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Assessment of groundwater contamination for fluoride , nitrate and health risk in Djemila area North east Algeria

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Abstract

The main aim of this study was to assess the groundwater quality and human health risks of fluoride and nitrate contamination in Djemila area, north east Algeria , employing a comprehensive analysis of samples collected from various locations, based on Twenty-five physicochemical parameters. Utilizing tools like the Nitrate Pollution Index (NPI), Water Quality Index (WQI) where groundwater is the primary source for drinking water. Hazard quotient (HQ) and total hazard index (THI) were calculated to estimate the non-carcinogenic risk to men, women, and children using the most substantial method recommended by United States Environmental Protection Agency (USEPA). The results of the study reveal that **26%** and **20.59%** of groundwater samples have significantly high nitrate and fluoride concentrations, exceeding the maximum permissible limits set by WHO (50 mg/L and 1.5 mg/L, respectively). Therefore, ingestion of high fluoride and nitrate water could be the chief reason for health risk in the study area. The total non-carcinogenic health risks for men, women, and children ranged from , 3.49 to 4.80, and 3.991 to 5.50, respectively. Moreover, 67.65%, 79.41%, and 82.35% of the total collected groundwater samples exceeded the permissible limit for acceptable total health index (THI D 1) for men, women, and children, respectively. Therefore, the health risk assessment suggests that children face higher health risk than men and women in the study region.

Key Word : Nitrate, Fluor, fluorose, health index, risk, pollution, Djemila, Algeria

Introduction

Environmental pollution and groundwater contamination pose significant threats to human health, particularly in arid and semi-arid regions globally (Adimalla and Venkatayogi, 2018; Li, 2016; Li et al., 2017b). Despite this awareness, groundwater quality continues to decline rapidly due to extensive changes in landscapes and increasing anthropogenic activities, resulting in a significant impact on human health through the consumption of contaminated water. Consequently, numerous studies have been conducted worldwide to investigate groundwater quality and its associated health risks (Li et al., 2017a; Zhang et al., 2018).

For instance, Had (2017) conducted an assessment of the health risks associated with high fluoride levels in groundwater in Punjab, India, highlighting the ingestion of water with high fluoride content as a major contributor to increased health risks. Marsha and Tabitha (2018) explored the spatial distribution and seasonal variations of groundwater fluoride contamination in South India, noting that the excessive input of high-fluoride water is the primary cause of deteriorating public health. Therefore, the quality of groundwater holds paramount importance for maintaining a healthy life and fostering sustainable development in a country.

Nevertheless, groundwater pollution is on the rise in the modern era, exacerbated by factors such as population growth, extensive changes in landscapes, increased prevalence of diseases, expanding industrial activities, erratic seasonal rainfall, etc. (Adimalla and Venkatayogi, 2018; Marsha and Tabitha, 2018). The high concentration of fluoride and nitrate in groundwater is a major contributing factor to health risks in thirsty and semi-arid regions worldwide (Adimalla et al., 2018; Li et al., 2018a). For instance, We et al. (2018) conducted a study on the threat assessment of high-nitrate-contaminated groundwater in northern China, concluding that the widespread use of nitrogen-based fertilizers was the primary source of groundwater pollution, resulting in adverse effects on human health.

Similar studies in various regions worldwide have been conducted by researchers such as SU et al. (2017), Li et al. (2016a), Ernesto et al. (2014), Animalia and Venkatayogi (2017, 2018), Marsha and Darshan (2017a, b, 2013, 2018a, b), Bubba Ran (2018), Bubba Ran et al. (2012), Sail Kumar (2017), Kunduz et al. (2001), Sudhakar and Marsha (2013), Anew and Gupta (2006), and Wu and Sun (2016).

This study focuses on the semi-arid Djemila area and aims to achieve the following objectives: (1) estimate the suitability of groundwater for drinking purposes, (2) assess fluoride and nitrate contamination in groundwater, and (3) evaluate non-carcinogenic health risks through ingestion for men, women, and children, using the United States Environmental Protection Agency system (USEPA)

Study area

Djemila is a municipality in the province of Sétif in northern Algeria, The population is approximately 33000 inhabitants (2023), surface of the area is 151,84 km² and density is 205 inhabitants/km². The municipality is home to the remains of the ancient Djemila, the old Roman city of Cuicul, listed as a World Heritage Site by Unesco. Known by its ancient name Cuicul, the site of Djémila is an establishment of an ancient Roman colony founded under the reign of Nerva (96–98 AD). The Roman city occupied a remarkable defensive site. Cuicul is one of the highlights of Roman architecture in North Africa. Being remarkably folded to the constraints of the mountainous site, a rocky spire that stretches, at 900 m of altitude, between the Guergour and the Betame, two mountain streams, the city possessed its own senate and its own forum. By the beginning of the 3rd century, it was overwhelmed by the creation of the temple of Septimius Severus, the arc of Caracalla, the marketplace, and the civil basilica. The site was also marked by a Christian foot print materialized by several worship buildings, including a cathedral, a church, and its baptistery, considered among the largest of the Paleocrisian period. The site of Djémila includes a remarkable collection of mosaic pavements, illustrating mythological stories and scenes from everyday life. Djemila (the beautiful among the Arabs and Cuicul among the Romans). Characterized by its very disorderly relief, the highlights exceed 1200 m: Djebel Laithou (1284 m), Djebel Tarker Aouedj (1238 m), and Moul el Djediane (1225 m). To the south, Chouf Aissa ben Zir is 1402 m. The surface waters are drained by Djemila wadis, Guergour wadis, Bitame wadis, Reggad wadis, and Mouroudj. Wadis (**Figure 1**). The average temperature over a period of 30 years is 24 °C, with the lowest recorded in January with a value of -10 °C and the maximum in August with a temperature of 48°C. ETR is 388 mm, and infiltration is 32 mm/year (Khemmoudj 2014).

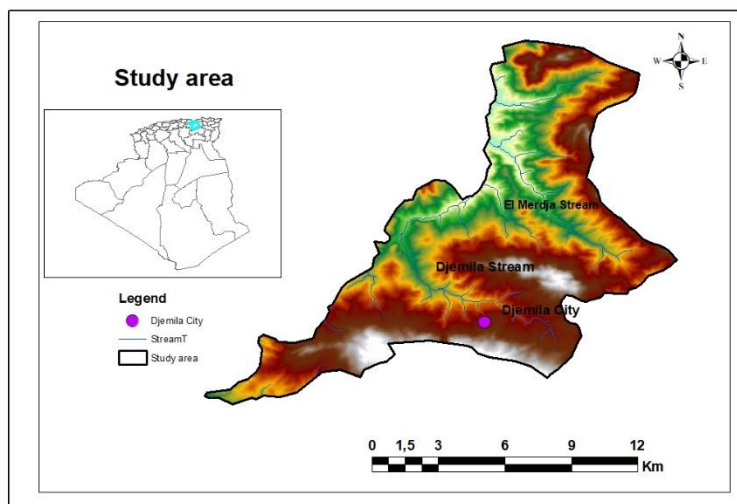


Fig (1) : Localization of the study area.

