



Article Identification of the Groundwater Quality and Potential Noncarcinogenic Health Risk Assessment of Nitrate in the Groundwater of El Milia Plain, Kebir Rhumel Basin, Algeria

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Abstract: In this study, we analyzed the quality and the potential noncarcinogenic health risk of nitrate in groundwater in the El Milia plain, Kebir Rhumel Basin, Algeria. Moran's I and the ordinary kriging (OK) interpolation technique were used to examine the spatial distribution pattern of the hydrochemical parameters in the groundwater. It was found that the hydrochemical parameters Ca, Cl, and HCO₃ showed strong spatial autocorrelation in the El Milia plain, indicating a spatial dependence and clustering of these parameters in the groundwater. The groundwater quality was evaluated using the entropy water quality index (EWQI). The results showed that approximately 86% of the total groundwater samples in the study area fall within the moderate groundwater quality category. The spatial map of the EWQI values indicated an increasing trend from the south-west to the northeast, following the direction of groundwater flow. The highest EWQI values were observed near El Milia city in the center of the plain. This spatial pattern suggests variations in groundwater quality across the study area, with potentially higher risks near the city center. The potential noncarcinogenic health risks associated with nitrate contamination in groundwater for adults and children through the drinking water pathway were assessed using the hazard quotient (HQ). The results revealed that approximately 5.7% of the total groundwater samples exceeded the HQ limit for adults, indicating potential health risks. Moreover, a higher percentage, 14.28%, of the total groundwater samples exceeded the HQ limit for children, highlighting their increased vulnerability to noncarcinogenic health hazards associated with nitrate contamination in the study area. Taking timely action and ensuring strict compliance with regulations in groundwater management are crucial for protecting public health, preserving the environment, addressing water scarcity, and achieving sustainable development goals.

Keywords: groundwater quality; health risk assessment; Moran's *I*; ordinary kriging interpolation; El Milia plain; Kebir Rhumel Basin

1. Introduction

Groundwater plays a vital role in water supply systems worldwide, serving various purposes such as drinking water, irrigation, and industrial use [1–11]. The demand for groundwater has increased significantly due to population growth, urbanization, and industrial activities. Excessive pumping of groundwater beyond its natural recharge rate has resulted in the depletion of aquifers in many regions, especially in arid and



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). semi-arid areas where surface water resources and precipitation are scarce [7,12,13]. This overexploitation can lead to a drop in water tables, land subsidence, and the drying up of wells. As groundwater gets depleted, there is an increased risk of contamination. Several human activities and geological factors have led to challenges in groundwater utilization, particularly in the presence of harmful substances such as nitrate (NO₃). To address these challenges and ensure the sustainable use of groundwater resources, it is necessary to enhance groundwater quality monitoring and assessment efforts in these regions.

Because groundwater quality is closely related to human health hazards, developing an appropriate tool to assess groundwater quality for drinking purposes has become a critical study in recent years [14,15]. The entropy weighted water quality index (EWQI) is a widely used mathematical tool for the evaluation of groundwater quality [16–18]. This method can measure the weights of groundwater hydrochemical attributes while ignoring artificial weight distribution, allowing for clear demarcation of groundwater quality classes.

Groundwater contaminated by nitrate has a direct negative effect on human health and agricultural activities. Nitrate can enter groundwater through multiple pathways, with the most significant sources being point and non-point sources, and natural processes can also contribute to their presence. The most common point sources of nitrate contamination in groundwater are septic tanks, dairy lagoons, wastewater effluent percolation, and livestock waste [19,20]. Elevated nitrate levels in groundwater can result from non-point sources such as fertilizers, pesticides, and manure application, as well as natural processes through rockwater interactions [13,21–23]. Also, nitrate contamination in groundwater can result from nitrogen fixation by legume plants and microbes. In addition, the extensive use of nitrogenbased fertilizers in agricultural areas is a major contributor to nitrate contamination in groundwater. When plants grow, they primarily take up nitrogen in the form of nitrate, an oxidized form of dissolved nitrogen. However, with intensive farming and continuous use of fertilizers, the soil may lose its natural ability to retain nitrates effectively. Consequently, excess nitrates can be washed into the groundwater by rainfall or irrigation, leading to elevated nitrate levels. Nitrates in groundwater pose health risks when they enter the food chain via contaminated groundwater and surface water. Drinking water with elevated nitrate levels can be harmful, particularly for vulnerable populations like infants and pregnant women. The World Health Organization [24] limit for nitrate in drinking water that is safe for drinking is <45 mg/L.

The health risk assessment method has been employed in numerous studies on pollutants in groundwater and soils worldwide [5,7,12,25]. In recent years, some studies have underscored the human health risk assessment of nitrate in groundwater [26,27]. This method provides a systematic and robust approach to evaluate the potential health risks associated with exposure to organic and inorganic pollutants in the environment, including those present in contaminated groundwater [3,5,28–30]. It considers factors such as the concentration and toxicity of contaminants, exposure pathways (e.g., drinking water consumption, dermal contact), exposure duration, and population characteristics. The results of the human health risk assessment method inform decision-making and risk management strategies. By quantifying the potential health risks associated with groundwater contamination, stakeholders can make informed decisions regarding contamination prevention, remediation measures, water treatment, and land-use planning. Risk assessment outcomes help prioritize actions to minimize exposure and protect public health. The estimation of health risks caused by concentrations of nitrate in drinking water has never been conducted in this study area. Therefore, in this study we aimed to evaluate the groundwater quality and assess the potential noncarcinogenic health risk of nitrate in the groundwater of the El Milia plain, Kebir Rhumel Basin.

