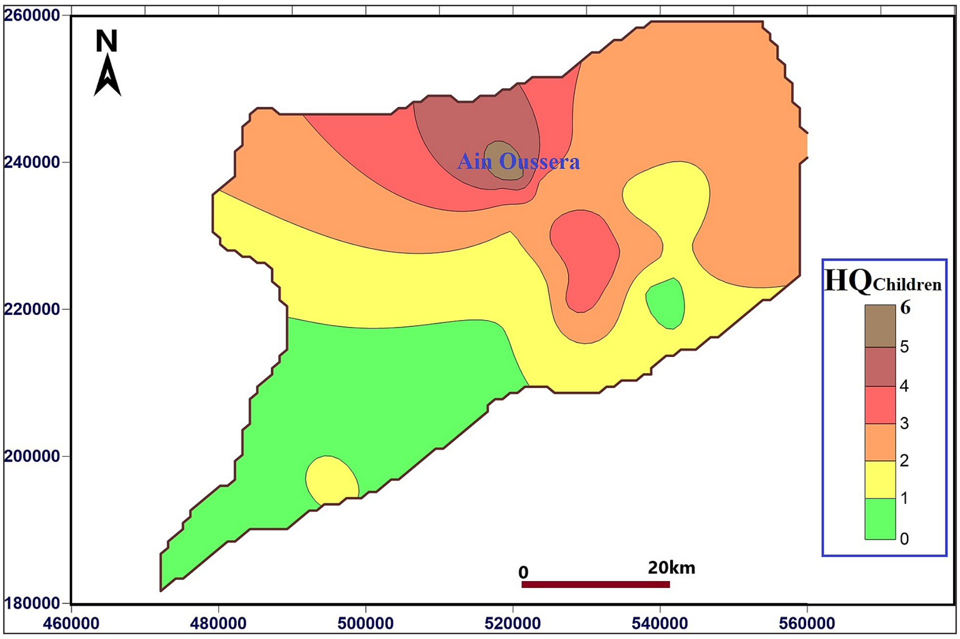

Figure 4. Adult HQ spatial distribution maps

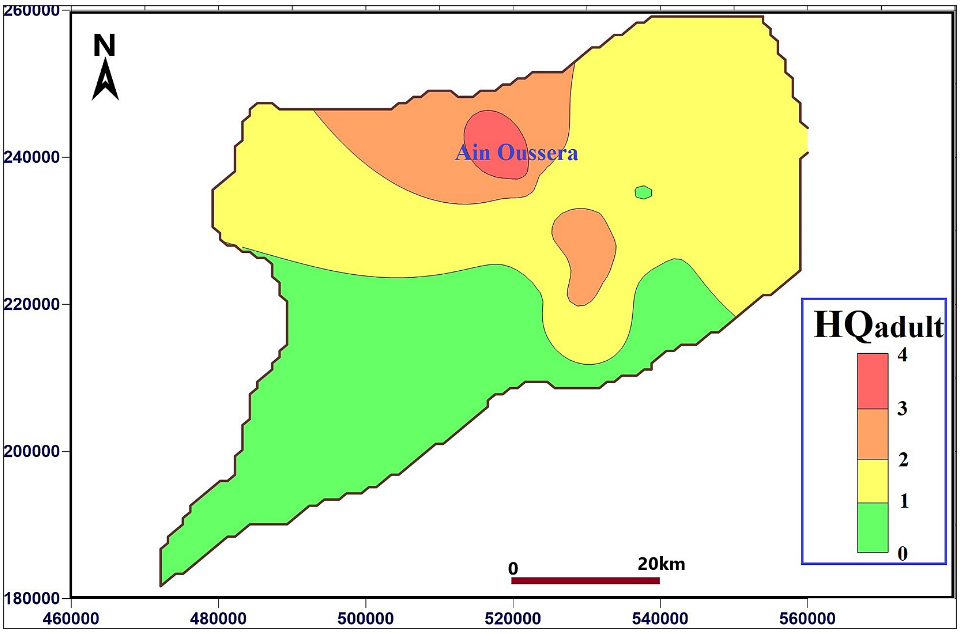

Figure 5. Children HQ spatial distribution maps

correlations among several variables and extracts coefficients indicating the influence variables have on each other. Examination of Table 5 related to the correlation matrix reveals that certain parameters are consistently correlated with each other in all analyses conducted, while others are correlated in one analysis but not in another.