Geology of the study area

The Djemila plateau comprises most of the landscape to the north of Sétif and El Eulma, and to the east, the surroundings of Beni Mérouane (**Figure 2**). It has quite sensitive variations from North to South and East to West. It is the only Tellian unit represented by a complete series ranging from the Lias to the end of the Eocene. For a simple reason of continuity of flourishing, the following units are rarely gathered under the name of "Djemila's unity": The inter-cutaneous scale of Benni-Ourtillane; the Bou Sellam series around the Djebel Guergour, Anini, and Hellel; the Djebel Babor; the vast sector of the "Sétifien domes" around the "Djebel Medjounés," the Djemila mountains, and the Ouled Sabor. The Djemila plateau, essentially represented by crystalline limestones of the Upper Senonian or limestone of the "Setifian domes," flows widely in the northern edge of Setifa. Bituminous limestone overlaid with black-calcareous alternations belonging to the Ypresian-Lutétien develops to the west of El Eulma. The Djemila active fault is a NE-SW trending and NW-dipping reverse fault. Historical seismicity around this fault is weak to moderate. However, field observations allowed us to observe differential uplifts of quaternary alluvial terraces on the hanging and foot walls. We interpret this as strong evidence of recent tectonic activity. The uplifted terraces suggest an uplift rate of 0.14 mm/year. Therefore, the historical seismicity of the region may not fully reflect the seismic potential of this fault.

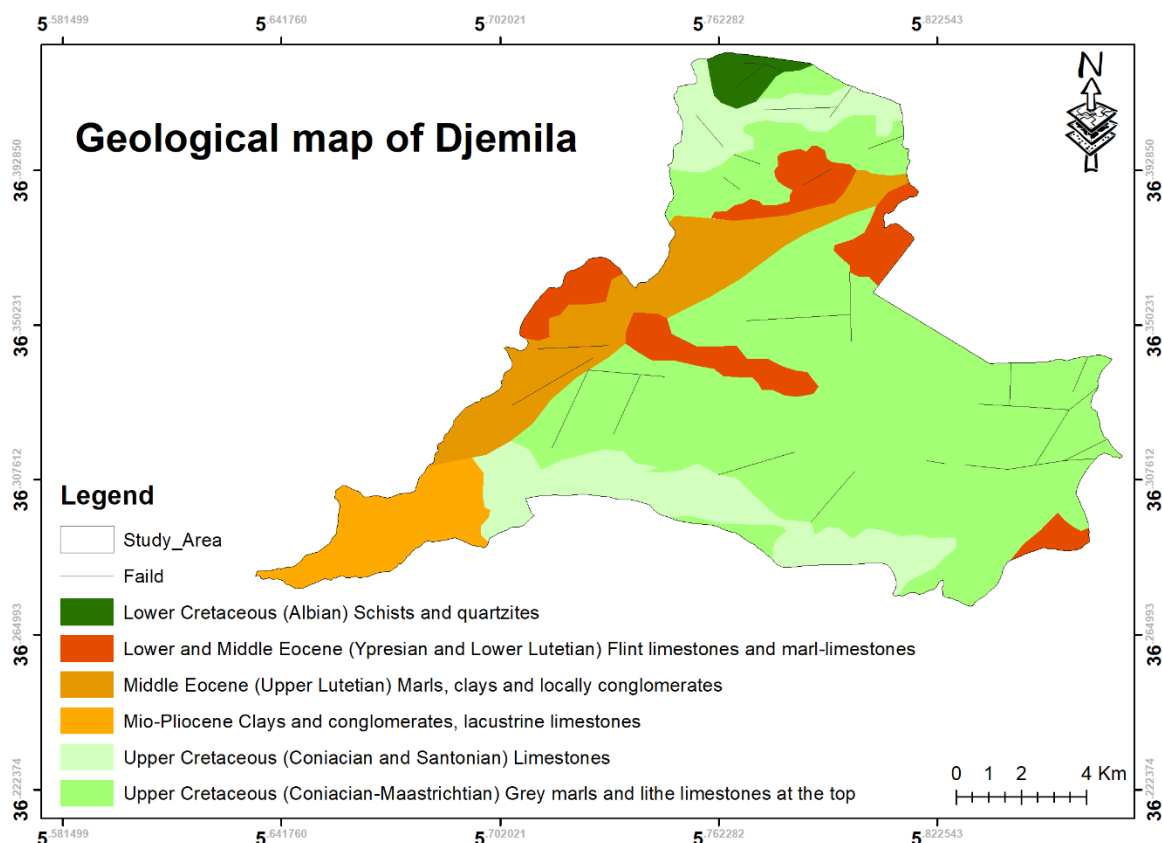


Fig 2 Geological Map of study area

Materials and Methods

The hydrochemical analysis was carried out in high waters (March 2023), in order to determine the physical and chemical parameters of groundwater. Twenty-five (25) samples were selected to determine the hydrogeochemical characteristics of groundwater (Table 1). Subsequently, the water samples were collected and transported in Water portable coolers, maintaining a constant low temperature of 4 °C, to the laboratory for further analysis

Physico-chemical parameters were measured in the field using a multi-parameter WMW(P3 multiline pH/LFSET). The samples were analyzed in the laboratory, Calcium, Potassium, Chlorine, Bicarbonates, Sulfates, Nitrates, and Fluorine were analysed using the standard method suggested by the American Health Association. (APHA,1989 ;1995). Ca, Mg, HCO₃, and Cl were analyzed by volumetric titration. The concentration of Ca and Mg was estimated by titration 0.05 N and 0.01 N EDTA, the bicarbonates HCO₃ and Cl by titrating H₂SO₄ and AgNO₃, The concentration of Na and K was measured using a flame photometer. Sulfates by the turbidimetric method. The NO₃ nitrates were analyzed by calorimetric with a UV-Vis spectrophotometer, the Fluor was analyzed with the MPM 1500 photometer. The spatial distribution maps of various physicochemical parameters were generated using GIS techniques and contouring methods with Arc-GIS 10.8.2. The spatial distribution maps for each parameter were prepared utilizing IDW interpolation techniques to illustrate variations across the study area. Furthermore, the NPI and WQI, were elaborated upon based on these spatial distribution maps.

Water quality indices

Water quality index (WQI) for drinking purpose was calculated using literature reported methods . The relative weight of each parameter (Wi) was calculated as Equa (1) Table (1):

$$Wi = \frac{wi}{\sum_i^n wi} \dots\dots\dots (1)$$

where wi is the weight of each parameters and n is the total number parameters included. Quality rating qi for each parameter was calculated as Equation 2:

$$qi = \frac{Ci}{Si} \times 100 \dots\dots\dots (2)$$

where Ci is the concentration of each parameter (mg/L) in the water samples and Si is WHO standard values (mg/L). Finally, water quality index (WQI) was calculated as Equation 3:

$$QWI = \sum_i^n Wi qi \dots\dots\dots (3)$$

Subsequently, the WQI scores for all groundwater samples are categorized into one of five water quality classes, as depicted in Table 2 .

Table 1 Rw and Wp

Parametrs	WHO (2017)	R _w	W _p
Ph	6,5 -8,5	4	0,093
EC	1000 (µs/cm)	5	0,116
TDS	1000 (mg/L)	2	0,046
Ca	75 (mg/L)	2	0,046
Mg	50 (mg/L)	2	0,046
Na	200 (mg/L)	5	0,116
K	10 (mg/L)	2	0,046
HCO ₃	120 (mg/L)	2	0,046
Cl	250 (mg/L)	5	0,116
SO ₄	250 (mg/L)	4	0,093
NO ₃	50 (mg/L)	5	0,116
F	1,5 (mg/L)	5	0,116
Total weight		43	0,996

Table 2. Classification of the WQI.