2. Study Area

The El Milia plain is situated in the Kebir Rhumel Basin, which is located in the northeastern part of the province of Jijel, Algeria (Figure 1). The study area is located between $36^{\circ}40'-36^{\circ}47'$ N latitude and $6^{\circ}10'-6^{\circ}20'$ E longitude. The Kebir Rhumel Basin is a

geological basin known for its agricultural significance, and it encompasses several plains, including the El Milia plain. The El Milia region experiences a Mediterranean climate with an average annual temperature and precipitation of 17 °C and 930 mm, respectively [4,7,31]. The El Milia plain is characterized by its fertile soils, which make it suitable for agricultural activities. The region is known for the cultivation of various crops, including cereals, vegetables, fruits, and olives. Agriculture plays a vital role in the economy of the area, and the El Milia plain is known for its agricultural productivity.



Figure 1. (a) location of the study area; (b) groundwater samples; (c) piezometric map; and (d) geological map of the study area.

The study area is located in the alluvial plain of the Mio-Plio-Quaternary (Figure 1). This designation indicates that the aquifer consists of sedimentary deposits from the Miocene, Pliocene, and Quaternary periods. Alluvial aquifers are typically composed of porous materials such as sand, gravel, and silt, which can store and transmit groundwater [7,31]. The potentiometric study conducted in the El Milia plain provides important insights into the groundwater flow patterns and hydrogeological characteristics of the area [7,31]. The potentiometric study reveals that the main axes of groundwater flow converge towards the center of the El Milia plain. This indicates that the groundwater in the area moves towards a central point, likely due to the topography and geological features of the region. Convergence of groundwater flow can have implications for the distribution and availability of groundwater resources in the plain (Figure 1).

3. Materials and Methods

3.1. Data Collection and Analysis Methods

Thirty-three groundwater samples were collected from wells in the El Milia plain during April 2015. The selected wells are used for domestic, agricultural, and domestic/agricultural purposes and are uniformly distributed over the study area. The hydrochemical parameter analyzed was described by Belkhiri et al. [4]. Figure 1 shows the locations of the groundwater samples collected. In situ measurements of pH and electrical conductivity (EC) were conducted at each sampling well. Major ions (Ca, Mg, Na, K, Cl, SO₄, HCO₃, and NO₃) in the groundwater samples were measured in the laboratory.

3.2. Moran's I (Index) Statistic

Moran's *I* statistic is a correlation coefficient that examines the spatial autocorrelation of the datasets [31–34]. It is defined as

$$\mu(x) = \frac{N}{W} \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} w_{ij}(x_i - \bar{x}) (x_j - \bar{x})}{\sum_{i=1}^{N} (x_i - \bar{x})^2}$$
(1)

where *N* is the number of spatial units indexed by *i* and *j*, *x* is the variable of interest, \overline{x} is the mean of x_i , w_{ij} are the elements of a matrix of spatial weights with zeroes on the diagonal (i.e., $w_{ii} = 0$), and *W* is the sum of all w_{ii}

$$W = \sum_{i=1}^{N} \sum_{j=1}^{N} w_{ij}$$
(2)

Resampling and randomization null hypotheses have been tested following the discussion of Goodchild [35]. To calculate the global Moran's *I* statistic, the function Moran's *I* in R was used with three arguments such as the coordinates of the observations, the number of nearest neighbors, and the variable for which the statistic is calculated.

3.3. Entropy Water Quality Index (EWQI)

The entropy water quality index (EWQI) is a robust technique that is widely used to provide precise and comprehensive information about the overall groundwater quality for human consumption and drinking purposes [16,18]. The EWQI offers a comprehensive assessment of groundwater quality by considering multiple water quality parameters. By combining and weighting these parameters, the EWQI provides an overall evaluation of groundwater quality. The weighting of each hydrochemical parameter is determined on the basis of its entropy value, which reflects the amount of variation or uncertainty in the data [36–38]. The process to calculate the EWQI is described below.

In this method, one must first assign an entropy weight to each hydrochemical parameter. For *n* number of groundwater samples, every groundwater sample has m number of hydrochemical parameters, generating an eigenvalue matrix (*X*).

$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1m} \\ x_{21} & x_{22} & \cdots & x_{2m} \\ \vdots & \vdots & \vdots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nm} \end{bmatrix} (i = 1, 2, \dots, n \text{ and } j = 1, 2, \dots, m)$$
(3)

The standardized value y_{ij} can be expressed following Equation (4), and the standard matrix is expressed as $Y = (y_{ij}) (n \times m)$ as shown in Equation (5).

$$y_{ij} = \frac{x_{ij} - (x_{ij})_{min}}{(x_{ij})_{max} - (x_{ij})_{min}}$$
(4)

$$Y = \begin{bmatrix} y_{11} & y_{12} & \cdots & y_{1m} \\ y_{21} & y_{22} & \cdots & y_{2m} \\ \vdots & \vdots & \vdots & \vdots \\ y_{n1} & y_{n2} & \cdots & y_{nm} \end{bmatrix}$$
(5)

where $(x_{ij})_{min}$ and $(x_{ij})_{max}$ are the minimum and maximum value of the hydrochemical parameter of the groundwater samples, respectively.