Most correlations among groundwater parameters are positive. There is a strong correlation between electrical conductivity on one hand and chlorides, sodium, calcium, sulfates, potassium, and nitrates on the other. Similar correlations are observed between these parameters and TDS. In both cases, the correlation is positive and helps deduce the major elements responsible for the increase in mineralization and salinity in the studied waters (Bouselsal and Saibi, 2022; Bouselsal and Belksier, 2018; Hao et al., 2022).

Other significant correlations are found between calcium and chlorides, sodium and

Table 4. Correlation matrixes of hydrogeochemical parameters of LC groundwater

Variables	pH	TDS	EC	SO_4^{2-}	Cl^-	HCO_3^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
pH	1	0.29	0.29	0.05	0.29	-0.29	0.46	0.25	-0.30	0.27	0.18
TDS		1	0.97	0.77	0.93	0.42	0.72	0.75	0.51	0.92	0.64
EC			1	0.776	0.93	0.42	0.72	0.75	0.51	0.92	0.68
SO_4^{2-}				1	0.80	0.73	0.34	0.89	0.82	0.81	0.26
Cl^-					1	0.34	0.54	0.79	0.51	0.99	0.47
HCO_3^-						1	0.06	0.62	0.79	0.39	0.09
NO_3^-							1	0.36	0.15	0.51	0.73
Ca^{2+}								1	0.75	0.79	0.30
Mg^{2+}									1	0.51	0.10
Na^+										1	0.43
K^+											1

chlorides, bicarbonate and calcium, bicarbonate and magnesium, sulfates and calcium, and sulfates on one hand and sodium, magnesium, and calcium on the other. These relationships illustrate the complexity of geochemical mechanisms governing the mineralization of groundwater in the Lower Cretaceous aquifers of the studied area, including the dissolution of sulfates, carbonates, and halite.

Principal component analysis

Ain Ouassera's groundwater data, which included thirty samples and eleven parameters for Principal Component Analysis (PCA), have provided important insights into the geochemical processes that determine the composition of the groundwater. The results show that the first two main components, which together account for 81.13% of the variance in the sample (Fig. 6), efficiently capture important differences. More specifically, a strong association is shown between total dissolved solids, electrical conductivity, and the amounts of calcium, magnesium, sulfate, nitrate, and chloride ions. PCA1 accounts for 61.06% of the variation. This association emphasizes how natural geological processes have a major influence in influencing the salinity and mineralization of the groundwater in this region (Ouarekh et al., 2022; Bousselsal and Saibi, 2022). Furthermore, the second principal component (PCA2), accounting for 20.07% of the variance, highlights the impact of human activities and reverse ion exchange mechanisms on the chemical composition of the waters. This clear distinction between natural and anthropogenic factors in the PCA provides valuable insights into the multiple forces at play in groundwater dynamics, emphasizing the importance of considering both geogenic and anthropogenic contributions in water quality assessments.