Water Quality Index	Type of Water
< 50	Excellent
50 - 100	Good
100 - 200	Poor
200 - 300	Very poor

➤ 300	Unsuitable
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Nitrate pollution assessment

The nitrate pollution index (NPI) (Panneerselvam et al. 2022; El Mountassir et al. 2022; Bhrami et al. 2022) is a tool designed to quantify the degree of nitrate pollution in groundwater. This index is calculated using equation 4, which considers C_s , the measured nitrate content in sample, and HAV representing the accepted value of NO_3 , taken as 20 mg/l. The NPI categorizes pollution into five levels: a score below zero indicates clean water, from 0 to 1 for slight pollution, from 1 to 2 represents moderate water pollution, from 2 to 3 signifies high water pollution, and a score above 3 is considered extremely high pollution (**Table 3**), particularly critical for drinking waters (Egbueri et al. 2023a, b). This systematic approach, central to assessing nitrate contamination, is essential to better comprehend the water quality within the area.

$$\text{NPI} = \frac{C_s - \text{HAV}}{\text{HAV}} \dots\dots\dots (4)$$

Table 3 NPI Categorizes

NPI	Categorizes
< 0	Clean (not polluted)
0- 1	Light Pollution
1-2	moderate Pollution
2-3	Significant Pollution
➤ 3	Very Significant Pollution

Human health risk assessment

Health risk assessment is beneficial to understand the probability of adverse health effects in human who may be exposed to chemicals in contaminated water. It is often the first step in safeguarding safety and health. The empirical models proposed by USEPA (1989) were applied to estimate the non-carcinogenic effects of contamination in this paper. The United States Environmental Protection Agency (USEPA) has established suitable models for human health risk assessment, and it is composed of four steps: hazard identification, dose response assessment, exposure assessment, and risk characterization (Narsimha and Rajitha 2018). Moreover, human beings are mostly exposed to contaminants through three pathways: ingestion of water, inhalation, and direct dermal contact (USEPA 2006). In this study, ingestion of contaminated drinking water was considered as a primary pathway, and fluoride and nitrate concentrations were selected as the parameters for HHRA in the current study. These two parameters are considered as non-carcinogenic pollutants by United States Environmental

Protection Agency. In exposure assessment, the average daily dose (ADD) of F^- and NO_3^- ingested from drinking of groundwater/borehole water in the study region was computed by Eq. 2 (U.S. EPA 2006; Li et al. 2014b):

$$CDI = \frac{C \times IR \times ED \times EF}{BW \times AT} \dots\dots\dots (5)$$

where ADD is the F^- and NO_3^- ingested (mg/kg/day), CPW is the concentration of pollutant in groundwater (mg/L), IR is the ingestion rate per unit time (L/day), ED is the exposure duration (years), EF is the exposure frequency (days/year), ABW is known as the average body weight of a person (kg), and AET indicates the average exposure time (years), which is equal to the life expectancy of a resident in the study region. The conversion factor from year to days is 365, and detailed description of obtained data is shown in Table 1. The reference dose is used as a measure of non-carcinogenic chronic hazards. Toxic effects are likely to ensue, when the exposure dose of the target contaminant exceeds the reference dose, which is generally articulated as hazard quotient (HQ):

$$HQ = \frac{CDI}{RfD} \dots\dots\dots (6)$$

where RfD signifies the reference dose for chronic oral exposure/non-carcinogenic risk, which is 0,6 and 1.6 mg/kg/day for F^- and NO_3^- , respectively (USEPA 2014). However, the total hazard index (THI) of non-carcinogenic risk is computed by Eq 3.

$$THI = \sum_{i=1}^n HQ_i \dots\dots\dots (7)$$

$$THI = HQ_{Nitrates} + HQ_{Fluorid} \dots\dots\dots (8)$$

According to the health risk assessment standard recommended by the USEPA, the allowable limit of non-carcinogenic THI is 1. If THI is larger than 1, it indicates the non-carcinogenic risk of contaminant exceeds the allowable limit, while if the THI is below 1 it suggests that the non-carcinogenic risk is within the acceptable limit (USEPA 2014)

In this study, all the people living here depend on groundwater for drinking, and thus EF is assigned 365 days per year for residents. ED value value is 12 years for children, and 30 years for adult man and woman (USEPA 1989). The value AT is equal to 365 days. The value of BW are 12 kg for children, respectively 72 and 65 are selected for man and woman (Table 7).

Table 4 Parameters for NO_3^- and F^- ingestion health risk assessment

Parameters /Frequency	Unit	Men	Woman	Children
Chronic daily intake CDI	mg/kg/day	-	-	-
Concentration in groundwater (C)	mg/L	-	-	-
Ingestion rate of water R, L/day	L/day	1,5	1,5	0,5
Exposure duration ED,	year	30	25	12
Exposure frequency EF	days /year	365	365	365
Average body weight BW	Kg	72	65	12
Average time AT	day	12000	8850	4450
Reference dose (RfD) NO_3^-	mg/kg/day	1.6	1.6	1.6
Reference dose (RfD) F^-	mg/kg/day	0.04	0.04	0.04

Result and discussion

Geochemistry of groundwater

Summary of minimum, maximum, mean and standard value of physico-chemical parameters measured in situ and in laboratory is presented in Table 5. pH is a measure of the hydrogen ion concentration of a solution; solutions with a high concentration of hydrogen ion normally have a low pH, while solutions with a low concentration of hydrogen ion have a very high pH. However, hydrogen ion concentration (pH) in groundwater is an important hydrochemical parameter, which has no direct impact on human health (Adimalla and Venkatayogi 2018). In the study, pH ranged from 7,2 to 8,6 , with a mean of 7.768 , indicating slightly alkaline condition of groundwater in the study area.

The concentration of EC in the study region groundwater ranged from 176.35 $\mu\text{S}/\text{cm}$ to 385 $\mu\text{S}/\text{cm}$, with a mean of 267.286 $\mu\text{S}/\text{cm}$ (Tables 2) not exceeding the permitted limit

TDS in the groundwater of the study area ranged from 275.55 to 601.mg/L, with a mean of 417.56 mg/L (Tables 2) not exceeding the permitted limit .

Results showed that the ranges of cation concentrations in the groundwater of Djemila area 32 to 128 mg/L, 10 to 76 mg/L, 151 to 103.15 mg/L, and 11.45 to 56.87 mg/L for Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , respectively (Tables 2). The mean values of these cations were 68.08, 29.96, 48.12, and 28.36 mg/L for Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , respectively (Table 2).

The anions of groundwater in study area ranged from 66.87 to 154.17, 16.86 to 146 , 21 to 133 for HCO_3^- , Cl^- , SO_4^{2-} resectively (table 2). The mean values of these anions were 89.618 , 52,852 and 52,491 mg/L for HCO_3^- , Cl^- , SO_4^{2-} resectively (table 2). The elevated Cl^- concentration in groundwater could be attributed to leaching of surface salts, anthropogenic untreated domestic sewage, and agricultural water return flow (Khemmoudj et al 2014)

Groundwater Type:

In assessing groundwater chemistry, hydrochemical facies play an essential role in determining the interactions between the main anions and cations and their behavior. This classification makes it possible to identify the origin and categorization of different types of water

Table 5 Summary of minimum, maximum, mean and standard value of physico-chemical parameters

Chemical parameters	Unité	Minimum	Maximum	Moyenne	SD
Ca	mg/L	32,000	128,000	68,080	28,504
Mg	mg/L	10,000	76,000	29,960	19,272
Na	mg/L	11,000	103,150	48,126	26,612
K	mg/L	11,450	56,870	28,369	12,744
HCO ₃	mg/L	66,870	154,170	89,618	21,521
Cl	mg/L	16,890	146,000	52,852	32,381
SO ₄	mg/L	21,000	133,000	52,491	27,577
NO ₃	mg/L	17,470	93,160	45,478	20,971
F	mg/L	0,430	2,790	1,277	0,746
TDS	mg/L	275,550	601,000	417,569	71,340
EC	µs/cm	176,352	385,000	267,286	45,699
pH		7,200	8,600	7,768	0,503

Water Quality Index (WQI)

The WQI was employed to assess the suitability of groundwater for drinking purposes in accordance with World Health Organization standards. The computed WQI values are presented in (Figure 3) (Table 6)

The spatial distribution of WQI, as depicted in Figure 8c, highlights that groundwater samples collected from the North east of the Djemila area are unfit for drinking purposes.

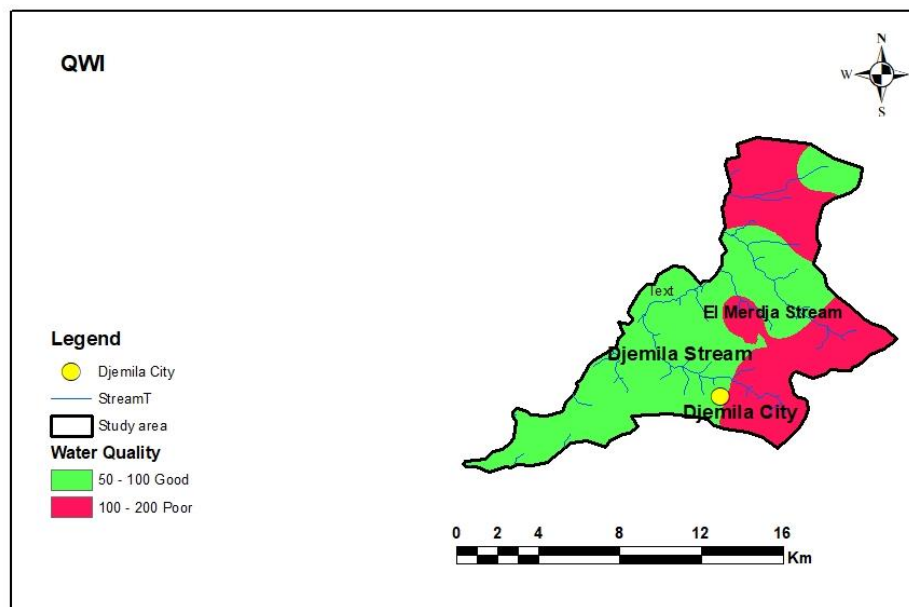


Fig 3 Water quality index

Nitrate Pollution Index (NPI)

The NPI serves as a valuable index for assessing groundwater pollution resulting from heightened nitrate concentrations. . The analysis of the NPI values (Figure 4) reveals that samples collected from locations . The spatial distribution depicted in Figure illustrates the NPI values, revealing that agricultural activities have been identified as significant contributors to groundwater pollution in various studies. Factors such as limited soil coverage, excessive fertilization, runoff and infiltration of surplus fertilizers, drainage systems, and the utilization of organic fertilizers from animal husbandry and wastewater reuse all contribute to nitrate pollution .

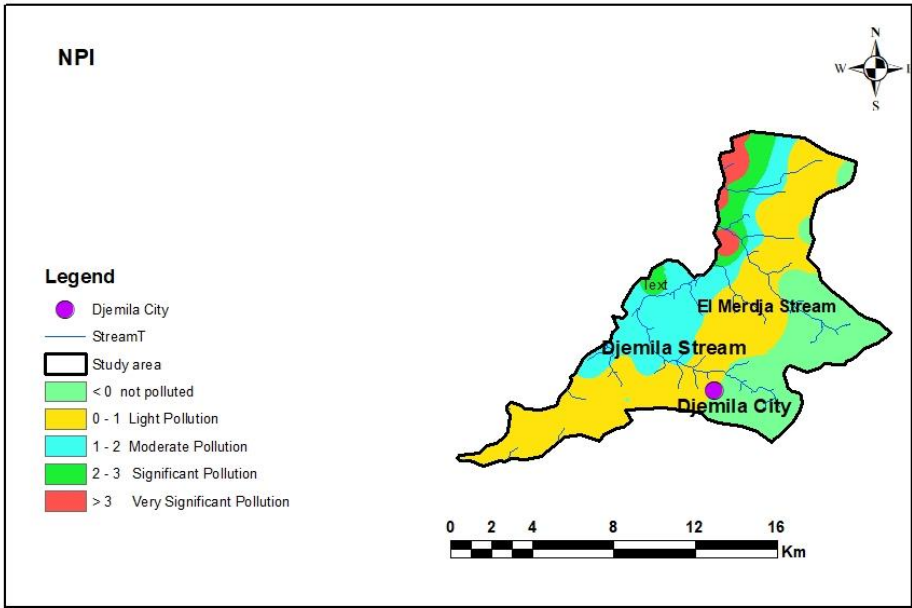


Fig 4 Nitrate pollution index (NPI))

Table 6 QWI and NPI index

Samples	QWI Values	Class	NPI Values	Class
P1	76,52	Good	0,78	Light Pollution
P2	87,89	Good	0,91	Light Pollution
P3	103,51	Poor	1,28	moderate Pollution
P4	89,02	Good	0,62	Light Pollution
P5	108,30	Poor	0,23	Light Pollution
P6	130,30	Poor	-0,13	not polluted
P7	112,70	Good	0,34	Light Pollution
P8	99,36	Good	1,45	moderate Pollution
P9	94,39	Good	1,46	moderate Pollution
P10	80,94	Good	1,69	moderate Pollution
P11	85,47	Good	1,54	moderate Pollution
P12	88,66	Good	2,34	Significant Pollution
P13	83,05	Good	1,44	moderate Pollution
P14	121,44	Poor	1,09	moderate Pollution
P15	78,77	Good	-0,02	not polluted
P16	83,43	Good	0,43	Light Pollution
P17	75,24	Good	0,66	Light Pollution
P18	107,84	Good	0,95	Light Pollution
P19	103,02	Poor	0,35	Light Pollution
P20	129,00	Poor	0,38	Light Pollution
P21	99,64	Good	0,89	Light Pollution
P22	135,66	Poor	2,94	Significant Pollution
P23	138,95	Poor	3,46	Significant Pollution
P24	116,15	Poor	3,11	Significant Pollution

P25	100,96	Poor	3,66	Significant Pollution
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Spatial distribution of nitrate and fluoride in the study area

Groundwater in the study area was adversely affected by nitrate concentration, and approximately 77% of the samples contained nitrate above its permissible limit (50 mg/L) for drinking purposes (WHO, 2017). Furthermore, nitrate concentrations in drinking water above 100 mg/L can affect congenital glucose-6-phosphate dehydrogenase insufficiency in adults and pregnant women. The nitrate concentration in the study area varied between 17,47 and 93,16 mg/L, with an average value of 45,478 mg/L. Infants are more likely to suffer from methaemoglobinemia, or newborn cyanosis, when exposed to excessive amounts of nitrate in their drinking water (Das et al., 2020). Worldwide reports of goiter, hypertension, and stomach cancer have also been linked to the consumption of nitrate-enriched water (Chabukdhara et al. 2017). Furthermore, nitrate concentrations in drinking water above 100 mg/L can affect congenital glucose-6-phosphate dehydrogenase insufficiency in adults and pregnant women. Elevated nitrate concentrations in groundwater may be caused by overuse of nitrogen fertilizer, home effluent, and sewage waste. Considering that drinking water with < 50 mg L⁻¹ of nitrate is in the low risk category, 50–100 mg L⁻¹ is in the high risk category, and >100 mg L⁻¹ is in the very high risk category (Adimalla 2020), approximately about 72%, 12% and of the total groundwater sample of the study area was in low risk, and high risk categories, respectively (Figure 6) .

