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ARTICLE

Groundwater quality evaluation and risk assessment of nitrate using monte carlo simulation and sensitivety analysis in rural areas of Divandarreh County, Kurdistan province, Iran

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ABSTRACT

During farming practices in rural areas, various fertilizers are used, which can lead to the contamination of groundwater resources with nitrate and, consequently, can affect the health of consumers. This study aimed to investigate the drinking suitability of the groundwater resources in rural areas of Divandarreh County, Kurdistan province, Iran using drinking water quality index (DWQI) and also estimation of the non-carcinogenic health risk induced by nitrate due to the drinking route. Sixty groundwater samples collected (2018) from active dug-wells and twelve parameters (TDS, pH, TH, EC, HCO_3^-, K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, and NO_3^-) were measured to calculate DWQI. Also, non-carcinogenic risk assessment was carried out for four exposed groupsusing two different approaches: deterministic andprobabilistic by Monte Carlo simulation.

The results of WQI showed that 61.66, 31.66, and 6.66% of samples fall within the class of excellent, good, and poor quality, respectively. The nitrate concentration in drinking water ranged from 36.06 ± 14.32 mg/L. The HQ mean for infants, children, teenagers, and adults were 0.90158, 1.17205, 0.90158, and 0.70436, respectively.Probability estimation showed the HQ values for the 5th, and 95th percentile in infants, children, teenagers, and adult groups were (0.52–2.53), (0.27–1.54), (0.25–1.40), and (0.15–0.71), respectively. Sensitivity analysis results showed that the most effective parameter in the non-carcinogenic risk in all exposed groups was NO_3^- concentration. Generally, nitrate concentration was relatively high and required more attention especially in agriculture and management of the use of fertilisers.

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1. Introduction

Drinking water safety has been a significant concern everywhere in the world and is an absolute obligation for sustainable development programmes [1,2]. Groundwater is one of the primary sources of drinking water. Significant parts of rural communities rely on this source for drinking, irrigation, and industrial purposes, especially in arid and semi-arid regions due to negligible rainfall and the scarcity of surface water resources [3–5]. In Iran, groundwater resources provide about 63% of drinking water for both urban and rural communities. In many parts, extraction wells are the primary sources of water supply for agriculture, irrigation, and drinking purposes [3,6]. But, in the last few decades, rapid population growth, urbanisation, industrialisation, and increasing human-made activities, such as disposal of urban wastewater and industrial wastes as well as agricultural runoff, have affected the quantity and quality of groundwater resources and cause to contamination for theses resources [7,8].

Groundwater contamination includes any physical, chemical, microbial, and radiological types that can threaten human health [9]. Given the fact of increasing demands for groundwater supplies, regular monitoring, and ensure the water quality all the time is an essential strategy for presenting healthy and safe drinking water to consumers [10]. So, in recent years, there has been an increasing amount of literature on conveying of groundwater quality in the worldwide [11–15].

Several methods have been applied for analysing water quality data, of which the Water Quality Index (WQI) has received much attention by researchers [16–18]. WQI is recommendeda tool with competence to facilitate analysis of water quality data by relating a group of parameters to a standard scale [4, 12], which provides a better understanding of the water quality parameters [19,20]. In this regard, Abbasnia et al.(2018) assessed the groundwater quality and its suitability for irrigation purposesin Chabahar city. In their study, electrical conductivity, sodium adsorption ratio, sodium, chloride, and bicarbonate parameters were utilised for computing the irrigation water quality index [21]. Also, Ramakrishnaiah et al. used twelve parameters including pH, total hardness, calcium, magnesium, bicarbonate, chloride, nitrate, sulphate, total dissolved solids, iron, manganese and fluoride to calculating the WQI, that this index in their samples ranges from 89.21 to 660.56 [14].

Moreover, Groundwater also may contain chemical contaminants such as nitrate (NO_3^-); as the prevalent pollutants in groundwater resources [22]. It can quickly beneath the soil to water tables and contaminate them [23]. Continuous ingestion of high concentrations of nitrate via drinking, cause harmful health effects such as methemoglobinemia, colloquially called blue baby syndrome (predominantly for infants under six monthsold), various forms of cancer, miscarriage in pregnant women, coronary cardiac diseases, ovarian cancer and hypertrophy of the thyroid [23,24]. The possible sources of groundwater pollution by nitrate are such as nitrogen-containing fertilisers, pesticides, improper waste management, and discharge of wastewater effluents into the environment [25]. So, this type of groundwater pollution because of adverse health effects should be considered for drinking water safety and also maintaining public health.

The harmful effects of human exposure to environmental pollutants can be determined through risk assessment. Risk assessment is a systematic approach that helps to identify significant risks and decide about the control measures to reduce exposure levels and attain acceptable levels of risk [16]. As the increase of NO_3^- concentration in water sources is the critical parameter in increasing the health risk, and it is vital to identify the main route of nitrate entry to groundwater resources to reduce its risk. Therefore, the present research aimedatthe evaluation of non-carcinogenic risk assessment for four exposed groups using two different approaches: deterministic and probabilistic by Monte Carlo simulation.Besides, WQI was applied for assessing the groundwater characteristic and also geographic information system (GIS) used for zoning spatial distributions of main chemical parameters.

2. Experimental

2.1. Description of study area

The Divandarreh county is located in Kurdistan province, west of Iran, encompassing an area of about 4203square kilometres, which approximately consists of 12.82% of the district of the province. The elevation of this region is about 1850 meters above sea level and geographically situated at the latitudes 35.9137°N and longitudes 47.0267°E.

According to the official census results of 2016 in the Kurdistan province, the urban and rural population of this district were 36,098 and 43942 persons, respectively. Due to the excellent weather conditions and relatively high annual precipitation (average precipitation of 517 mm/year), Kurdistan province is one of the important agricultural regions of Iran and Divandarreh is one of the important centres of wheat cultivation of the Kurdistan province due to the existence of two vast plains [26]. Over 80% of the inhabitants in this region mainly rely on agriculture for their livelihood. Consequently, different kinds of nitrogen fertilisers and other agrochemicals are used in farming practices to improve farm yields [6].

In terms of climate, this area has a cold temperate with long winters, and relatively mild spring and summer, and is considered as one of the cold and snowy regions of Iran. The average annual temperature and average yearly precipitation of studied area have been estimated to be 5ºC and 500 mm, respectively. Figure 1 shows the location of Kurdistan province, Divandarreh city, and water sampling points.

2.2. Sample collection

To select sampling points, the standard criteria such as collecting the representative samples, notice the pollutants, gathering proper and enough number of quality control samples, and sufficiently distributed (In space and time)has been considered [27]. Water samples were collected from 60 active dug-wells, located in Divandarreh rural areas, within the two time repetition period (2018).

All the sampling containers (polythene bottles of 1-L capacity) were rinsed by deionized water before sample collection. Before groundwater sampling, all bore-wells were pumped for 10–15 minutes to abolish theinfluence of stagnant water. After sampling, the groundwater samples were labelled, stored at fourºC, and transported to the laboratory for chemical analysis. The samples were analysed for significant parameters according to the Standard Method for Examinations of Water and Wastewater [28].

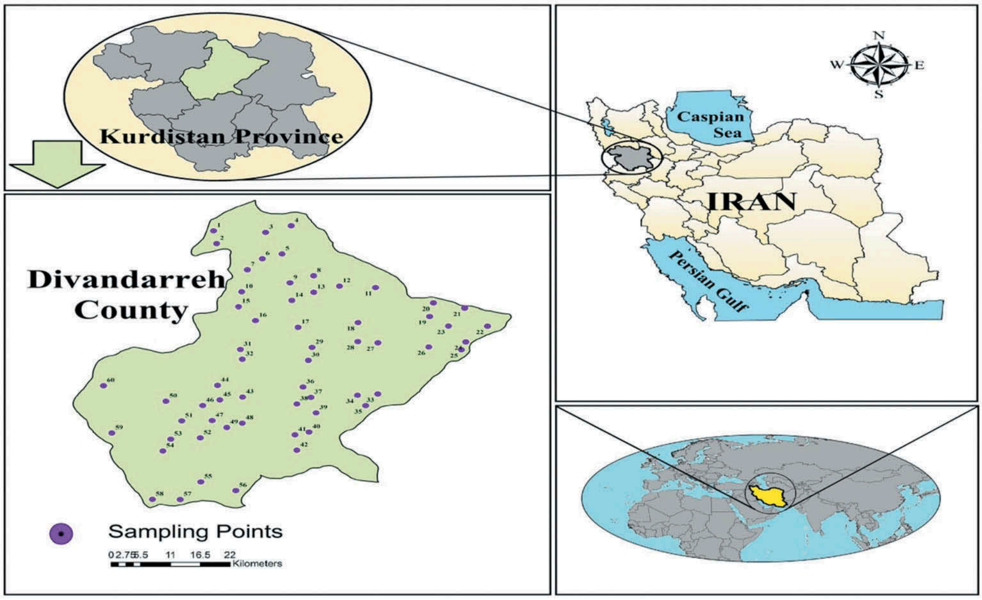

Figure 1. Location map of the study area and sampling points.

2.3. Data analysis& spatial analysis

In the present study for data analysis, the Pearson correlation coefficient did correlation analysis. All data have been investigated using statistical package IBM SPSS Version 16.00 (SPSS Inc., Chicago, IL, USA). It should be noted that significance tests were at 95% confidence level [29].

Geographic information system (GIS) was used for investigating the spatial distribution of groundwater samples in the study region. For this aim, Arc GIS 10.3 software (ESRI, Redlands, CA, USA) was applied [30]. To locating the sampling points, a global positioning system (GPS) was applied. These points were drawn on GIS by using the world geodetic system (WGS-1984). Finally, the Inverse Distance Weight (IDW) method was employed for developing the spatial distribution maps of water quality parameters [31].

2.4. Laboratory analysis

According to guidelines, delivery time was about 6–7 hours from sample collection to laboratory receipt and analytical experiments [27,32]. Samples were analysed to measure the concentrations of total dissolved solids (TDS), pH, total hardness (TH), electrical conductivity (EC), bicarbonate ($HCO3^-$), potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chloride (Cl^-), sulphate (SO_4^{2-}), and nitrate (NO_3^-).

The parameters of magnesium, total hardness, calcium, bicarbonate, and chloride were measured by the titrimetricmethod. The metals (sodium and potassium) were determined with the flame photometric method, electrical conductivity (EC) and pH by pH metre (model 7020. E.I.L., Kent). Also, nitrate and sulphate concentrations were analysed with spectrophotometer UV (HACH DR/5000) in the wavelength of 220 and 420 nm [15,21,33,34].

2.5. Drinking water quality index (DWQI)method

The water quality index (WQI) represents a reliable picture of surface and groundwater quality for most domestic usages [35]. DWQI is commonly used for evaluating drinking water quality throughout the world. This index is also specified for groundwater quality assessment. The WQI was created by Horton et al [36]. and afterward developed and modified by Brown et al. [37], and so far, it has been used in many studiesallover the world.Tocalculating the DWQI, Physico-chemical parameters including pH, TDS, TH, EC, $^{-}$, K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, $SO_4{}^{2-}$, and $NO_3{}^-$were used [4,18].

To computing the WQI, the weight (wi) has been assigned based on the relative importance of each parameter in the quality of water for drinking aims. The maximum weight has been considered for nitrate and total dissolved solids because generally, these two parameters affect the quality of groundwater resources often. For some of the settings, the weights were adopted from several investigations and determined according to the groundwater condition of the study area [13,15,21,38,39].

The following equation was used in the calculation of the relative weight [40]:

$$W_i = \sum \frac{w_i}{\sum_{i=1}^{n} w_i} \tag{1}$$

Where;

W_i: relative weight

w_i: the weight of each parameter

n: number of studied parameters

The weight (wi) and relative weight (Wi) of all parametershave been indicated in Table 1.

In the next step, the quality rating scale was measured for each parameter by dividing its concentration in each water sample to its standards (World Health Organisation 2011) [41] and finally multiplied the results by 100.

Table 1. The weight (wi) and relative weight (Wi) of studiedPhysico-chemical chemical parameter.

S. No	Parameter	Unit	WHO Standard [41]	Weight ($_{wi}$)	Relative weights $W_i = \sum \frac{w_i}{\sum_{i=1}^{n} w_i}$ [40]
1	K^+	mg/l	12	2	0.054
2	Na^+	mg/l	200	4	0.081
3	Mg^{2+}	mg/l	75	3	0.054
4	Ca^{2+}	mg/l	75	3	0.081
5	$HCO_3{}^-$	mg/l	500	2	0.054
6	Cl^-	mg/l	200	3	0.081
7	$SO_4{}^{2-}$	mg/l	250	4	0.108
8	pH	-	6.5–8.5	3	0.083
9	TDS	mg/l	500	5	0.128
10	$NO_3{}^-$	mg/l	50	5	0.135
11	EC	µS/cm	1000	3	0.081
12	TH	-	200	3	0.081
-	**Σ**	-	-	**Σ_{wi} = 1**	**Σ Wi = 1**

$$Q_i = \left(\frac{C_i}{S_i}\right) \times 100 \quad (2)$$

Where,

Qi: quality rating

Ci: concentration of specific chemical parameter in each sample (mg/L)

Si: standard limit for each chemical parameter (mg/L) (WHO guideline 2011) [41].

In the following, after the definition of the SIifor each parameter, the sum of Si values calculated for the WQI of any sample.

$$SI_i = W_i \times Q_i \quad (3)$$

$$WQI = \sum_{i=1}^{n} SI_i \quad (4)$$

Where;

SI_i: sub-index of the i_{th}parameter

Qi:a rating based on the concentration of the i_{th} parameter

n: number of parameters [39].

Based on the findings of WQI, water quality can be categorised into five types, including excellent water to unsuitable for drinking and irrigation purposes, which are tabulated in Table 2.

2.6. Risk assessment methodology

In the present study, a risk assessment was carried out to determine the adverse health effects of exposure to nitrate in groundwater resources of the Divandarreh rural areas. The human can be exposed to contaminants through three main routes including oral, dermal and inhalation routes. Generally, ingestion is the primary exposure route of nitrate. Therefore, only this route was considered in the present study. For this aim, the exposed population was classified intofour groups: infant (<2 years), children (2–6 years), teenager (6–16 years), and adult (>16 years) and were surveyed regarding non-carcinogenic risk [43]. For the non-carcinogenic risk to be determined, the Reference Dose (RFD) is of great significance.RFD is an exposure that, if contacted by a human population (including sensitive groups) daily, is likely to cause no significant risk of harmful effects throughout life [44].

The RFD is expressed in mg/kg body weight per day. In other words, if one person has a single dose of n-mg of a pollutant per kilogram throughout his or her lifetime, the toxic effect would not be observed in it. IRIS_EPA, has determined RFD = 1.6 mg/kg BW day for

Table 2. General DWQI classifications [42].

WQI Range	Type of Groundwater
<50	Excellent water
50–99.99	Good water
100–199.99	Poor Water
200–299.99	Very poor water
≥300	Unsuitable for drinking/Irrigation purpose

nitrate from the digestive tract [45]. Hazard Quotient is estimated by having RFD and determination of nitrate intake per day (through drinking water consumption). HQ <1, the harmful effects of exposure cannot be expected. A potential hazard, HQ >1, represents a potential risk of additional non-carcinogens and exposure to harmful effects [46].The HQ was calculated using the following formula [47]:

$$HQ = \frac{C_i \times IR \times E_{fr} \times ED}{RfD \times BW \times AT} \tag{5}$$

Where;

HQ: Hazard Quotient

Ci: Average contamination concentration in water (mg/L)

IR: Ingestion rate of water (L/d)

Efr: Exposure frequency (d/year)

ED: exposure duration for cancer risk assessment (year)

RfD: Oral reference dose (mg/Kg.day)

BW: Average body weight (kg)

AT: Averaging time (day) = (ED×365)

The formula parameters for exposed groups are described in Table 3.

Given the values presented in Table 3, the HQ point value was estimated using the above formula. Then the uncertainty analysis was performed using the Monte Carlo Simulation (MCS) method by 10,000 repetitions in Oracle Crystal Ball®.

2.7. Monte Carlo simulation & sesitivity analysis

MCS (what-if analysis) – as one of the most broadly used methods for probabilistic risk assessment (PRA) modelling- is an approach that can evaluate the variability and uncertainty in the several parameters of the human health risk assessment procedure [51]. In the present study, the variability and sensitivity analysis of the predictions of the risk assessment model was carried out by using the Monte Carlo simulation technique. A simplified approach to perform MCS is to create the model without uncertainty in Microsoft Excel software, then use the spread sheet-based application, such as Crystal Ball® software [52,53].

The sensitivity analysis (SA) was carried out by Monte Carlo Simulation (MCS) method by 10,000 repetitions in Oracle Crystal Ball® (version 11.1.34190) [54]. The MCS method chooses the values of the parameters from their distribution fitted to input data and consequently calculates both point value and the distribution of exposure and risk. Risk analysis using Crystal Ball relies on developing a mathematical model in Excel that represents the situation of interest. After you develop a deterministic model, you replace point estimates with probability distribution assumptions and forecast the distribution of

Table 3. Values of parameters used in health risk assessmentmethod.

Parameters	Unit	Infant	Children	Teenager	Adults	References
IR	L/day	0.4	0.78	2	2.5	[48]
E_{fr}	Day/year	350	350	350	350	[49]
ED	Year	1.5	4	13	40	[48]
Rfd	mg/kg.day	1.6	1.6	1.6	1.6	[71]
BW	Kg	10	15	50	80	[50]
AT	Day	525	1400	4550	14,000	[34]

Table 4. Parameters used in Monte Carlo Simulation and uncertainty analysis of nitrate.

Parameter	Age group (years)				Probability Distribution	Ref
	(<2 years)	(2–6 years)	(7–16 years)	(>16 years)		
Ingestion Rate (L/d)	0.45 ± 0.12*	0.51 ± 0.14	1.12 ± 0.27	1.23 ± 0.27	Log normal	[55,59]
NO_3^- concentration (mg/L)	36.06 ± 14.33				Log normal	[74]
Body weight (kg)	7.98 ± 1.02*	16.41 ± 3.78*	39.83 ± 10.16*	77.45 ± 13.6*	Log normal	[60]
Exposure Duration (year)	1.5	4	13	40	-	[48]
Exposure Frequency (day/year)	350					[61]
Averaging Time (Exposure Duration*350)	1.5*350	4*350	13*350	40*350		
RfD(mg/kg.day)	1.6				-	[62]

*** Mean±S.D**

the output. The forecasted output distribution is used to assess the riskiness of the situation [55,56]. Table 4 indicates the parameters for determining sensitivity analysis by the MCS technique. The probability distribution functions used in the Monte Carlo simulation and sensitivity analysis (SA) are obtained from the US Environmental Protection Agency [57,58].

3. