



Assessment of the quality of groundwater intended for consumption and its impact on human health: case of the Sidi Rached Mitidja West basin, Algeria

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ABSTRACT: The quaternary aquifer of Sidi Rached basin located in the West Mitidja represents an important source for water supply. Groundwater is widely recognized as an essential source of drinking water in Sidi Rached basin. The objective of the present study is to evaluate the groundwater quality of Mitidja, to determine its suitability for consumption using the Groundwater Quality Index (GWQI) and to determine its impact on human health. Physico-chemical analysis were carried out on 38 groundwater samples taken from different locations in the study area. Groundwater quality index (GWQI), electrical conductivity (EC), total hardness (TH) and total dissolved solids (TDS) were used to assess groundwater quality. While HHRA (Human Health Risk Assessment) was used to assess human health risks. The GWQI showed that 64.86% and 35.14% of the sampling sites are classified as medium and poor drinking water quality respectively. The total hazard index (HI) based on human health risk assessment model for cumulative NO₃⁻ toxicity through oral was computed as 100%, 97.85% and 96.77% for infants, children and adults populations respectively. The HQ (nitrate) >1 through ingestion pathway was in 84.95%, 68.82% and 62.37% of the groundwater samples were recorded for infants, children and adults population respectively. The risk assessment study highlighted very high toxicity and severe health impact of ingestion of contaminated groundwater on public health. The study made it possible to identify polluted areas and also to assess the risks to human health, according to the HHRA, infants are at high risk compared to children and adults in the study area.

Keywords: HHRA, Groundwater, GWQI, Nitrate pollution, Mitidja, Sidi Rached.

I. INTRODUCTION

The Groundwater constitutes an important source of fresh water, essential and widely used in development and most human activities (for consumption and agriculture in arid and semi-arid regions). It depends mainly on irregular and unevenly distributed rainfall in space; it can be rare in some places, such as arid and semi-arid are, or simply of poor quality in other places. The quaternary aquifer of West Mitidja is exposed to various sources of pollution linked mainly to agriculture, livestock and urban and industrial discharges, which causes the contamination of groundwater by various pollutants including nitrates (Saida and al., 2017). Significant concentrations ranging from 14 mg/L to 115 mg/L were determined in the groundwater of the study area (Saida and al., 2017). In recent years, the protection and conservation of natural environments, in particular water quality, has become a major concern and a main objective in development programs. Indeed, groundwater quality generally has considerable potential for contamination particularly in agricultural areas dominated by intense activities involving the use of fertilizers and pesticides (Chae and al., 2004). Nitrates are one of the parameters used to qualify the state of water. Their presence in excess can contribute to unbalancing aquatic environments, for example with eutrophication phenomena in waterways due to the absence of filtration and exposure to light. This phenomenon corresponds to a significant proliferation of chlorophyll plants, which causes a reduction in the quantities of dissolved oxygen available. While groundwater will only be affected later, due to the presence of vadose zone (area between the ground surface and the aquifer). Nitrate losses from non-point agricultural sources, mainly emitted by fertilizer application, have been recognized as one of the most serious threats to groundwater pollution (Salemi and al., 2012). The level of nitrate in drinking water is an indicator of water quality (Keeney DR., 1984; Khosravi R. and al. 2018) Consumption of water with high nitrate content can cause harmful effects on human health. Following long-term exposure, diuresis, hardening of the spleen and foci of bleeding foci are observed (USEPA, 2006). It is known that ingestion of nitrate through drinking water causes the development of methemoglobinemia, known as blue baby syndrome), in infants less than 06 months old (Chambon and al., 1983). This disease results from the reaction of nitrites with hemoglobin in the blood, preventing it from transporting oxygen from the lungs to the rest of the body. Ingesting nitrate-laden water can cause

diabetes in children and can be a precursor to many chemicals that can be toxic to the pancreas (Parslow RC. 1997). Nitrites can also combine with amino compounds to form nitrosamines (N-nitroso) which can cause goiter disease (Seffner W. 1995) and stomach cancer in adults. Nitrate can cause the formation of methemoglobin leading to insufficient blood flow to vital organs and tissues (Kaya S., 2002). Zaldivar (1997) found in her study that in babies aged 0 to 6 months with a gastric pH greater than 4.9, in foods prepared with water containing more than 20 mg/L of nitrate, nitrate transforms into nitrite, leading to the formation of methemoglobin as a result of nitrite binding to hemoglobin and preventing it from oxidizing (Zaldivar R., 1997). Diffuse pollution affects soil and water in a widespread manner. It essentially results from certain agricultural practices such as the spreading of fertilizers or pesticides in agricultural fields. Nearly half of the nitrogen fertilizers provided are not used by crops and are lost to the ecosystem through volatilization, runoff or leaching (Billen, G; 2013). In fact, the agricultural sector is responsible for 60% of this increase (FAO Faostat 2020, Bodirsky B.L. and al. 2014). In 1977, a WHO expert committee set the maximum admissible concentration of nitrates for water intended for human consumption at 50 mg/L. In 1977, a WHO expert committee set the maximum admissible concentration of nitrates for water intended for human consumption at 50 mg/L. Numerous studies have been established in this context and have shown that the nitrate concentration of groundwater is often higher than 50 mg/L, the standard recommended by the WHO (World Health Organization). A study carried out in the Mitidja plain, the concentration increased from 130 mg/L in 2002 to 260 mg/L in 2004 (Salem, 2007), greatly exceeding the WHO standard (50 mg/L). In fact, the fertilization rate has reached nearly 400 kg of nitrogen/hectare in its western region (Hadjoudj, 2008). Another study carried out on the Ghrib Ain Defla dam (North West Algeria) during the period from April to October 2007 showed that the concentration of nitrates in July is double that found in April, this corresponds during the period of introduction of fertilizers into the agricultural lands in the vicinity of this dam (Hamaidi, 2009). A very alarming situation was observed in 2004 in Oued Mezzouze Collo W de Skikda (Chabour, 2004) where the concentration reached 570 mg/L. Values of 80 to 120 mg/L were obtained in numerous wells tapping the Chéria aquifer (Baali and al, 2007). This increase in concentration is due to the use of nitrogen fertilizers in quantities significantly higher than the plants' needs. The current level of water pollution by nitrates justifies taking measures to prevent any increase in this pollution. However, appropriate protection of water resources, particularly against pollution from intensive agriculture, requires understanding the mechanisms that determine this pollution at different scales. The water quality of the alluvial aquifer of Sidi Rached located in the far west of the Mitidja plain, considered as a potential source of drinking water supply, irrigation and industry for the wilaya of Tipaza and its surroundings, has suffered a qualitative deterioration in recent years due to inadequate agricultural practices. This work is a continuation of numerous works carried out in the study area and which have dealt with the problem of water resource management, agricultural practices and nitrate pollution. We can cite: Cavero and al. (2011), Salhi and al. (2015), Sbgoud S. (2013), Saida and al. (2017). In this study, the objective was to evaluate the drinking groundwater quality index (GWQI), identify polluted areas and also determine the non-carcinogenic human health risk factor (HHRA) resulting from the ingestion of nitrates through drinking water for three different age groups: adults, children and infants, using the level of nitrates measured in groundwater samples taken from different water points in the Sidi Rached area.

II. MATERIALS AND METHODS

2.1. Study area

The study area is located in the far west of the Mitidja agricultural plain. The area is bordered to the north by the Sahel and the province of Tipaza; to the east by Attatba and El Affroun; to the west by Hadjout and to the south by the Atlas Mountains of Blida and it contains 03 communes, Sidi Rached, Ahmeur el Ain and Bourkika (Figure 1). The climate is subject to a coastal sub humid Mediterranean climate. Precipitation is often irregular, varying from 500 to 625mm. The average temperature in the region is 18°C.

The fluvial system of the basin is characterized by a set of watercourses which drain the alluvial outcrops. More than 200 boreholes and wells are currently exploited at the level of the groundwater for irrigation and drinking water supply. According to geophysical studies carried out in 1967 (C.G.G., 1967), there are two superimposed aquifers under the Mitidja plain: the Eocene aquifer (formed during the Tertiary age) and the Quaternary alluvium aquifer.

The Eocene aquifer is confined with an average thickness which varies from 100 to 150 m, it is very deep (250 and 300 m). The Quaternary alluvial layer is entirely free and rests on the yellow marls of El Harrach. Its thickness varies from 100 to 200 m.

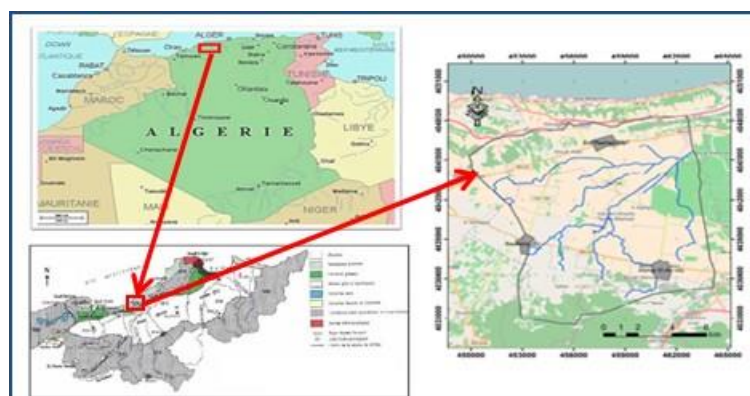


Figure 1. Location map of the Sidi Rached plain.

2.2. Sample collection and analysis

Groundwater sampling and physicochemical analysis were carried out on groundwater samples taken from boreholes and wells located within the study area (Figure 2). The parameters measured in the laboratory are cations and anions (Ca^{+2} , Mg^{+2} , $\text{Na}^+\text{SO}_4^{-2}$, HCO_3^{-} , NO_3^{-} , NO_2^{-} , NH_4^+ , PO_4^{-3}) while pH and electrical conductivity (EC) were measured in situ.

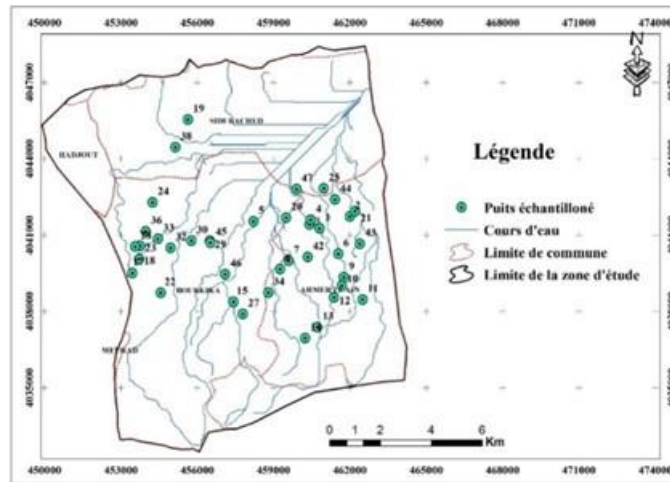


Figure 2. Location map of groundwater sampling wells.

The analytical methods used are:

- Colorimetric method of elements (Cl^- , SO_4^{2-} , HCO_3^{-} , NO_3^{-} , NO_2^{-} , NH_4^+ , PO_4^{3-}).
- Atomic absorption spectrophotometry method: (Ca^{2+} , Mg^{2+} , Na^+) analyses were carried out in the laboratories of the National Water Resources Agency (ANRH).

Results of the chemical analyses were tested by the cations and anions percent charge balance error (%CBE) in order to determine their degree of precision. It was calculated by lenntech on line software (Domenico and Schwartz 1990). The equation (Equation 1) to calculate the CBE is as follows:

$$\%CBE = \left(\frac{\sum m_c z_c - \sum m_a z_a}{\sum m_c z_c + \sum m_a z_a} \right) * 100 \quad (1)$$

Where “m” is molar concentration of major solutes and “z” is charge of cation (c) or anion (a). In this study, the charge balance error of all samples is 0.17%. These results are in agreement with previous studies for the statistical treatment of datasets (Li P. and al., 2015; Zghibi A. and al., 2014).

2.3. Suitability of Groundwater for drinking water

For the evaluation of the quality of drinking water, the results relative to TDS, TH, CE and GWQI were compared to the standards of the World Health Organization (WHO).

2.4. GWQI computing

Groundwater quality index (GWQI) was calculated for assessing suitability of groundwater for drinking use based on WHO standards (WHO 2011), it indicates the quality of water and it is calculated using various parameters that are truly reflective of the water's quality. It is considered as one of the most reliable tools to classify groundwater contamination levels (Sahu and Sikdar, 2008; Belkhir et al., 2018). In the current study, nine important parameters for each well were chosen for the GWQI calculation. International standards were used to assess the quality of different water samples (See Table 1). The following steps were taken to calculate the GWQI:

1. Calculating relative weight for each water quality parameter was done by assigning weightage to each measured parameter which between 1 and 5. The relative weight for each water quality parameter was calculated using the following formula:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (2)$$

Where W_i represents the relative weight of each sampled parameter, w_i represents the weight of each parameter, and n represents the total number of parameters.

2. Calculating Q value: a quality rating score (q_i) or sub index for all parameters was calculated by dividing the concentration of each parameter by its respective standard, the result was then normalized as follows:

$$q_i = C_i * 100/S_i \quad (3)$$

Where q_i is quality rating, C_i is concentration of each parameter (mg/L), and S_i is derived from the WHO water quality standard.

3. Finally, the overall GWQI for each sample was calculated using the following equation:

$$GWQI = \sum_{i=1}^n w_i q_i \quad (4)$$

The computed WQIs were then classified into five groups excellent water at water unsuitable for drinking purpose, using Sahu and Sikdar (Gibbs, R.J., 1970) classification model (Table 1).

Table 1. Relative weight of chemical parameters

Parameters	units	WHO	Weight (wi)	Relative weight
Ca ²⁺	mg/L	100	2	0.056
Mg ²⁺	mg/L	50	5	0.139
Na ⁺	mg/L	150	5	0.139
Cl ⁻	mg/L	250	5	0.139
SO ₄ ²⁻	mg/L	250	5	0.139
HCO ₃ ⁻	mg/L	250	1	0.028
NO ₃ ⁻	mg/L	50	5	0.139
CE	µs/cm	1500	5	0.139
pH	/	8.5	3	0.082
			∑wi=36	

The classification of groundwater quality is made according to the water quality index (GWQI) in five classes (table 2)

Table 2. Classification of groundwater quality according to water quality index (GWQI) (Sahu and Sikdar 2008).

WQI	Water type
< 50	Excellent water
50 – 100	Good quality water
100 – 200	Poor quality water
200 – 300	Eau très mauvaise
> 300	Eau impropre à la consommation

2.5.Human Health Risks Assessment

Human health risk assessment is a process to estimate the nature and probability of adverse health effects in humans that may be exposed to chemicals in a contaminated environment (Li P. and al., 2014). In the present study, nitrate ion (NO₃⁻) was selected as parameter for human health risk assessment (HHRA) because we found that the groundwater in the Sidi Rached basin is loaded by nitrates. Intensive human activities have caused this contamination of the quality of groundwater by a nitrate which consequently affects human health and poses a high-risk health. These ions are considered to pose a non-carcinogenic risk to human health for adults, children and infants.

The model Human health risk assessment (HHRA) has been proposed par US Environmental Protection Agency (USEPA). The HHRA is calculated using the current concentration values of a contaminant in groundwater) and the intensity of drinking per kg body weight and day. The possible health hazards of high NO₃ intake were estimated using USEPA human health risk assessment (HHRA) model for adults, childes and infants (USEPA 1989; Zhou and al. 2016; Wu J. and Sun Z., 2015):

$$EN = \frac{CxIRxEFxED}{BWxAT} \quad (5)$$

Where EN average daily dosage of nitrate in mg/kg/day is the ingestion dose from drinking water (mg/kg/day); C: is the concentration of NO₃ estimated in groundwater samples (mg/L);

IR: is the average daily ingestion rate of drinking water (L/day), and the values of IR (2.5 L/day for an adult, 1 L/day for a child and 0.5 L/day for an infant were used for this model as taken from published literature as suggested by Asante-Duah (2002);

EF: is the exposure frequency (365 days/year),

ED: is the exposure duration (standard exposure during in literature is suggested 30 years for adults, 12 years for children and 1 year for infants);

BW: is the body weight (70 kg for an adult, 30 kg for a child and 09 kg for an infant; Asante-Duah 2002), and AT: is the average exposure time. The non-carcinogenic health risk of NO₃⁻ estimated by the hazard quotient (HQ_N) values, which is estimated through following equation 6.

$$HQ_N = EN/RfD \quad (6)$$

Where RfD is reference dose (1.6 mg/kg/day) for non-carcinogenic health risk (Su H. and al. 2017). The calculation of HQ_N> 1 potentially known to cause health risks and values of HQ_N< 1 constitute an acceptable level of non-carcinogenic risk in individuals due to ingestion of NO₃⁻contaminated groundwater.

2.6.Mapping Spatial Distribution of Groundwater Quality

ArcGIS 10.2.2 software was used to delineate the sampling sites and the geostatistical “spatial analyst” extension of ArcGIS 10.2.2 was used by inverse distance weighted (IDW) interpolation to construct spatial distribution maps, water quality indices (GWQI), and human health risk assessment (HHRA). Figure 3 illustrates the methodological steps adopted.

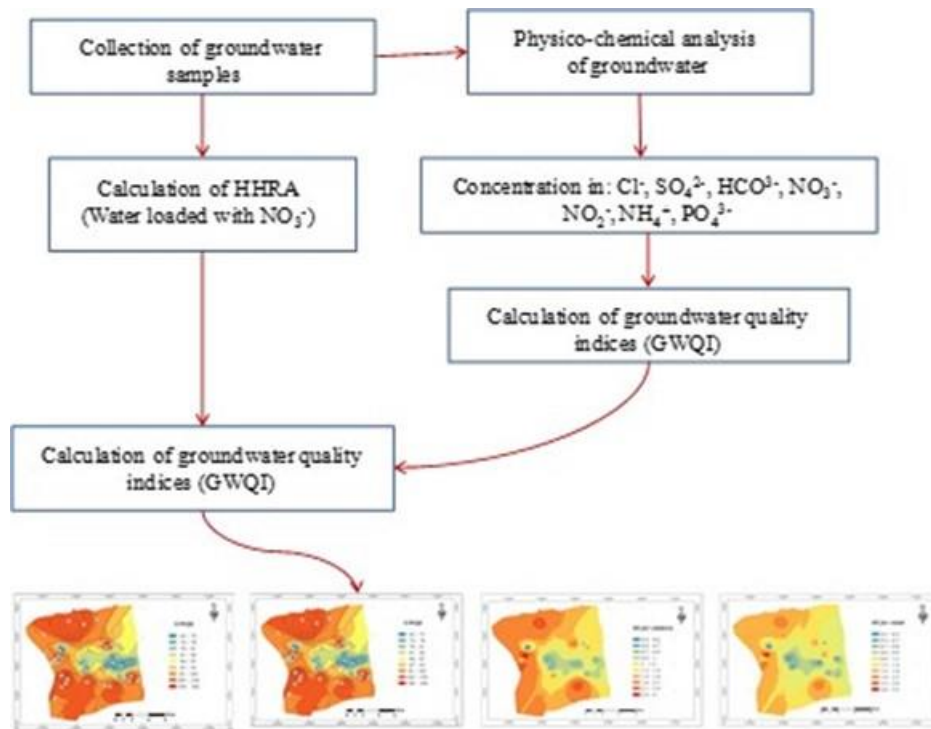


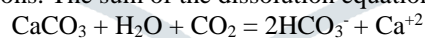
Figure 7. Spatial distribution of the overall potential non carcinogenic health risks through drinking pathway for (a) Infants, (b) Children and (c) Adult.

III. RESULTS AND DISCUSSION

3.1. Physicochemical analysis of groundwater

A summary of the basic statistical analysis of the various hydrochemical parameters of the Sid Rached basin is presented in Table 3. The latter also includes the contribution of these hydrochemical parameters and the WHO standards for comparative studies. The pH is a physical parameter that determines acidity or alkalinity. Usually, pH values range from 6.5 to 8.5 in natural waters (Chapman D. and Kimstach V. 1996). The pH measurements of groundwater in Sidi Rached vary between 6.8 and 8.2, which shows no significant variation and that all wells are within the range of the WHO drinking standard and indicate a low alkalinity of groundwater.

The electrical conductivity of groundwater varied from 1020–2650 $\mu\text{S}/\text{cm}$ with an average value of the 1562.6 $\mu\text{S}/\text{cm}$ indicating high ionic activity in the area. Looking into the analysed water quality data for major ions, anionic abundance was in the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ while cationic abundance was found in the order of $\text{Ca}^{+2} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. The presence of bicarbonates in water is due to the dissolution of carbonate formations (cipolin, limestone) by water loaded with carbon dioxide and to the presence of carbonaceous sandstones in the aquifers and weathering of carbonate minerals in rain water followed by subsequent precipitation of HCO_3^- along with other cations. The sum of the dissolution equations is given as follows:



The concentrations observed in the plain are higher than the norm (250 mg/L), which explains why CO_2 is produced in the aquifer from the mineralization of organic matter. The more the weathering process advances, the more the HCO_3^- content increases. The high levels are recorded during the high-water period with 636 mg/L and a minimum of 206 mg/L, following the dissolution of limestones. The concentrations vary slightly (standard deviation varies between 31.1 and 46.9 mg/L).

Higher Cl^- and SO_4^{2-} concentrations also classified as secondary salt mainly came from the leaching of sewage effluent, especially due to poor wastewater management in the informal settlements. In addition, higher concentrations of SO_4^{2-} can also be attributed to the leaching of organic matter and agricultural runoff carrying unutilized SO_4^{2-} . Chlorides are important inorganic anions found in varying concentrations in natural waters, usually as sodium (NaCl) and potassium (KCl) salts. They are often used as an index of pollution. They have an influence on the aquatic fauna and flora as well as on the growth of plants. The concentrations of chloride ions found in the groundwater of Sidi Rached range between 131 mg/L and 608 mg/L. Values exceeding the norm are recorded in 28.8% of water points indicating higher anthropogenic pressures (leaching of wastewater effluent, leaching of organic matter and agricultural runoff) in these areas.

The presence of sulphate ions (SO_4^{2-}) in water is linked to the dissolution of gypsum formations contained in marls and to the leaching of evaporite deposits according to the relationship:



The sulphate concentrations vary from 52 to 134.3 mg/L. The spatial distribution map of the sulphate concentration shows that the high concentrations are located to the south of the aquifer, at water point's wp13, wp14, wp15 and wp25. Only in 07.7% of wells exceeded the potability standard. The lowest values are recorded in Sidi Rached and Ahmer El Ain, where gypsum marls are absent.

Table 3. Statistical descriptive of the hydrochemical parameters and GWQI.

Parameters	Units	WHO	Max ¹	Min ²	Mean ³	Sd ⁴	CV ⁵ (%)	Nbre ⁶	%
pH	-	6.5-8.1	7.5	6.9	7.2	0.2	2.8	0	0
EC	μ.S.cm	750	2650	1020	1562.6	392.7	25.1	17	45.9
HCO ₃ ⁻	mg/L	250	636	206	327.1	60.5	18.5	37	100
SO ₄ ²⁻	mg/L	250	346.5	52	134.3	61.2	45.6	2	5.41
Cl ⁻	mg/L	250	608	131	236.4	92.6	39.2	11	29.7
Ca ²⁺	mg/L	100	332	62	136.7	41.7	30.5	33	89.2
Mg ²⁺	mg/L	50	90.3	27	46.1	15	32.5	11	29.7
Na ⁺	mg/L	150	195	63	114.8	33.7	29.4	5	13.5
NO ₃ ⁻	mg/L	50	115	13.9	49.8	25.2	50.7	15	40.5
TH	mg/L	500	1047.9	323.9	550.9	163.8	29.7	21	56.8
TDS	mg/L	1000	1786.6	697.6	1018.8	272.7	26.8	14	37.8
GWQI	/	< 100	187.7	62.3	93.3	26	19.6	26	70.3

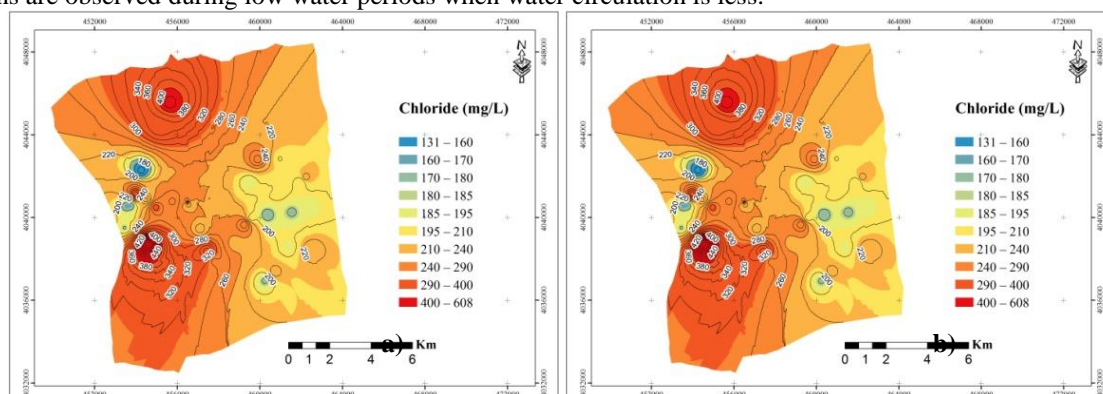
¹ Maximum, ² Minimum, ³ 95% confidence interval, ⁴ Standard deviation, ⁵ Coefficient of variation, ⁶ Numbers of groundwater samples exceeding the standard.