The groundwater fluoride concentration (Figure 5) varied between 0.43 and 2,79 mg /L with a mean value of 1,277 mg/L and approximately, 32% of the samples had fluoride concentrations over the permissible limit of 1.5 mgL⁻¹ (WHO 2011). and almost 20% of the sample had fluoride concentrations above the permitted limit of 2.0 mg L⁻¹ (USEPA, United States Environmental Protection Agency, 2010). Fluoride, which causes skeletal fluorosis in both adults and children when exposed in excess, is one of the most important pollutants in the aquifer (Narsimha and Rajitha 2018). One very common dental condition that affects children globally throughout the period of tooth growth is fluorosis (Yadav et al. 2019).

The speciation of fluoride (F⁻) in groundwater is significantly influenced by the acid-base environment. Alkaline groundwater conditions reduce the activity of calcium (Ca²⁺), This lessens the inhibitory influence of F⁻ buildup in groundwater and promotes the production of high-fluoride groundwater. Additionally the release of F is encouraged by the concentration of hydroxide ions (OH⁻) in alkaline settings from minerals containing fluorine (such as muscovite, biotite, and fluorapatite), leading to increased F concentrations.

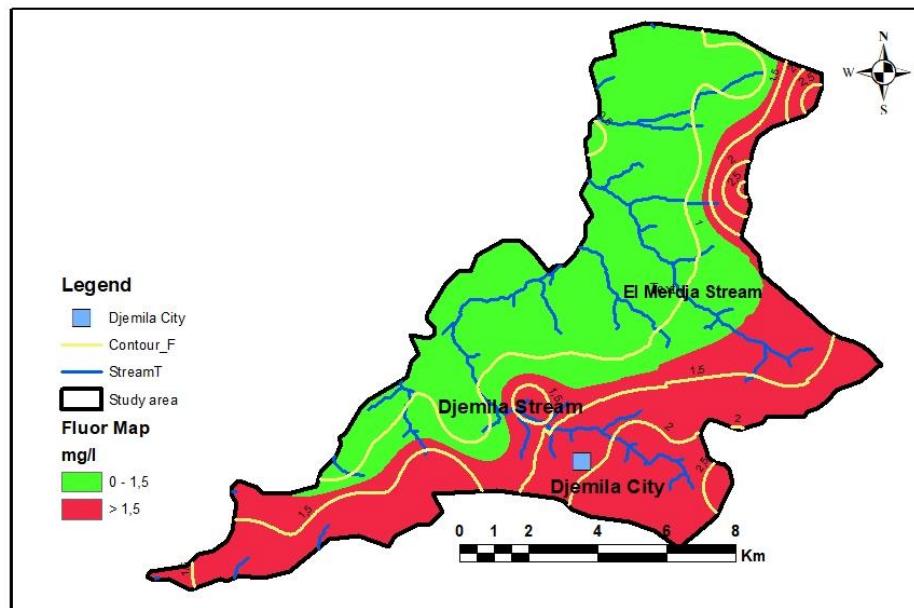


Figure 5 Spatial distribution of Fluor in the study area

The factors controlling the nitrate concentrations in groundwater

Surface and groundwater can readily dissolve and contain nitrate ions. Nitrate in groundwater comes from a variety of sources, including both natural and man-made processes such as biological denitrification fixation by bacteria, leaching of industrial effluent, untreated wastewater, fertilizers, and animal dung (Barnes et al. 2013 ; annicke et al. 1992). Although geogenic sources contribute less to nitrate pollution than do anthropogenic sources, the weathering of rocks is linked to the process of nitrate conversion from nitrogen leaching (Holloway and Dahlgren 2002; Shukla and Saxena 2020). Groundwater containing more than 50 mg/L of NO_3 is thought to be contaminated by human activities such as animal waste and the overuse of nitrogen-based fertilizers from excessive irrigation. according to Guo et al. (2008), Alam et al. (2023 , 2020), and Wang et al. (2023) for agricultural output. Nitrate is a significant non-carcinogenic pollutant in areas with intensive agricultural activities (Adimalla 2020; Adimalla and Qian 2019a). While nitrate is essential for DNA, RNA, proteins, and enzymes, elevated levels in groundwater are becoming a serious global health concern. Typically, nitrate concentrations in surface and groundwater are low, but human activities such as intensive agriculture with excessive nitrogen fertilizer use, animal manure, organic matter decay, domestic wastewater, industrial effluents, landfills, and irrigation runoff can increase nitrate levels (Qian et al. 2012; Karunanidhi et al. 2019; Marghade et al. 2019; Adimalla and Qian 2019a). In the study area, located in the eastern Algerian plain with alluvial soils, agriculture is the primary activity. The indiscriminate use of nitrogenous fertilizers to boost crop yields, despite decreasing nitrogen factor productivity, has led to nitrate leaching and elevated nitrate

levels in groundwater. Fertilizer application also increases concentrations of calcium (Ca), chloride (Cl), and nitrate (NO₃) in groundwater, indicating the impact of animal manure and livestock waste. Surface activities, such as percolation of wastewater from septic tanks and fertilizers along with irrigation water, can further elevate nitrate and ammonia concentrations in groundwater (Chen et al. 2018). In paddy fields, ammonia is converted to nitrate by bacteria under anoxic conditions.

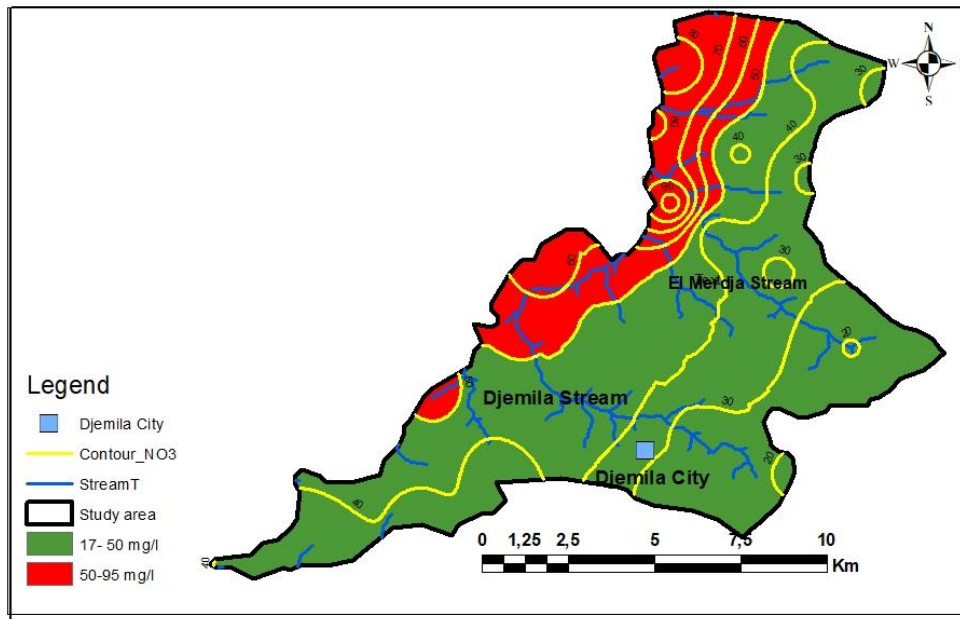


Figure 6 Spatial distribution of nitrates in study area

Factors controlling fluoride hydrogeochemistry

Geological factors, different hydrogeochemical processes that take place within the groundwater system, and human activity close to the groundwater source can all have an impact on the enrichment of fluoride in groundwater. The results of general statistical analysis showed that fluoride levels were higher. Furthermore, showing how hydrogeochemical processes affect groundwater indicated that rock weathering is common in the studied area. This demonstrates that evaporites and minerals containing fluorine can dissolve in groundwater. Dissolution of evaporites, like gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), in samples ranging from shallow to deep groundwater occurs in the evaporation regime. Fluoride may become more enriched as a result of halite (Na-Cl) and mirabilite (Na_2SO_4) (Gao in 2007). However, most of the samples are rock weathering dominant illustrate the role of dissolution of the fluorine-bearing minerals. The fluorine-bearing