Then the ratio of the index value of *i* groundwater sample and *j* index can be expressed as Equation (6).

$$P_{ij} = \frac{1 + y_{ij}}{\sum_{i=1}^{n} (1 + y_{ij})}$$
(6)

Information entropy (e_i) can be expressed as Equation (7).

$$e_{j} = -\frac{1}{\ln(n)} \sum_{i=1}^{n} P_{ij} \ln(P_{ij})$$
(7)

As the value of e_j becomes smaller, the effect of index j becomes bigger. The entropy weight (w_j) is given in Equation (8).

$$w_j = \frac{1 - e_j}{\sum_{j=1}^m (1 - e_j)}$$
(8)

For the next step, assign a quality rating scale for every hydrochemical parameter (q_i) .

$$q_j = \frac{C_j}{S_j} \times 100 \tag{9}$$

$$q_{pH} = \begin{cases} \frac{C_{pH} - 7}{8.5 - 7} & C_{pH} > 7\\ \frac{7 - C_{pH}}{8.5 - 7} & C_{pH} < 7 \end{cases}$$
(10)

where C_j is the concentration of each hydrochemical parameter (mg/L), C_{pH} is the measured pH value, and S_j is the permissible limit of each hydrochemical parameter given by the World Health Organization [24].

After calculating all the parameters of equations from 2 to 8, the last EWQI can be expressed as

$$EWQI = \sum_{j=1}^{m} w_j q_j \tag{11}$$

According to the EWQI value, groundwater quality can be classified as: excellent (EWQI \leq 25), good (25 < EWQI \leq 50), moderate (50 < EWQI \leq 100), poor (100 < EWQI \leq 150), and extremely poor (EWQI > 150).

3.4. Health Risk Assessment

Nitrate in groundwater is generally considered to be a noncarcinogenic substance. However, it can still pose risks to human health through different exposure pathways, primarily via drinking water (e.g., oral pathway) and skin contact (e.g., bathing) [12,21,39]. Nitrate can be absorbed by the human body through the consumption of contaminated groundwater. In the digestive system, nitrate can be converted to nitrite, which can further react with other compounds in the body to form nitrosamines. High levels of nitrosamines have been associated with various health concerns. Moreover, excessive levels of nitrate in drinking water can lead to methemoglobinemia, also known as "blue baby syndrome," which affects the ability of blood to carry oxygen, particularly in infants. In addition, the nitrate can be absorbed through the skin and enter the bloodstream. However, the extent of absorption through the skin is generally lower compared to ingestion. Because human health risks from drinking are much higher than that through skin contact, only the health risk of the drinking water pathway is appraised [40,41]. Therefore, the current study considered only the effect of the drinking water pathway on children and adults. In this study, the hazard quotient (HQ) was used to measure the noncancer risk of the nitrate parameter in groundwater. The HQ was calculated as follows [42–44]:

$$HQ = \frac{C_{NO_3} \times IR \times EF \times ED}{BW \times AT \times RfD}$$
(12)

where C_{NO_3} is the observed concentration of NO₃ (mg/L), IR is the ingestion rate (L/Day; for child: 1.5; adult: 2.5), EF is the exposure frequency (Days/Year; for both child and adult: 365), ED is the exposure duration (Years, for child: 12, and adult: 30), BW is the body weight (kg, for child: 36, and adult: 70), and AT is the average time (days/year, for both child and adult: ED × 365). The RfD (reference dose) value for NO₃ is 1.6 mg/kg/day [12,45,46].

4. Results and Discussion

4.1. General Characteristics of Hydrochemical Parameters

The statistical analysis of the hydrochemical parameters in groundwater is highly valuable for understanding the enrichment and variation in hydrochemical components in groundwater. It helps identify patterns, characterize variations, assess trends, evaluate relationships, develop spatial maps, and support data-driven decision making in groundwater management and protection efforts. A statistical summary of hydrochemical parameters for groundwater in the El Milia plain was discussed by Belkhiri et al. [7]. The results presented in Table 1, based on the pH values, indicate that the groundwater ranges from slightly acidic to slightly alkaline in nature. The majority of the groundwater samples exhibited high values of electrical conductivity (EC), above the WHO permissible limit [24], indicating that these groundwater samples are classified as saline water quality. Eighty percent of the total groundwater samples had Ca concentrations above the limits set by the World Health Organization [24]. Additionally, 14% of the samples had Mg concentrations above the WHO limits. All the groundwater samples for both Na and K had concentrations lower than the World Health Organization standard levels. The mean concentrations of anions in the groundwater samples were 150.08, 125.97, 232.02, and 23.47 mg/L for Cl, HCO₃, SO₄, and NO_3 , respectively. From the results, it can be observed that only one groundwater sample for chloride and bicarbonate, and two groundwater samples for sulfate and nitrate, were lower than the World Health Organization [24] standard levels. On the other hand, the remaining groundwater samples were within the WHO standard for drinking water.