Hierarchical cluster analysis

The technique of hierarchical clustering analysis is widely used for categorizing water samples in numerous investigations, is grounded in a comprehensive analysis of multiple parameters, resulting in the grouping of samples by their mutual similarities (Egbueri, 2019; Kharroubi et al., 2024). The dendrogram produced by this approach, which employs Euclidean distance, uncovers distinct clusters. Within each cluster, samples exhibit greater resemblance to each other than to samples from different clusters. In the context of this research, Hierarchical Cluster Analysis (HCA) identified three main clusters (Fig. 7):

- Cluster 1: This group comprises samples with an electrical conductivity exceeding 2280 µS/cm and exceptionally high nitrate levels (81 ± 25 mg/l), primarily located in and around the city of Ain Ouassera. The high electrical conductivity and nitrate concentrations can be attributed to anthropogenic contamination, resulting from industrial activities and the percolation of wastewater, contributing to an increase in dissolved ions.
- Cluster 2: Samples in this group, characterized by an electrical conductivity ranging between 2280 and 1900 µS/cm and relatively high nitrate contents (45 ± 17 mg/l),

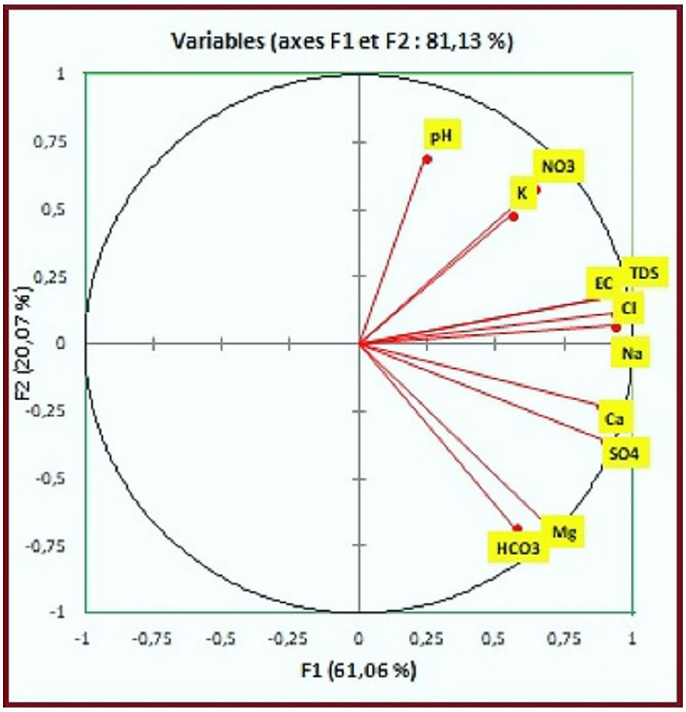

Figure 6. Principal component analysis

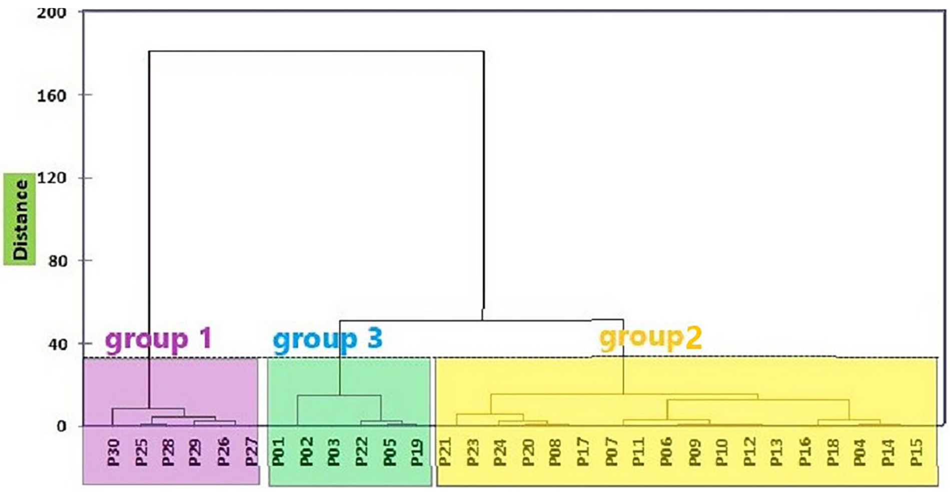

Figure 7. Hierarchical cluster analysis CI Ain Ouessara

mainly come from the agricultural areas of the central and eastern parts of the region. These groundwater sources are influenced by the infiltration of irrigation waters laden with chemical fertilizers and dissolved salts, a consequence of evaporation under a semi-arid climate.