Nitrates are the final stage of nitrogen oxidation, and represent the highest oxidized form of nitrogen found in water. Groundwater concentrations are at the limit of the potability standard. The nitrate concentrations recorded in groundwater are between 13.9 and 115 mg/L. If the minimum value is equal to 13.9 mg/L, recorded at the level of the wp23 water point located north of Bourkika, indicating the presence of an optimal water quality for consumption, there are on the other hand excessively nitrate levels. High with a maximum of 115 mg/L recorded at a water point (wp14) located southwest of Ahmer El Ain. More than 35% of water points have concentrations above the international standard recommended by WHO showing concentrations up to 115 mg/L. The standard deviation calculated between the different periods represents a low variability (25.5), which makes it possible to conclude that the studied waters present a risk of pollution by nitrates which, mainly come from point sources and diffuse agricultural sources and which attests to its origin. Anthropogenic linked mainly to the application of nitrogen fertilizers. Indeed, any excess of nitrate at soil level and not absorbed by the plant finds its way into groundwater when pedo-climatic conditions are favorable. The nitrate map shows the spatial distribution of nitrate concentrations in the groundwater of the Sidi Rached aquifer. More than 73% of the study area, their groundwater has a nitrate concentration higher than the standard established by the World Health Organization WHO (>50mg/L), of which more than 14% show levels, which exceed 75 mg/L.

The presence of Ca²⁺ ions in water is mainly linked to two natural origins: either to the dissolution of carbonates formations (CaCO₃), or to the dissolution of gypsum formations (CaSO₄). 77% of water points have levels above the standard for drinking water. The spatial distribution map of calcium concentration shows that the highest values with a maximum of 332 mg/L are observed in the South-East of the study area (Bourkika) and in the North between Hadjout and Sidi Rached. The lowest values with an average minimum of 62 mg/L are observed in the South East of Ahmer El Ain and concern the wells bordering the limestone borders.

Its origins come from the dissolution of carbonate formations with high magnesium contents (magesite and dolomite). The recorded values oscillate between 90.3mg/L and 27mg/L. The variations in concentration are small; the standard deviation values confirm this. The evolution of magnesium is very different from that of calcium (Ca²⁺). Because the latter has very high contents coming from two origins, which are mentioned above. The spatial distribution map, of the magnesium concentration shows that the highest values (90 mg/L > Mg > 65 mg/L) are located in the centre of the basin and the lowest (35mg/L > Mg > 25 mg/L) at Ahmer El Ain and Bourkika.

The concentrations by sodium (Na⁺) vary between 63 and 195 mg/L. The map shows that the concentrations are important in the central zone of the Sidi Rached basin. Rather high levels are observed in the center of the aquifer, this can be explained by the fact that the points of the Triassic dolomites hidden under the covering of the filling are at their origin. It is reported that the low concentrations are located upstream of the aquifer, there where the groundwater is at the beginning of its path, that is to say is not yet too mineralized. Cretaceous clays, which are found in the aquifer, can give sodium by the phenomenon of Base Exchange by fixing one Ca²⁺ ion after the release of two Na⁺ ions. The sodium content map shows that the North-West sector has water with low sodium content. High concentrations are observed in the center of the basin and south of Ahmer El Ain. These high concentrations are observed during low water periods when water circulation is less.



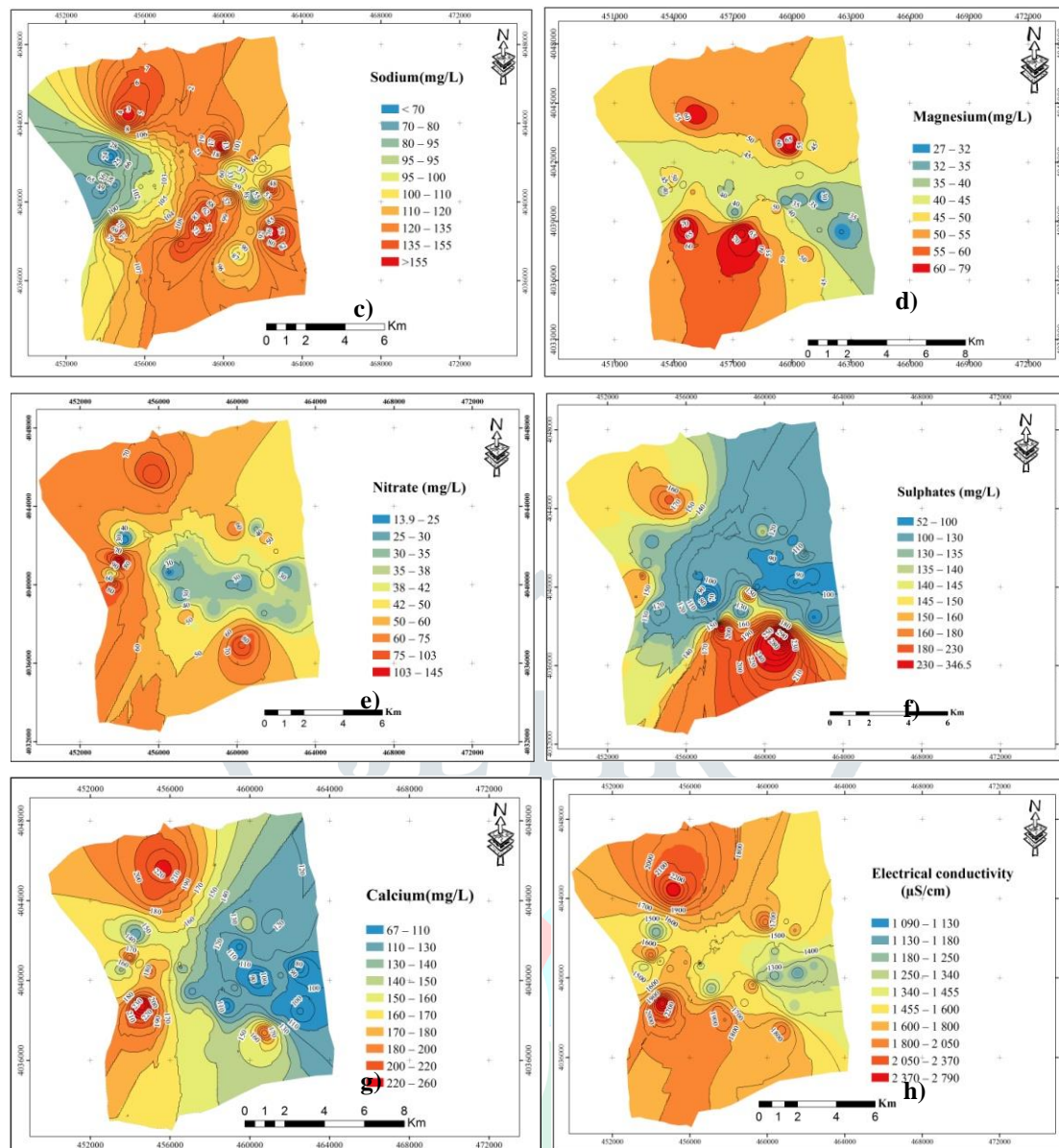


Figure 4. Graphical presentations of water quality data.

These results are evidence for the deterioration of groundwater resources intended for human consumption and agricultural irrigation in the study area. This contamination is at the origin of the intense agricultural activity, with different speculations and different practices (fertilization and irrigation), the share of sanitation and urban discharges are not considered in this study. This also contributes to the increase in the concentration of nitrates while weakening the environment and seriously threatening human health. The map shows that only 26.8% of the area with nitrate concentrations below 50 mg/L, located in the center of the plain. The soils in this zone are of fine texture with low permeability, which could play in favour of non-propagation of nitrates in depth. This refers to the adsorbent power of clays (Richa et al., 2015). In terms of area, only 4183.9 ha remain which can be considered as unpolluted areas.

3.2. Groundwater suitability for Drinking Purposes

The waters of Sidi Rached are used for the consumption and irrigation of agricultural perimeters. The assessment of the suitability of groundwater in the Sidi Rached basin for drinking purposes was evaluated according to standards recommended by the WHO (WHO, 2017). Drinking suitability of groundwater in the study region is assessed using EC, TH and TDS and also GWQI.

3.2.1. Electrical conductivity (EC): EC is an utmost main parameter to assess groundwater suitability for ingestion and irrigation practices (Panneerselvam et al., 2020a). The CE is one of the most prominent parameters to measure GWQI especially in coastal areas. The EC value in the groundwater of the study area varied from 1020–2650 $\mu\text{S}/\text{cm}$ with an average value of 1562.6 $\mu\text{S}/\text{cm}$ (Table 2). All groundwater samples fall outside the desirable limit ($\text{EC} < 750 \mu\text{S}/\text{cm}$) prescribed by the HWO (58).

3.2.2. Total Dissolved Solids (TDS): The range of TDS values in the groundwater of Sidi Rached basin aquifer was found to be in the range of 697.6–1785.6 mg/L with an average of 1018.8 mg/L. According to the WHO specification, TDS up to 1000 mg/L is desirable for drinking water, 37.8% of the total samples exceeded the drinking water limit (1000 mg/L) recommended by the WHO (58). The spatial distribution of TDS in groundwater (Figure 5a) shows that 30.82% and 69.18% of the area falls into the desirable (<1000 mg/L) and admissible (>1000 mg/L) categories respectively. The TDS in the groundwater samples in this study

was high due to enrichment of salts in the water. Excessive use of chemical fertilizers in the agricultural field and Excessive withdrawal of groundwater are the reasons for the decrease in water quality in terms of CE and TDS.

3.2.3.Total hardness (TH): Total hardness of water is a measure of dissolved Ca^{+2} and Mg^{+2} in water expressed as $CaCO_3$ (Mitra et al. 2007), expressed in mg/L is determined by Todd in 1980 (Equation 11). The concentrations values of calcium and magnesium were between 62–332 and 27–90.3 mg/L respectively as $CaCO_3$. High amount of calcium and magnesium could cause some negative effects like health effects such as abdominal ailments as well as economic and hydraulic effect such as scaling.

The total hardness of groundwater samples from Sidi rached aquifer was found in the range of 432.8-1047.9mg/L with an average of 550.9mg/L. The classification of groundwater based on TH shows (Table 2) that 43.2% (< 500mg/L) of the groundwater samples fall in the tolerable water categories, and 56.8% (>500 mg/L) of the groundwater samples fall in the hard water categories (WHO).

Spatial distribution of the TH concentration in the groundwater is illustrated in Figure 5b, the TH concentration the highest is with the highest TH concentration located in the Eastern and Southern portions of the study area (Figure 5b). In principle, Hardness has no known adverse effects on health, but it can prevent formation of lather and increase the boiling point of water. The high TH may cause encrustation on water supply distribution systems. There is some suggestive evidence that long-term consumption of extremely hard water may lead to an increased incidence of urolithiasis, anencephaly, parental mortality, some types of cancer, and cardio-vascular disorders (Derry CW. and al., 1990).

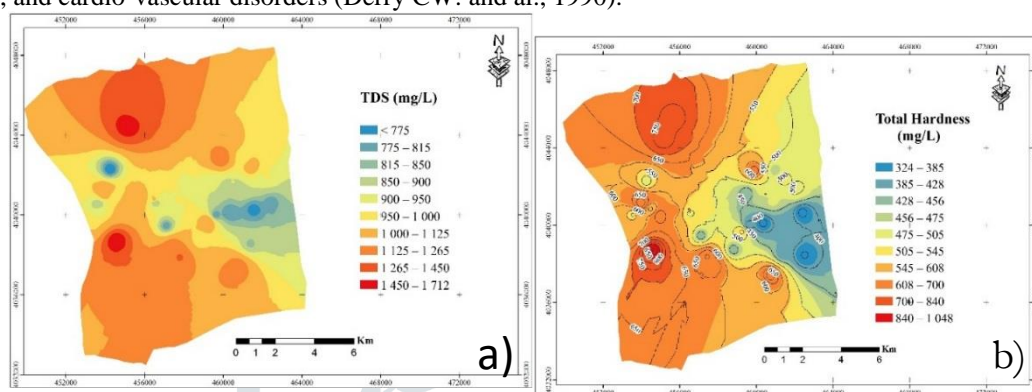


Figure 5. Spatial distribution map of TDS and TH.

The estimation of groundwater suitability for drinking purposes in the Sidi Rached basin is achieved using the relative weight GWQI model. The selection of the parameters for calculating the index depends on the importance of the parameter and its availability. Groundwater quality classification details based on index range is presented in Table 3. The computation of the GWQI values varies from 64.4mg/L to 187.7mg/L (Table 3) and it was classified into two categories: Class II (Good) and Class III (Poor) according to classification shown in Table 4. According to this classification, 64.86% of samples show good water quality drinking purpose (Class II) and 35.14% of the samples fall into the poor water quality category (Table 5). None of the samples were found in excellent, very poor and unfit water quality category (Class I, IV et V).

Table 3. Classification of groundwater based on GWQI (Sahu and Sikdar, 2008)

Range	Type of water	Numbers of samples	% of samples	% of area
< 50	Excellent water	0	0	0
50-100	Good water	26	64.86	47.82
100-200	Poor water	12	35.14	52.18
200-300	Very poor water	0	0	0
>300	Unfit for drinking purpose	0	0	0

WQI in the study area may be due to intensive irrigation practices and extensive intensive groundwater exploitation, and geogenic forces like rock weathering mineral dissolution and also anthropogenic practices are responsible for founding high WQI values in this region. The spatial distribution map of water quality indices is presented in Figure 6. It shows that the areas in the center of the basin fall into the good quality category (47.82% of the total surface), while the areas located to the north and south of the basin show poor water quality (52.18%) of the total surface of the basin of sidi rached).

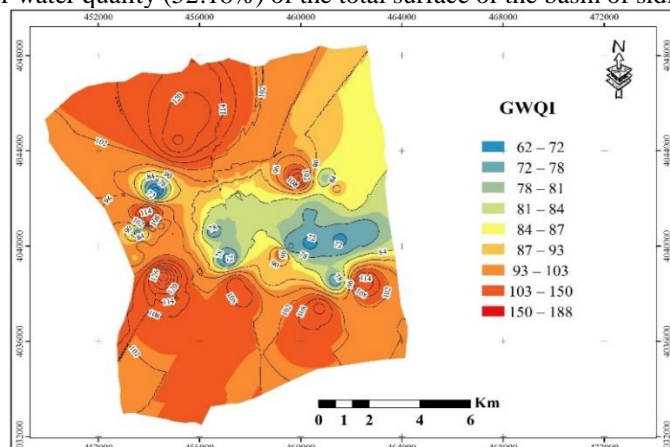


Figure 6. Spatial distribution map of groundwater quality Indices (GWQI)

Table 4. GWQI at individual sampling station

N° of wells	GWQI	Groundwater quality status	N° of Wells	GWQ I	Groundwater quality status
P1	80.6	Good water	P21	79.3	Good water
P2	85.1	Good water	P22	111.3	Poor water
P3	72.1	Good water	P23	71.7	Good water
P4	80.9	Good water	P24	88.6	Good water
P5	69.0	Good water	P25	90.6	Good water
P6	70.3	Good water	P26	102.1	Poor water
P7	101.1	Poor water	P27	85.6	Good water
P8	120.0	Poor water	P28	85.7	Good water
P9	74.3	Good water	P29	74.2	Good water
P10	116.8	Poor water	P30	187.7	Poor water
P11	108.8	Poor water	P31	127.0	Poor water
P12	113.7	Poor water	P32	68.3	Good water
P13	92.3	Good water	P33	72.7	Good water
P14	99.7	Good water	P34	91.5	Good water
P15	124.3	Poor water	P35	64.4	Good water
P16	81.9	Good water	P36	69.0	Good water
P17	84.9	Good water	P37	120.6	Poor water
P18	142.9	Poor water			
P19	81.7	Good water			
P20	62.3	Good water			

3.3. Correlation coefficient

Pearson correlation matrices of the various parameters of groundwater samples were calculated and are presented in Table 5. The correlation coefficient matrix shows that the strong correlations between the variables are positive therefore their concentrations evolve in the same direction. Calcium is good correlated with TH, CE, GWQI, and Cl⁻, NO₃⁻ and Mg⁺² (0.65-0.97) but was less correlated with other parameters. Magnesium is positively good correlated with Cl⁻, CE, TH and GWQI (0.74-0.86) but was less correlated with other parameters. Sodium is fairly good correlated with Cl⁻, CE and HCO₃⁻ (0.50-0.51) but non with other parameters. The groundwater quality indices (GWQI) was less correlated with Na⁺, SO₄⁻², HCO₃⁻ and pH but was good correlated with other parameters (0.76-0.87). The correlation showed that the major parameters were good correlated with each other indicating that these samples were in the similar locations (Table 5).

The correlation matrix shows that CE was good positively correlated with Ca⁺², Mg⁺², Na⁺, Cl⁻, NO₃⁻, TH and GWQI (0.51-0.93). This indicates the impact of multiple processes such as ion exchange, mineral dissolution, saline water intrusion and anthropogenic activities like use of fertilizers and sewage disposal on water chemistry.

Tableau 5. Correlation determination of the parameters

Variables	Ca ⁺²	Mg ⁺²	Na ⁺	Cl ⁻	k ⁺	SO ₄ ⁻²	CO ₃ H ⁻	NO ₃ ⁻	EC	pH	TH	GWQI
Ca ⁺²	1	0,65	0,06	0,80	0,10	0,32	-0,02	0,76	0,85	-0,10	0,97	0,82
Mg ⁺²	0,65	1	0,46	0,74	-0,03	0,32	0,42	0,48	0,86	-0,01	0,82	0,76
Na ⁺	0,06	0,46	1	0,50	-0,05	-0,02	0,51	0,06	0,51	0,33	0,20	0,49
Cl ⁻	0,80	0,74	0,50	1	0,06	-0,02	0,20	0,56	0,89	0,08	0,85	0,84
k ⁺	0,10	-0,03	-0,05	0,06	1	-0,05	0,07	-0,08	0,04	-0,02	0,06	-0,02
SO ₄ ⁻²	0,32	0,32	-0,02	-0,02	-0,05	1	-0,15	0,19	0,32	-0,11	0,35	0,29
CO ₃ H ⁻	-0,02	0,42	0,51	0,20	0,07	-0,15	1	-0,02	0,27	-0,14	0,13	0,20
NO ₃ ⁻	0,76	0,48	0,06	0,56	-0,08	0,19	-0,02	1	0,65	0,16	0,73	0,79
EC	0,85	0,86	0,51	0,89	0,04	0,32	0,27	0,65	1	0,05	0,93	0,92
pH	-0,10	-0,01	0,33	0,08	-0,02	-0,11	-0,14	0,16	0,05	1	-0,08	0,10
TH	0,97	0,82	0,20	0,85	0,06	0,35	0,13	0,73	0,93	-0,08	1	0,87
GWQI	0,82	0,76	0,49	0,84	-0,02	0,29	0,20	0,79	0,92	0,10	0,87	1

3.4. Human Health Risks Assessment

As described previously, the groundwater of the study area is contaminated by nitrates; these concentrations exceed the permissible limits for drinking purposes. Continuous consumption of contaminated drinking water affects human health. Thus, a human health risk assessment (HHA) was conducted to figure out the potential overall health risks of this contaminant to human beings. The human health risk (HHR) is determined by a method developed by USEPA (United Environment Protection

Agency). The results of the nitrate human health risk assessment for infants, children, and adults were expressed as HQ and HI, and are statistically listed in Table 6 and presented Figure 7.