	Min	Max	Mean	SD	Cv	S_j	ej	w_j
pН	6.00	7.50	6.77	0.26	0.04	8.5-7	0.9982	0.0530
ĒC	228	1411	821	279	0.34	500	0.9966	0.0997
Ca	16.19	198.18	95.56	32.50	0.34	75	0.9979	0.0606
Mg	11.02	61.32	37.39	12.01	0.32	50	0.9966	0.0993
Na	12.47	38.14	24.57	4.99	0.20	200	0.9976	0.0698
Κ	1.78	5.45	3.51	0.71	0.20	12	0.9976	0.0698
Cl	63.90	255.60	150.08	53.12	0.35	250	0.9951	0.1441
SO_4	61.39	270.00	125.97	49.93	0.40	250	0.9957	0.1252
HCO ₃	97.60	524.60	232.02	90.22	0.39	500	0.9966	0.0989
NO ₃	0.02	47.54	23.47	14.77	0.63	45	0.9938	0.1795
EWQI	41.54	94.42	63.35	12.51	0.20			

Table 1. Statistical summary of hydrochemical parameters and EWQI.

The unit of each hydrochemical element is mg/L, except for pH and EC, μ S/cm for EC. S_j : the WHO permissible limit. e_j : Information entropy. w_j : entropy weight. Min: Minimum; Max: Maximum; SD: Standard deviation; Cv: Coefficient of variation.

4.2. Spatial Distribution Pattern of Hydrochemical Parameters

In this study, the Moran's *I* was used to analyze the spatial distribution pattern of hydrochemical parameters in groundwater. Moran's *I* is a statistical measure that assesses the degree of spatial autocorrelation and helps identify any spatial patterns in the hydrochemical parameters. The values of Moran's *I* typically range from -1 to +1. Positive values indicate a higher degree of spatial autocorrelation, suggesting a pattern of spatial clustering. This means that neighboring spatial units tend to have similar values for the hydrochemical parameters. This indicates that there is spatial dependence in the data. On the other hand, negative values of Moran's *I* indicate a lower degree of spatial autocorrelation. This suggests that the data are more dispersed or randomly distributed in space, with neighboring spatial units having dissimilar values. A lower negative value indicates a stronger dispersal or randomness in the distribution of the hydrochemical parameters. A Moran's *I* value of zero in spatial autocorrelation analysis indicates that the results are completely randomly distributed in space. This means that there is no spatial autocorrelation or pattern observed in the data [33,47].

The results of the spatial autocorrelation analysis based on Moran's *I* values for each hydrochemical parameter in the study area are presented in Table 2. From the results, it can be observed that the Moran's *I* values range from -0.0950 (Mg) to 0.3837 (HCO₃). Three hydrochemical parameters, namely Ca, Cl, and HCO₃, exhibit strong spatial autocorrelation in the El Milia plain. Each of these hydrochemical parameters has a Moran's *I* value more than or close to 0.3. Furthermore, it is clear that all three of these hydrochemical parameters have Z-score values larger than 2.58 and *p*-values less than 0.01. This indicates that the high and/or low values of each hydrochemical parameter are geographically clustered in the dataset.

Table 2. Moran's I values for each hydrochemical parameter.

	Moran' I	Expected I	Z Resampling	<i>p</i> -Value Resampling	Z Randomization	<i>p</i> -Value Randomization
рН	0.1556	-0.0294	2.2510	$2.44 imes10^{-2}$	2.3744	0.0176
EC	0.0999	-0.0294	1.5736	$1.16 imes 10^{-1}$	1.5647	0.1176
Ca	0.2695	-0.0294	3.6360	$2.77 imes10^{-4}$	3.7808	0.0002
Mg	-0.0950	-0.0294	-0.7974	$4.25 imes10^{-1}$	-0.7940	0.4272
Na	-0.0806	-0.0294	-0.6223	$5.34 imes10^{-1}$	-0.6352	0.5253
Κ	-0.0805	-0.0294	-0.6216	$5.34 imes10^{-1}$	-0.6345	0.5258
Cl	0.3360	-0.0294	4.4453	$8.78 imes10^{-6}$	4.3863	0.0000
SO_4	0.0810	-0.0294	1.3435	$1.79 imes10^{-1}$	1.3828	0.1667
HCO ₃	0.3837	-0.0294	5.0257	$5.02 imes 10^{-7}$	5.1597	0.0000
NO ₃	-0.0738	-0.0294	-0.5403	$5.89 imes10^{-1}$	-0.5336	0.5936

4.3. Spatial Interpolation of the Hydrochemical Parameters

In the present study, the spatial distribution of the three hydrochemical parameters, namely Ca, Cl, and HCO₃, was analyzed using the ordinary kriging (OK) interpolation technique, and the results are displayed in Figure 2. As shown in Figure 3, the spatial distribution of calcium in the El Milia plain indicates that the highest Ca values, exceeding 100 mg/L, are primarily concentrated in the central region of the plain. Furthermore, these high Ca values tend to follow the direction of groundwater flow in the area. This suggests that the movement of groundwater is influencing the distribution of calcium concentrations. The observed spatial distribution of chloride and bicarbonate concentrations in the El Milia plain shows an increase in values from the western to the eastern part of the plain. The concentrations of Cl reach up to 200 mg/L, while the concentrations of HCO₃ reach up to 300 mg/L in the same direction. The spatial trend of increasing Cl and HCO_3 concentrations from west to east may be indicative of the direction of groundwater flow in the El Milia plain. As groundwater moves through the subsurface, it can interact with different geological formations, which can influence the solute composition, including Ca, Cl, and HCO₃, in the groundwater. Geological factors such as the composition and mineralogy of the aquifer materials can play an important role in the release and transport of Ca, Cl, and HCO₃. Another factor to consider is the impact of human activities on the hydrochemical composition of groundwater. Industrial processes, agricultural practices, and domestic wastewater can introduce Ca, Cl, and HCO_3 into the groundwater system. These anthropogenic inputs can contribute to the spatial patterns and variations observed in the hydrochemical distribution.



Figure 2. Spatial distribution map of (**a**) Ca; (**b**) Cl; and (**c**) HCO₃ parameters (mg/L); and (**d**) EWQI using OK method.



Figure 3. Spatial distribution of HQ for children and adults. The red and blue dots represent medium risk ($1 < HQ \le 4$) and no risk ($HQ \le 1$), respectively.

4.4. Comprehensive Assessment of Groundwater Quality

The application of the entropy water quality index (EWQI) method can provide a comprehensive understanding of the overall groundwater quality in the El Milia plan. The EWQI method is a robust technique used to assess and summarize the overall quality of water resources, including groundwater. In this method, the hydrochemical parameters, including pH, EC, Ca, Mg, Na, K, Cl, SO₄, HCO₃, and NO₃, were involved in the calculation of the EWQI. Table 2 summarized the general statistics of EWQI in the study area. The percentage of the total groundwater samples for each category of EWQI is presented in Table 3. The spatial distribution map of EWQI using the ordinary kriging method is displayed in Figure 2.

Table 3.	The EWQI	range and	percentage of	groundwater sam	ples in	the study	v area.
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Range	Water Type	No. of Samples	% of Samples
$EWQI \le 25$	Excellent	0	0
$25 < EWQI \le 50$	Good	5	14
$50 < EWQI \le 100$	Moderate	30	86
$100 < EWQI \le 150$	Poor	0	0
EWQI > 150	Extremely Poor	0	0

From the results, it was observed that the values of EWQI in the groundwater ranged from 41.54 to 94.42, with a mean value of 63.35. These values provide an overview of the overall groundwater quality in the study area. The distribution of EWQI values indicates that a majority, approximately 86% of the groundwater samples, fall within the moderate groundwater quality category. This suggests that most of the groundwater in the study area is classified as having a moderate environmental groundwater water quality. This implies that there might be some level of contamination or pollutants present in the groundwater, albeit not to an extent that classifies it as poor or very poor in terms of quality. On the other hand, only a smaller portion, around 14% of the total groundwater samples, fall within the good groundwater quality category. This indicates that a relatively small proportion of the groundwater samples likely exhibit lower levels of contamination or pollutants compared to the majority of the groundwater samples. This implies that these specific groundwater samples meet the criteria for good environmental grou

The spatial distribution of the EWQI in the study area provides valuable insights into the variability of groundwater quality across different locations. The spatial distribution of EWQI indicates a trend of increasing values from the southwest to the northeast part of the study area. This pattern follows the direction of groundwater flow, suggesting a potential influence of groundwater movement on groundwater quality. In other words, as the groundwater flows from the southwest to the northeast, the EWQI values tend to increase. The highest values of EWQI are observed in the center of the plain, particularly near El Milia city. This suggests that the groundwater quality in that particular area is relatively poor compared to other parts of the study area. The factors contributing to the high EWQI values, such as industrial discharges, agricultural runoff, and other human activities, indicate potential pollution sources in the study area. Excessive release of nutrients like nitrogen from industries can lead to nutrient pollution in water bodies, causing harmful algal blooms and oxygen depletion. The runoff from agricultural fields can carry excess fertilizers containing nitrogen, leading to nutrient pollution in water bodies and causing eutrophication. Agricultural activities involve the use of pesticides and herbicides, which can be washed off of fields and enter water bodies, affecting aquatic life and human health. Improperly treated or untreated sewage and wastewater from residential and commercial sources can introduce pathogens, organic matter, and nutrients into water bodies. Furthermore, these sources could introduce pollutants or contaminants into the groundwater, affecting its quality. Identifying and understanding these pollution sources is crucial for effective groundwater management and protection.

4.5. Noncarcinogenic Health Risk Assessment of Nitrate

Nitrate is commonly used as a good indicator of groundwater quality and vulnerability, especially in agricultural regions where it can be associated with fertilizer use and other agricultural activities [12,21,39]. The presence of high levels of nitrate in groundwater can pose potential health risks, particularly through the drinking water pathway [40,41]. In the present study, the hazard quotient (HQ) was used to assess the noncancer health risk assessment with the nitrate parameter in groundwater, specifically for children and adults through the drinking water pathway. The HQ is a commonly used method in health risk assessment to estimate the potential adverse effects of exposure to a particular chemical or contaminant.

Table 4 presents a statistical summary of the HQ values of nitrate for children and adults. As presented in Table 4, the HQ values for children ranged between 0.00052 and 1.23802, with a mean value of 0.61127. The HQ values for adults varied from 0.00045 to 1.06116 with a mean of 0.52395. This indicates that the HQ values for children are higher than those for adults, indicating in turn that the hazards to human health by nitrate are higher among children than among adults.

Table 4. Statistical summary of HQ for children and adults.

HQ	Min	Max	Mean	SD	CV
HQ _{Children}	0.00052	1.23802	0.61127	0.38451	0.62903
HQ _{Adults}	0.00045	1.06116	0.52395	0.32958	0.62903

To quantify the degree of noncarcinogenic health risk, Xiao et al. [41] classified the HQ values into three categories: low risk (HQ \leq 1), medium risk (1 < HQ values \leq 4), and high risk (HQ > 4). Table 5 presents the classification of groundwater quality based on HQ for children and adults. The spatial map of the HQ values for children and adults in the study area is shown in Figure 3. It can be observed that the health risk results revealed that 14% and 6% of the groundwater samples exceeded the acceptable limit for noncarcinogenic risk of 1.0 for children and adults, respectively. Thus, the evaluation of the HQ reveals that children were more vulnerable to noncarcinogenic health hazards than adults in the study area.

Range	Risk	Ch	ild	Adult		
		No. of Samples	% of Samples	No. of Samples	% of Samples	
$HQ \leq 1$	No risk	30	86	33	94	
$1 < HQ \le 4$	Medium	5	14	2	6	
HQ > 4	High	0	0	0	0	

Table 5. The HQ range and percentage of groundwater samples in the study area.

These results indicate that nitrate contamination in the groundwater of the study area is a potential risk to human health, especially for children. It suggests that long-term consumption of contaminated groundwater as drinking water can be harmful. To mitigate this health risk, the treatment of discharged waste water and the management of fertilizer applications are recommended.

5. Conclusions

In this study, we analyzed the quality and the potential noncarcinogenic health risk of nitrate in the groundwater in the El Milia plain, Kebir Rhumel Basin, Algeria. In order to understand the spatial distribution pattern of the hydrochemical parameters in the groundwater, the Moran's I and the irdinary kriging (OK) interpolation technique were applied. It was found that the hydrochemical parameters Ca, Cl, and HCO₃ exhibited strong spatial autocorrelation in the El Milia plain, indicating a spatial dependence and clustering of these hydrochemical parameters in the groundwater. The entropy water quality index (EWQI) method was employed to evaluate the groundwater quality in the study area. The results indicated that approximately 86% of the total groundwater samples fell under the moderate water category based on the EWQI classification. This suggests that the majority of the groundwater samples in the El Milia plain have moderate environmental groundwater quality. The spatial map of the EWQI values revealed a gradual increase from the southwest to the northeast, following the direction of groundwater flow. The highest values were observed near El Milia city in the center of the plain. This spatial pattern suggests variations in groundwater quality across the study area, with potential implications for water resource management and protection.

The hazard quotient (HQ) was used to assess the potential noncarcinogenic health risks associated with nitrate contamination in groundwater for both adults and children through the drinking water pathway. From the results, it was observed that approximately 6% of the groundwater samples exceeded the limit for adults, while a higher percentage, 14%, exceeded the limit for children. This highlights the increased vulnerability of children to noncarcinogenic health hazards associated with the contaminated groundwater in the El Milia plain. Therefore, the findings suggest that the nitrate contamination of groundwater in the El Milia plain poses a human health risk, particularly through long-term consumption of contaminated groundwater as drinking water. In order to mitigate this health risk, we recommend implementing management approaches that focus on limiting nitrate contamination. This may include improving the treatment of discharged wastewater and implementing better management practices for fertilizer application.