- Cluster 3: Including samples with an electrical conductivity below 1900 µS/cm and lower nitrate levels (20 ± 6 mg/l), this group is located in the southern part of the region, an area less affected by urbanization and agricultural activities.

Groundwater hydrochemistry

Hydrochemical facies

The Piper plot, developed in 1944, is a graphical tool for analyzing the cationic and anionic compositions of waters, visually displaying major trends and clusters. It features two triangles for cations and anions and a central diamond for overall analysis, facilitating the identification of water's chemical facies. Used to compare multiple analyses and track water quality, the plot allows for the visualization of precipitation or dissolution processes. However, since it expresses

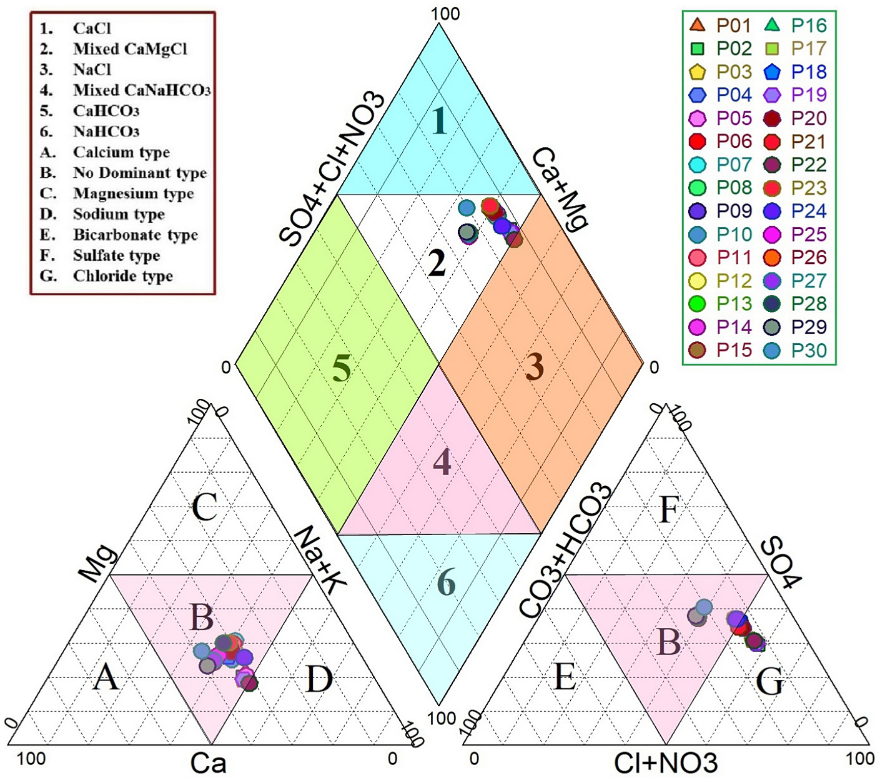

Figure 8. Piper plot of LC groundwater samples

analyses in percentages, it requires careful interpretation for direct comparisons due to the lack of visibility on absolute concentration variations.

The representation of the chemical analysis results on the Piper plot (Fig. 8) highlights a significant variation in the chemical composition of the examined groundwater. The projection of the analysis data onto this plot reveals that the predominant chemical facies of the waters in the study area is mixed CaMgCl type. This composition is in conformity with the lithology of the aquifer, which consists of a mixture of sandstone, limestone, clay, and marl. Interactions between these types of rocks and groundwater lead to significant variations in the proportions of chemical ions, thus influencing the hydrochemical facies of the groundwater.