Tableau 6. Statistics of health risks assessment results through drinking water intake.

Parameters	HI _N		
	Infant	Children	Adult
Min.	0.48	0.39	0.33
Max.	3.99	3.22	2.76
Mean	1.73	1.39	1.23
SD	0.85	0.69	0.61
Samples groundwater acceptable	08	12	18
Samples groundwater (%)	21.62	32.43	48.65

To identify this problem, hazard quotient (HI_N) is an essential tool to determine non-carcinogenic health risk. The higher concentration of nitrate ions is observed in Bourkika region (GW30 with 115mg/L).

It can be seen that there existed potential non carcinogenic health risks to all populations, including infants, children and adult, based on the overall assessment results. HI values of nitrate in the study area range from 0.3 to 2.8 (Adults), 0.4 to 3.2 (Children), and 0.5 to 3.99 (Infants) with the average value >1 of 1.23, 1.39, and 1.73, respectively (Table 10). 78.38%, 67.57%, and 51.35% of the groundwater samples are above the acceptable limit > 1 (Table 10) and may cause a health risk to adults, children, and infants, respectively. The figure 17 denotes comparison of HI_N in the studied groups as shown, the HI_N in each of the three groups was greater than 1, which has to be taken care of and proper precautionary measures.

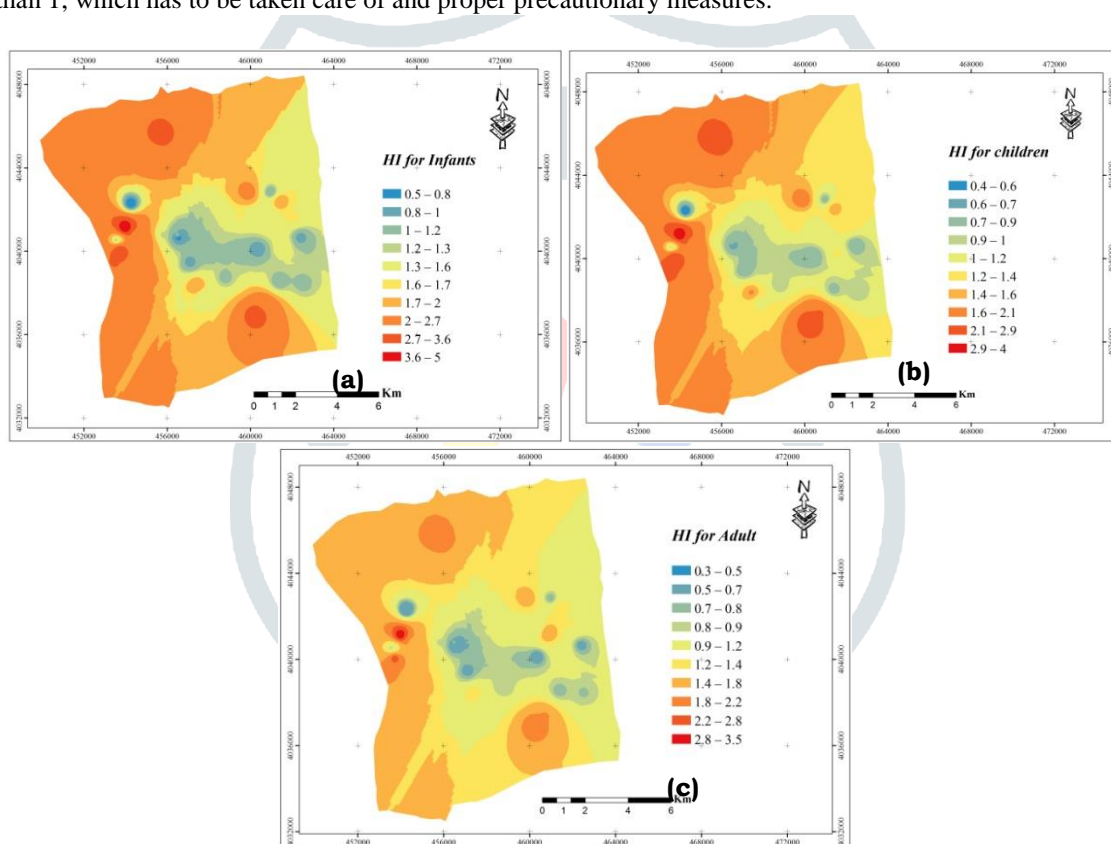


Figure 7. Spatial distribution of the overall potential non carcinogenic health risks through drinking pathway for (a) Infants, (b) Children and (c) Adults.

CONCLUSIONS

This work allowed us to possible to define the water classes in the study area according to GWQI, to identify polluted areas and also to assess the risks to human health (HHRA).

In this study, it was considered that the high nitrate concentrations in the groundwater analysed in the sampling areas were largely due to agricultural activities. It made it possible to define the water classes in the study area according to the GWQI, to identify polluted areas and also to assess the risks to human health (HHRA). The GWQI values range from 62 (poor) to 188 (unfit for drinking) and 35.14% of the samples indicate poor water quality around the study area. No samples fall into the “Excellent” category. The study reveals that 35.14% of groundwater samples (52.18% of the total area studied) are of poor quality, unfit for consumption. The average QG values for all age categories are greater than 1, which reveals the existence of potential risks to human health due to the high concentration of nitrates in the groundwater of the study area and shows also that infants are at high risk compared to children and adults.

In our study, nitrate-induced risk (HQ) levels calculated for three different age groups: adults, children and infants, and the CDI values used in the calculation of HQ were found to be higher in infants and children. In children, more particularly in infants, compared to adults, it can be said that babies are particularly more sensitive to concentrations of pollutants and, therefore, the health risk increases in this age group. The reason for the increase in the HQ value in babies can be explained by the increase in CDI values, which are used in the calculation of the HQ value and are defined as the amount of a pollutant in contact with the weight body per unit of time.

The spatial distribution maps of GWQI and HHRA produced in this work will help water resource managers develop policy guidelines for effective management and protection of groundwater resources from further deterioration due to anthropogenic activities.

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