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References

- 1. Belkhiri, L.; Boudoukha, A.; Mouni, L.; Baouz, T. Application of multivariate statistical methods and inverse geochemical modeling for characterization of groundwater—A case study: Ain Azel plain (Algeria). *Geoderma* **2010**, *159*, 390–398.
- Belkhiri, L.; Narany, T.S. Using multivariate statistical analysis, geostatistical techniques and structural equation modeling to identify spatial variability of groundwater quality. *Water Resour. Manag.* 2015, 29, 2073–2089. [CrossRef]
- 3. Belkhiri, L.; Mouni, L.; Narany, T.S.; Tiri, A. Evaluation of potential health risk of heavy metals in groundwater using the integration of indicator kriging and multivariate statistical methods. *Groundw. Sustain. Dev.* **2017**, *4*, 12–22. [CrossRef]
- 4. Belkhiri, L.; Mouni, L.; Tiri, A.; Narany, T.S.; Nouibet, R. Spatial analysis of groundwater quality using self-organizing maps. *Groundw. Sustain. Dev.* **2018**, *7*, 121–132. [CrossRef]
- 5. Tiri, A.; Belkhiri, L.; Mouni, L. Evaluation of surface water quality for drinking purposes using fuzzy inference system. *Groundw. Sustain. Dev.* **2018**, *6*, 235–244. [CrossRef]
- 6. Wang, W.; Zhang, Z.; Duan, L.; Wang, Z.; Zhao, Y.; Zhang, Q.; Dai, M.; Liu, H.; Zheng, X. Response of the groundwater system in the Guanzhong Basin (central China) to climate change and human activities. *Hydrogeol. J.* **2018**, *26*, 1429–1441.
- Belkhiri, L.; Tiri, A.; Mouni, L. Spatial distribution of the groundwater quality using kriging and Co-kriging interpolations. *Groundw. Sustain. Dev.* 2020, 11, 100473. [CrossRef]
- 8. Wu, J.; Wang, L.; Wang, S.; Tian, R.; Xue, C.; Feng, W.; Li, Y. Spatiotemporal variation of groundwater quality in an arid area experiencing long-term paper wastewater irrigation, northwest China. *Environ. Earth Sci.* **2017**, *76*, 460. [CrossRef]
- 9. Li, P.; He, X.; Li, Y.; Xiang, G. Occurrence and health implication of fluoride in groundwater of loess aquifer in the Chinese Loess Plateau: A case study of tongchuan, northwest China. *Expo. Health* **2019**, *11*, 95–107. [CrossRef]
- 10. Karunanidhi, D.; Aravinthasamy, P.; Deepali, M.; Subramani, T.; Bellows, B.C.; Li, P. Groundwater quality evolution based on geochemical modeling and aptness testing for ingestion using entropy water quality and total hazard indexes in an urban-industrial area (Tiruppur) of Southern India. *Environ. Sci. Pollut. Res.* **2021**, *28*, 18523–18538. [CrossRef]
- 11. Tiri, A.; Belkhiri, L.; Asma, M.; Mouni, L. Suitability and assessment of surface water for irrigation purpose. In *Water chemistry*; IntechOpen: London, UK, 2020; pp. 1–18.
- Liu, J.; Peng, Y.; Li, C.; Gao, Z.; Chen, S. Characterization of the hydrochemistry of water resources of the Weibei Plain, Northern China, as well as an assessment of the risk of high groundwater nitrate levels to human health. *Environ. Pollut.* 2021, 268, 115947. [CrossRef]
- 13. Shukla, S.; Saxena, A. Appraisal of groundwater quality with human health risk assessment in parts of indo-gangetic alluvial plain, north India. *Arch. Environ. Contam. Toxicol.* **2021**, *80*, 55–73. [CrossRef]
- 14. Singaraja, C. Relevance of water quality index for groundwater quality evaluation: Thoothukudi District, Tamil Nadu, India. *Appl. Water Sci.* 2017, 7, 2157–2173. [CrossRef]
- 15. Belkhiri, L.; Mouni, L.; Tiri, A.; Narany, T.S. Evaluation of groundwater quality and its suitability for drinking and agricultural purposes using self-organizing maps. *Int. J. Geol. Environ. Eng.* **2017**, *11*, 705–709.
- 16. Shannon, C.E. A mathematical theory of communication. Bell. Syst. Tech. J. 1948, 27, 623-656. [CrossRef]
- 17. Adimalla, N. Controlling factors and mechanism of groundwater quality variation in semiarid region of South India: An approach of water quality index (WQI) and health risk assessment (HRA). *Environ. Geochem. Health* **2020**, *42*, 1725–1752. [CrossRef]
- Gao, Y.Y.; Qian, H.; Ren, W.H.; Wang, H.K.; Liu, F.X.; Yang, F.X. Hydrogeochemical characterization and quality assessment of groundwater based on integrated-weight water quality index in a concentrated urban area. *J. Clean. Prod.* 2020, 260, 121006. [CrossRef]
- Kalaivanan, K.; Gurugnanam, B.; Pourghasemi, H.R.; Suresh, M.; Kumaravel, S. Spatial assessment of groundwater quality using water quality index and hydrochemical indices in the Kodavanar sub-basin, Tamil Nadu, India. *Sustain. Water Resour. Manag.* 2018, 4, 627–641. [CrossRef]
- 20. Nawale, V.P.; Malpe, D.B.; Marghade, D.; Yenkie, R. Non-carcinogenic health risk assessment with source identification of nitrate and fluoride polluted groundwater of Wardha sub-basin, central India. *Ecotoxicol. Environ. Saf.* **2021**, 208, 111548. [CrossRef]
- 21. Zhai, Y.; Lei, Y.; Wu, J.; Teng, Y.; Wang, J.; Zhao, X.; Pan, X. Does the groundwater nitrate pollution in China pose a risk to human health? A critical review of published data. *Environ. Sci. Pollut. Res.* **2017**, *24*, 3640–3653. [CrossRef]
- 22. Kom, K.P.; Gurugnanam, B.; Bairavi, S. Non-carcinogenic health risk assessment of nitrate and fluoride contamination in the groundwater of Noyyal basin, India. *Geod. Geodyn.* **2022**, *13*, 619–631. [CrossRef]
- Noori, R.; Farahani, F.; Jun, C.; Aradpour, S.; Bateni, S.M.; Ghazban, F.; Hosseinzadeh, M.; Maghrebi, M.; Naseh, M.R.V.; Abolfathi, S. A non-threshold model to estimate carcinogenic risk of nitrate-nitrite in drinking water. *J. Clean. Prod.* 2022, 363, 132432. [CrossRef]
- 24. WHO (World Health Organization). Guidelines for Drinking-Water Quality, 4th ed.; WHO: Geneva, Switzerland, 2017.
- 25. Shil, S.; Singh, U.K. Health risk assessment and spatial variations of dissolved heavy metals and metalloids in a tropical river basin system. *Ecol. Indic.* 2019, *106*, 105455. [CrossRef]
- 26. Zhang, Y.; Wu, J.; Xu, B. Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China. *Environ. Earth Sci.* 2018, 77, 273. [CrossRef]
- 27. Adimalla, N. Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. *Hum. Ecol. Risk. Assess.* **2019**, *26*, 310–334. [CrossRef]