Groundwater source solute

The fundamental hydrochemical mechanisms influencing the mineralization of groundwater include ion exchange reactions with surrounding rocks, the dissolution of saline minerals, acid-base interactions, ion exchanges, and human activities. The chemical composition of groundwater is often analyzed using bivariate diagrams, based on the concentrations of compounds in meq/l (Hao et al., 2022; Kharroubi et al., 2022). The selection of these diagrams follows an examination of the lithological composition of the aquifer and the establishment of correlation links between the different chemical compounds present in the water.

Theoretically, the main cations and anions in the waters result from the dissolution of evaporites like halite (Equation 6) and gypsum (Equation 7), or from the alteration of carbonates through the dissolution of dolomite and calcite (Equation 8 and 9). Under such conditions, the Na/Cl and Ca + Mg/HCO_3 + SO_4 ratios should theoretically balance to 1. Therefore, for bivariate analyses of Na^+ relative to Cl^- and Ca^{2+}+ Mg^{2+} relative to HCO_3^- + SO_4^{2-}, water samples are positioned on the line representing the 1:1 ratio.

$$NaCl \rightarrow Na^+ + Cl^- \quad (6)$$

$$CaSO_4 \cdot 2H_2O \rightleftarrows Ca^{2+} + SO_4^{2-} + 2H_2O \quad (7)$$

$$CaCO_3\,(calcite) + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (8)$$

$$CaMg\,(CO_3)_2\,(dolomite) + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4(HCO_3^-) \quad (9)$$

The bivariate plot of Na^+ against Cl^- (Fig. 9a) indicates that most points slightly deviate from the 1:1 line, signaling that sodium concentration is affected by reverse ion exchange with the reservoir clays, which absorb Na and release Ca^{2+} and Mg^{2+}, although the source of sodium and chloride is mainly due to the dissolution of halite (Hao et al., 2020; Xiao et al., 2021). The graph of (Ca^{2+} + Mg^{2+}) against (SO_4^{2-} + HCO_3^-) illustrates the dissolution of sulfates and carbonates as well as the alteration of silicates (Touahri et al., 2022). As shown in Fig. 9b, samples from the CI aquifers of Ain Ouassera distribute slightly below the 1:1 line, revealing that in addition to the dissolution of carbonates and sulfates influencing water mineralization, CI groundwater is also affected by reverse ion exchange, leading to a decrease in Na^+ and K^+ ions and an increase in Ca^{2+} and Mg^{2+} ions. The chloro-alkaline index (CAI-1), according to Schoeller (1965), is crucial for evaluating the composition of groundwater and their interactions with geological formations. CAI-1 identifies the ion exchange processes influencing the chemistry of groundwater in the studied area and is calculated as follows, using meq/l unit for each ion:

$$CAI-1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \quad (10)$$

Schoeller (1965) said that reverse ion exchange is signaled by positive values of CAI-1, whereas negative values indicate normal ion exchange. According to Zhang et al. (2021), 80% of the study's samples have positive CAI-1 values (Fig. 9c), indicating that these samples go through a reverse ion exchange process in which Ca^{2+} and Mg^{2+} ions from the aquifer's constituent materials replace Na^+ and K^+ ions. The saturation index (SI) is used to quantify the tendency of minerals to dissolve or precipitate in waters, indicating supersaturation (SI > 0), equilibrium (SI = 0), or undersaturation (SI < 0). The PHREEQC software is utilized to determine the SI of key aquifer minerals, providing insights into the hydrogeochemical processes affecting the quality of the studied groundwater. Figure 9d shows that, for carbonate minerals such as calcite, dolomite, and aragonite, in 60% of the analyzed wells, the saturation index values exceed zero, meaning a propensity for these minerals to