minerals that responsible for occurrence of fluoride in the groundwater are fluorite (CaF_2), fluorspar, fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), cryolite, amphibole, topaz ($\text{Al}_2(\text{SiO}_4)\text{F}_2$), villiaumite (NaF), muscovite, biotite, hornblende (Avtar et al. 2013; Wu et al. 2018; Chicas et al. 2022).

Fluoride is an essential micronutrient for human health, necessary for healthy teeth and bones. However, long-term consumption of water with fluoride concentrations above permissible limits can cause fluorosis (Aghapour et al. 2018). Fluoride in groundwater can be geogenic or anthropogenic, influenced by factors such as the type of rock (Rao 2017), fertilizer use, industrial effluents, rock-groundwater interaction duration, and weathering processes (Chen et al. 2018). Alkaline water mobilizes fluoride from fluorite, precipitating calcium carbonate (Wang et al. 2019). Sodium bicarbonate in water accelerates fluoride dissolution, increasing its concentration (Jha et al. 2013). Alkaline pH, combined with high sodium and bicarbonate levels, is favorable for fluoride dissolution. Similar findings have been reported in various areas within the study region. The fluoride content in groundwater varies with rock type, as rocks release fluoride during the weathering of minerals like muscovite, biotite, apatite, and fluorite (Kumar et al. 2017). The higher clay content in the aquifers of the study area facilitates prolonged interaction between groundwater and aquifer materials in an alkaline environment, increasing fluoride release (Manikandan et al. 2014). Anthropogenic sources of elevated fluoride levels include chemical fertilizers used in agriculture and industrial waste (sewage, sludge) (Tiwari et al. 2017). Fluoride is a micronutrient that is vital to human health and is required for healthy tooth and bone development. Long-term ingestion of drinking water with fluoride concentrations over recommended levels can lead to fluorosis. The origin of fluoride in groundwater is recognized to be either geogenic or anthropogenic, depending on many aspects such as the kind of rock, fertilizer use, industrial effluent, rock-groundwater interaction duration, and weathering process (Rao, 2017). impact the amount of fluoride present in groundwater (Chen et al. 2018). Higher clay content, as seen in the research area's aquifers, is found to allow groundwater to interact with aquifer materials for longer periods of time in an alkaline environment, increasing the groundwater's release of fluoride. Industrial waste (sewage, sludge) and chemical fertilizers used in agriculture are other potential human sources of the elevated fluoride level in groundwater ..

Non-carcinogenic human health risk assessment

Globally, and particularly in Algeria, where groundwater is a primary source for household and drinking purposes, there is significant evidence of health risks linked to fluoride and nitrate exposure. Our findings reveal that groundwater fluoride and nitrate levels exceeded permissible limits, potentially posing health hazards. We conducted a non-carcinogenic health risk assessment for fluoride and nitrate in drinking water using a model outlined by USEPA (1989). Hazard quotients (HQ) for fluoride (HQ Fluoride) and nitrate (HQ Nitrate) were calculated for three age groups: children, man, and women (Table 7). The permissible limit of HQ and hazard index (HI) is 1.0 (USEPA 1989) whereas the average $\text{HQ}_{\text{Nitrate}}$ for children , man and woman were 2.75, 2.21 and 2.10 respectively in our study area and 63%, 58% and 56% of the samples were above 1.0 ($\text{HQ} > 1$) with respect to Children, man and women. HQ Fluoride for infant, children and adult varied from 0.16-22.44, 0.14-13.88 and 0.12-13.88 respectively with mean of 4.26, 3.74 and 3.47 respectively and 88.13, 84.67 and 82.78% of groundwater samples were above 1.0 ($\text{HQ} > 1$) with reference to children, man and woman respectively. with reference to children, man and woman respectively. It can be inferred that children and man were at higher risk of non-carcinogenic effects due to intake of drinking water high in nitrate and fluoride than woman probably due to the lower body weight and less developed enzymatic metabolism of children and man as comparison to woman.

HQ Nitrate depicts children population of the study area were most vulnerable to health risk hazard due to ingestion of nitrate-rich groundwater than the central region of the study area, which has a few hazard free patches. Increased use of nitrogen fertilizer to attain higher crop yield in recent years has increased the nitrate concentration in groundwater and excessive use of nitrogen fertilizer raised the nitrate concentration in the groundwater to as high as 179.65 mg. Elevated rate of fertilizer, high permeability, and intensive irrigation increased the nitrate concentration in the groundwater the study area whereas agriculture has been reported to be the primary source of nitrate pollution in the groundwater. The cumulative health risk associated with nitrate and fluoride was estimated using the HI and it was found that approximately 99% of the samples in the study were above the permissible limit ($HI > 1$), indicating that considerable non-carcinogenic health risk was associated with using such water for drinking and domestic purposes and the health risk associated with fluoride was greater than nitrate in the study area. The population of the study area was more prone to non-carcinogenic risk due to intake of fluoride-rich groundwater, especially in case of infants and children which can cause dental and skeletal fluorosis. Pretreatment of drinking water to lower its content well within the permissible limit is necessary to curb the non-carcinogenic effect of fluoride. Similar results were reported in the studies by various researchers in the world (Adimalla and Qian 2019b; Kaur et al. 2020). Moreover the present study estimates fluoride intake through drinking water only and does not take into account the other source of fluoride ingestion through food, vegetable and beverages. Therefore, the actual dose of fluoride exposure through ingestion by the local residents is much higher than the value estimated in our study. This study reported high levels of fluoride in groundwater and the occurrence of various forms of fluorosis in the Djemila area.

Table 7 HQ_{Nitrates} , HQ_{Fluor} and HI Parametrers

Parameters	Age group	Minimum	Mean	Maximum	% sample above 1
HQ _{Nitrates}	Children	0,05	2,75	21 ,11	63
	Man	0,03	2,21	17,35	58
	Woman	0,02	2,10	13,57	56
HQ _{Fluoride}	Children	0,16	4,26	22,44	88,13
	Man	0,14	3,74	17,99	84,67
	Woman	0,12	3,47	13,88	82,78
HI	Children	0,69	7,98	25,83	97,15
	Man	0,58	5,42	20 ;34	95,63
	Woman	0,49	4,92	16,12	93,88

Conclusion

Algeria relies heavily on groundwater as a resource to supply its water needs, but it faces many obstacles. The combination of rising water demands and decreased precipitation due to climate change has significantly strained groundwater reserves across the country. An important consideration in evaluating human growth and well-being is the quality of groundwater. In an agricultural area of the Djemila area, this study aims to assess and identify the causes of groundwater contamination linked to both natural and human sources. The study reported elevated concentrations of nitrate and fluoride in groundwater with little awareness about the health risk due to elevated nitrate and fluoride concentration among the agrarian population of the study area utilizing hydrochemical approaches, index methods (such NPI, WQI, HQ and HI) . This research is unique because it takes a holistic approach to identifying and understanding the origins of groundwater pollution. It does this by integrating a variety of approaches. Twenty-five groundwater samples were taken from different places for the experiment in order to evaluate their features. The NPI ranges from -0,13 to 3.66, indicating dangerously high levels of nitrate contamination linked to human activities such as the usage of fertilizer and sewage intrusion. 64% of samples are of "good" quality for drinking, according to the WQI analysis and 36% are judged unsuitable (or "poor").

This study gives a thorough summary of the state of the groundwater in the study area and offers insightful information to relevant authorities and policymakers. In tackling the issues of groundwater pollution in the research region adoption of appropriate water management techniques, efficient land use, and sustainable agricultural It is essential to have management plans. Promoting the use of techniques like precision irrigation, crop rotation, and efficient water use can greatly reduce the amount of contaminants that seep into groundwater reservoirs. Making fertilizer management a priority is vital to stop too much nitrate from seeping into groundwater supplies. Putting into Practice actions include controlling the amount and timing of fertilizer applications and using Utilizing organic leftovers as substitute fertilizers can assist in preserving the balance of nutrients and minimize leaching.

References

1. **Adimalla N, Li P, Qian H. 2018.** Evaluation of groundwater contamination for fluoride and nitrate in semi-arid region of Nirmal Province, South India: a special emphasis on human health risk assessment (HHRA). *Hum Ecol Risk Assess Int J.* doi:10.1016/j.chemer.2019.125548
2. **Adimallaa, N., & Rajitha, S. (2018).** Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. *Human and Ecological Risk Assessment*. <https://doi.org/10.1080/10807039.2018.143817>.
3. **Adimalla N, Qian H. 2019a.** Groundwater quality evaluation using water quality index (WQI) for drinking purposes and human health risk (HHR) assessment in an agricultural region of Nanganur, south India. *Ecotoxicol Environ Saf.* 176:153–161. doi:10.1016/j.ecoenv.2019.03.066
4. **Adimalla, N. (2019)** 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* 2019, 42, 1725–1752.
5. **Adimalla N. 2020.** Spatial distribution, exposure, and potential health risk assessment from nitrate in drinking water from semi-arid region of South India. *Hum Ecol Risk Assess Int J.* 26(2): 310–334. doi:10.1080/10807039.2018.1508329
6. **Alam I, Rehman JU, Nazir S, Nazeer A, Akram M, Batool Z, Ullah H, Hameed A, Hussain A, Hussain A, et al. 2021.** Health risk assessment in different age-group due to nitrate, fluoride, nitrite and geo-chemical parameters in drinking water in Ahmadpur East, Punjab, Pakistan. *Hum Ecol Risk Assess Int J.* 27(7):1747–1763. doi:10.1080/10807039.2021.1902264
7. **Alam SK, Li P, Fida M. 2023.** Groundwater nitrate pollution due to excessive use of N-fertilizers in Rural Areas of Bangladesh: pollution status, health risk, source contribution, and future impacts. *Expo Health.* 16(1):159–182. doi:10.1007/s12403-023-00545-0.
8. **Al-Aizari, H.S.; Aslaou, F.; Al-Aizari, A.R.; Al-Odayni, A.-B.; Al-Aizari, A.-J.M.(2023)** Evaluation of Groundwater Quality and Contamination Using the Groundwater Pollution Index (GPI), Nitrate Pollution Index (NPI), and GIS. *Water*, 15, 3701.
9. **Azhari, H.E.; Cherif, E.K.; Sarti, O.; Azzirgue, E.M.; Dakak, H.; Yachou, H.; Esteves Da Silva, J.C.G.; Salmoun, F.** Assessment of Surface Water Quality Using the Water Quality Index (IWQ), Multivariate Statistical Analysis (MSA) and Geographic Information System (GIS) in Oued Laou Mediterranean Watershed, Morocco. *Water* 2022, 15, 130. [CrossRef]
10. **Avtar R, Kumar P, Surjan A, Gupta LN, Roychowdhury K. 2013.** Geochemical processes regulating groundwater chemistry with special reference to nitrate and fluoride enrichment in Chhatarpur area, Madhya Pradesh, India. *Environ Earth Sci.* 70(4):1699–1708. doi:10.1007/s12665-013-2257-7.
11. **Barakat, A.; Mouhtarim, G.; Saji, R.; Touhami, F. 2020** Health Risk Assessment of Nitrates in the Groundwater of Beni Amir Irrigated Perimeter, Tadla Plain, Morocco. *Hum. Ecol. Risk Assess. Int. J.* 26, 1864–1878.
12. **Barnes CJ, Jacobson G, Smith GD. 1992.** The origin of high-nitrate ground waters in the Australian arid zone. *J Hydrol.* 137(1–4):181–197. doi:10.1016/0022-1694(92)90055-Z.
13. **Bouita, M.; El Mahdi, Y.; Sbai, H.; Bouita, I.; El Bakouri, A.; Ibrahimi, E.M.; Chakir, E.M. (2021)** Assessment of Nitrogen Pollution of Groundwater in the Maamora Gharb Aquifer, Morocco. *Egypt. J. Aquat. Biol. Fish.*, 25, 739–758
14. **Chabukdhara M, Gupta SK, Kotecha Y, Nema AK. 2017.** Groundwater quality in Ghaziabad district, Uttar Pradesh, India: Multivariate and health risk assessment. *Chemosphere.* 179: 167–178. doi: 10.1016/j.chemosphere.2017.03.086
15. **Chen J, Wu H, Qian H, Li X. 2018.** Challenges and prospects of sustainable groundwater management in an agricultural plain along the Silk Road Economic Belt, north-west China. *Inter J Water Resour Dev.* 34(3):354–368. doi:10.1080/07900627.2016.1238348

16. Chicas SD, Omine K, Prabhakaran M, Sunitha TG, Sivasankar V. 2022. High fluoride in groundwater and associated non-carcinogenic risks at Tiruvannamalai region in Tamil Nadu, India. *Ecotoxicol Environ Saf.* 233:113335. doi:10.1016/j.ecoenv.2022.113335.
17. Das A, Das SS, Chowdhury NR, Joardar M, Ghosh B, Roychowdhury T. 2020. Quality and health risk evaluation for groundwater in Nadia district, West Bengal: An approach on its suitability for drinking and domestic purpose. *Groundw Sustain Dev.* 10:100351. doi:10.1016/j.gsd.2020. 100351
18. El Mountassir, O.; Bahir, M.; Chehbouni, A.; Dhiba, D.; El Jiar, H. (2022) Assessment of Groundwater Quality and the Main Controls on Its Hydrochemistry in a Changing Climate in Morocco (Essaouira Basin). *Sustainability* , 14, 8012. [CrossRef]
19. Gao X, Wang Y, Li Y, Guo Q. 2008. Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. *Environ Geol.* 53(4):795–803. doi:10.1007/s00254-007-0692-z
20. Gao X, Wang Y, Li Y, Guo Q. 2007. Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. *Environ Geol.* 53(4):795–803. doi:10.1007/s00254-007-0692-z
21. Holloway JM, Dahlgren RA. 2002. Nitrogen in rock: occurrences and biogeochemical implications. *Global Biogeochem Cycles.* 16(4):65–61. doi:10.1029/2002GB001862.
22. Kachroud, M.; Trolard, F.; Kefi, M.; Jebari, S.; Bourrié, G. (2019) Water Quality Indices: Challenges and Application Limits in the Literature. *Water* , 11, 361
23. Kadri, A.; Baouia, K.; Kateb, S.; Al-Ansari, N.; Kouadri, S.; Najm, H.M.; Mashaan, N.S.; Eldirderi, M.M.A.; Khedher, K.M. (2022) Assessment of Groundwater Suitability for Agricultural Purposes: A Case Study of South Oued Righ Region, Algeria. *Sustainability* , 14, 8858
24. Marghade D, Malpe DB, Subba Rao N. 2019. Applications of geochemical and multivariate statistical approaches for the evaluation of groundwater quality and human health risks in a semi-arid region of eastern Maharashtra, India. *Environ Geochem Health.* doi:10.1007/s10653-019- 00478-1
25. Shukla S, Saxena A. 2020. Groundwater quality and associated human health risk assessment in parts of Raebareli district, Uttar Pradesh, India. *Groundw Sustain Deve.* 10:100366
26. Shukla S, Saxena A. 2020. Sources and leaching of nitrate contamination in groundwater. *Current Science.* 118(6):883–891. doi:10.18520/cs/v118/i6/883-891.
27. Subba Rao, N. (2012). PIG: a numerical index for dissemination of groundwater contamination zones. *Hydrological Processes*, 26(22), 3344–3350. <https://doi.org/10.1002/hyp.8456>
28. Subba Rao, N. (2018) Groundwater Quality from a Part of Prakasam District, Andhra Pradesh, India. *Appl. Water Sci.* 8, 30.
29. Sunitha, V.; Reddy, B.M. (2022) Geochemical Characterization, Deciphering Groundwater Quality Using Pollution Index of Groundwater (PIG), Water Quality Index (WQI) and Geographical Information System (GIS) in Hard Rock Aquifer, South India. *Appl. Water Sci.* , 12, 41. [CrossRef]
30. Oyedele, A. A., Ayodele, O. S., & Olabode, O. F. (2019). Groundwater quality assessment and characterization of shallow basement aquifers in parts of ado ekiti metropolis, Southwestern Nigeria. *SN Applied Sciences*, 1(7). <https://doi.org/10.1007/s42452-019-0683-1>
31. Rao, N. S., Sunitha, B., Rambabu, R., Rao, P. V. N., Rao, P. S., Spandana, B. D., Sravanthi, M., & Marghade, D. (2018). Quality and degree of pollution of groundwater, using PIG from a rural part of Telangana State, India. *Applied Water Science*, 8(8). <https://doi.org/10.1007/s13201-018-0864-x>
32. Panneerselvam B, Karuppannan S, Muniraj K (2021) Evaluation of drinking and irrigation suitability of groundwater with special emphasizing the health risk posed by nitrate contamination using nitrate pollution index NPI and human health risk assessment HHRA. *Hum Ecol Risk Assess.* 27(5):1324–1348. <https://doi.org/10.1080/10807039.2020.1833300>

33. **Egbueri, J. C., & Unigwe, C. O. (2019).** An integrated indexical investigation of selected heavy metals in drinking water resources from a coastal plain aquifer in Nigeria. *SN Applied Sciences*, 1(11). <https://doi.org/10.1007/s42452-019-1489-x>
34. **Singh, P. S. (2017).** Small-Angle Scattering Techniques (SAXS/SANS). In *Membrane Characterization*. Elsevier B.V. <https://doi.org/10.1016/B978-0-444-63776-5.00006-1>
35. **Solangi, G. S., Siyal, A. A., Babar, M. M., & Siyal, P. (2019).** Evaluation of drinking water quality using the water quality index (WQI), the synthetic pollution index (SPI) and geospatial tools in Thatta district, Pakistan. *desalination and water treatment*, 160, 202–213. <https://doi.org/10.5004/dwt.2019.24241>
36. **Liu, J., Peng, Y., Li, C., Gao, Z., & Chen, S. (2021).** A characterization of groundwater fluoride, influencing factors and risk to human health in the southwest plain of Shandong Province, North China. *Ecotoxicology and Environmental Safety*, 207, 111512. <https://doi.org/10.1016/j.ecoenv.2020.111512>
37. **Raja, V., & Neelakantan, M. A. (2021).** Evaluation of groundwater quality with health risk assessment of fluoride and nitrate in Virudhunagar district, Tamil Nadu, India. *Arabian Journal of Geosciences*, 14(1). <https://doi.org/10.1007/s12517-020-06385-5>
38. **Rao NS. 2017.** Controlling factors of fluoride in groundwater in a part of South India. *Arab J Geosci*. 10(23):524.
39. **Naderi, M., Jahanshahi, R., & Dehbandi, R. (2020).** Two distinct mechanisms of fluoride enrichment and associated health risk in springs' water near an inactive volcano, southeast Iran. *Ecotoxicology and Environmental Safety*, 195, 110503. <https://doi.org/10.1016/j.ecoenv.2020.110503>
40. **Narsimha A, Rajitha S. 2018.** Spatial distribution and seasonal variation in fluoride enrichment in groundwater and its associated human health risk assessment in Telangana State, South India. *Hum Ecol Risk Assess Int J*. 24 (8):2119–2132. [doi:10.1080/10807039.2018.1438176](https://doi.org/10.1080/10807039.2018.1438176)
41. **USEPA (U.S. Environmental Protection Agency) 2010.** Fluoride: Exposure and Relative Source Contribution Analysis. EPA 820-R-10e015. Washington, D.C: U.S. Environmental Protection Agency, Health and Ecological Criteria Division, Office of Water.
42. **Yadav KK, Kumar V, Gupta N, Kumar S, Rezanian S, Singh N. 2019.** Human health risk assessment: study of a population exposed to fluoride through groundwater of Agra city, India. *Regul Toxicol Pharmacol*. 106:68–80. [doi:10.1016/j.yrtph.2019.04.013](https://doi.org/10.1016/j.yrtph.2019.04.013)
43. **Wannicke N, Korth F, Liskow I, Voss M. 2013.** Incorporation of diazotrophic fixed N₂ by mesozooplankton Case studies in the southern Baltic Sea. *J Mar Syst*. 117–118:1–13. [doi:10.1016/j.jmarsys.2013.03.005](https://doi.org/10.1016/j.jmarsys.2013.03.005)
44. **Wang D, Li P, Yang N, Yang C, Zhou Y, Li J. 2023.** Distribution, sources and main controlling factors of nitrate in a typical intensive agricultural region, northwestern China: vertical profile perspectives. *Environ Res*. 237(Pt 1):116911. [doi:10.1016/j.envres.2023.116911](https://doi.org/10.1016/j.envres.2023.116911)
45. **Wu C, Wu X, Qian C, Zhu G. 2018.** Hydrogeochemistry and groundwater quality assessment of high fluoride levels in the Yanchi endorheic region, northwest China. *Appl Geochem*. 98:404–417. [doi:10.1016/j.apgeochem.2018.10.016](https://doi.org/10.1016/j.apgeochem.2018.10.016)
46. **WHO. (2011).** Guidelines for drinking-water quality (4th ed.). Geneva: World Health Organization
47. **WHO World Health Organization.** Guidelines for Drinking-Water Quality: Fourth Edition Incorporating First Addendum; World Health Organization: Geneva, Switzerland, **2017**; ISBN 978-92-4-154995-0