- 28. Zhang, Q.; Qian, H.; Xu, P.; Hou, K.; Yang, F. Groundwater quality assessment using a new integrated-weight water quality index (IWQI) and driver analysis in the Jiaokou Irrigation District, China. *Ecotoxicol. Environ. Saf.* **2021**, 212, 111992. [CrossRef]
- 29. Liu, J.; Gao, Z.; Feng, J.; Wang, M. Identification of the hydrochemical features, genesis, water quality and potential health hazards of groundwater in Dawen River Basin, North China. *Ecol. Indic.* **2023**, *149*, 110175. [CrossRef]
- 30. Singh, G.; Rishi, M.S.; Herojeet, R.; Kaur, L.; Sharma, K. Evaluation of groundwater quality and human health risks from fluoride and nitrate in semi-arid region of northern India. Environ. *Geochem. Health* **2020**, *42*, 1833–1862. [CrossRef]
- 31. Moran, P.A.P. The interpretation of statistical maps. J. R. Stat. Society 1948, 10, 243–251. [CrossRef]
- 32. Moran, P.A.P. Notes on continuous stochastic phenomena. Biometrika 1950, 37, 17–23. [CrossRef]
- 33. Cliff, A.D.; Ord, J.K. Spatial Autocorrelation; Pion: London, UK, 1973.
- 34. Cliff, A.D.; Ord, J.K. Spatial Processes: Models and Applications; Pion: London, UK, 1981.
- 35. Goodchild, M.F. Spatial Autocorrelation; Catmog 47; Geo Books: Kattappana, India, 1986.
- 36. Adimalla, N. Application of the entropy weighted water quality index (EWQI) and the pollution index of groundwater (PIG) to assess groundwater quality for drinking purposes: A case study in a rural area of telangana state, India. *Arch. Environ. Contam. Toxicol.* **2021**, *80*, 31–40. [CrossRef]
- Li, X.; Huang, X.; Zhang, Y.H. Spatio-temporal Analysis of Groundwater Chemistry, Quality and Potential Human Health Risks in the Pinggu Basin of North China Plain: Evidence from High-Resolution Monitoring Dataset of 2015–2017. *Sci. Total Environ.* 2021, 800, 149568. [CrossRef]
- 38. Wu, C.; Wu, X.; Qian, C.; Zhu, G. Hydrogeochemistry and groundwater quality assessment of high fluoride levels in the Yanchi endorheic region, northwest China. *Appl. Geochem.* **2018**, *98*, 404–417. [CrossRef]
- Sheng, D.; Meng, X.; Wen, X.; Wu, J.; Yu, H.; Wu, M.; Zhou, T. Hydrchemical characteristics, quality and health risk assessment of nitrate enriched coastal groundwater in northern China. J. Clean. Prod. 2023, 403, 136872. [CrossRef]
- 40. Chen, J.; Wu, H.; Qian, H. Groundwater nitrate contamination and associated health risk for the rural communities in an agricultural area of ningxia, northwest China. *Expo. Health* **2016**, *8*, 349–359. [CrossRef]
- Liu, J.; Gao, Z.; Zhang, Y.; Sun, Z.; Sun, T.; Fan, H.; Wu, B.; Li, M.; Qian, L. Hydrochemical evaluation of groundwater quality and human health risk assessment of nitrate in the largest peninsula of China based on high-density sampling: A case study of Weifang. J. Clean. Prod. 2021, 322, 12916. [CrossRef]
- 42. USEPA (U.S. Environmental Protection Agency). *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual* (*Part A*); Office of Emergency and Remedial Response: Washington, DC, USA, 1989.
- 43. USEPA (U.S. Environmental Protection Agency). *Exposure Factors Handbook*; General Factors; Office of Research and Development: Washington, DC, USA, 1997; Volume 1.
- 44. USEPA (U.S. Environmental Protection Agency). *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites;* Office of Emergency and Remedial Response: Washington, DC, USA, 2002.
- 45. Tran, D.A.; Tsujimura, M.; Loc, H.H.; Dang, D.H.; Le Vo, P.; Ha, D.T.; Nguyen, T.V. Groundwater quality evaluation and health risk assessment in coastal lowland areas of the Mekong Delta, Vietnam. *Groundw. Sustain. Dev.* **2021**, *15*, 100679. [CrossRef]
- Xiao, Y.; Liu, K.; Hao, Q.; Xiao, D.; Zhu, Y.; Yin, S.; Zhang, Y. Hydrogeochemical insights into the signatures, genesis and sustainable perspective of nitrate enriched groundwater in the piedmont of Hutuo watershed, China. *Catena* 2022, 212, 106020. [CrossRef]
- 47. Wang, Z.; Liu, Y.; Zhang, Y.; Liu, Y.; Wang, B.; Zhang, G. Spatially varying relationships between land subsidence and urbanization: A case study in Wuhan, China. *Remote Sens.* **2022**, *14*, 291. [CrossRef]

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