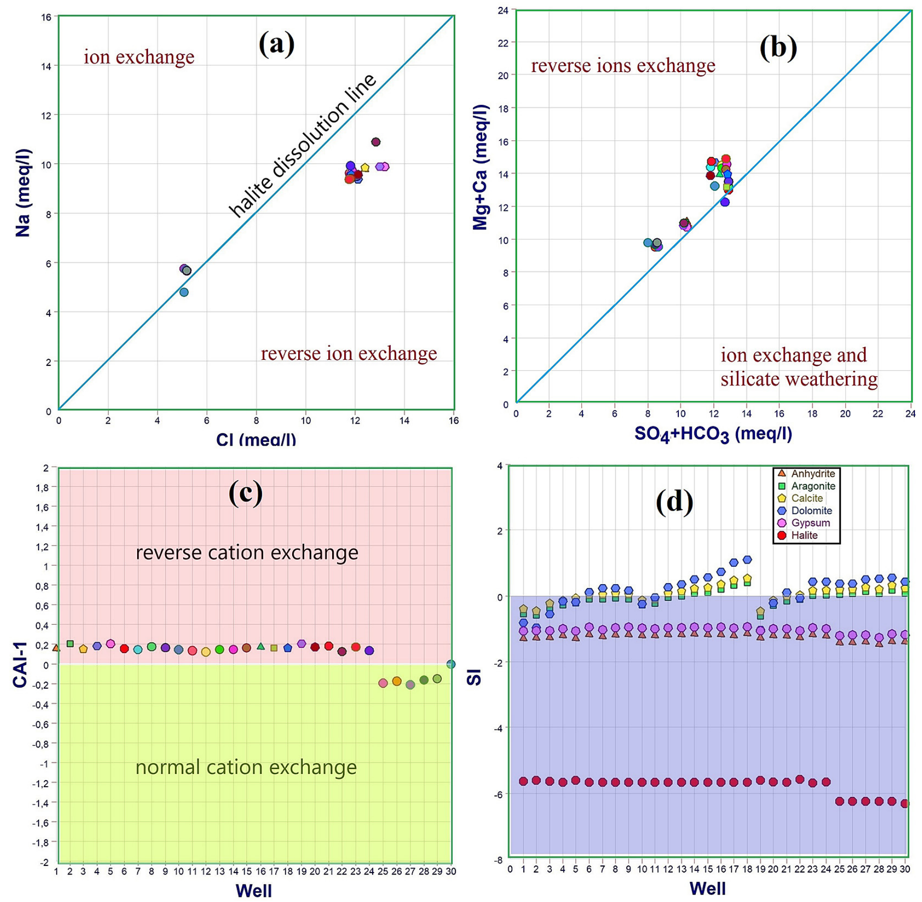

Figure 9. Diagrams (a to d) showcasing the interactions between major ions highlight the processes governing the chemical composition of CI groundwater

precipitate (Karmakar et al., 2021; Hao et al., 2020; Bouselsal, 2016). Conversely, for gypsum, anhydrite, and halite, the saturation indices are consistently negative for all tested groundwater samples, indicating that these minerals are in the process of dissolution in the examined area.

CONCLUSIONS

The current study was driven by two principal objectives: to evaluate the potability and safety of the Lower Cretaceous aquifer water in Ain Ouassera in terms of human consumption, and to quantify the health risks associated with nitrate presence across different age demographics within the local population. Employing a rigorous methodological approach that included statistical analyses, water quality indexing, and health risk assessments in accordance with USEPA models, this research provides a solid foundation for developing water management policies and risk mitigation strategies in the region.

Our findings indicate that the groundwater quality of the studied aquifer is predominantly classified as "poor" for consumption purposes, with nitrate concentrations exceeding the WHO permissible limits in 40% of the cases. Moreover, health risk analysis revealed that the local population, especially children, is exposed to heightened health risks due to the presence of nitrates. These observations underscore the urgency to intervene to improve the water quality of the Lower Cretaceous aquifer and to reduce nitrate exposure. This includes implementing more sustainable agricultural practices, enhancing water treatment systems, improving the sanitation systems, and formulating targeted public policies. Such actions are vital to ensuring safe drinking water and to protecting the health of local populations, while laying the groundwork for sustainable water resource management in the Ain Ouassera region.

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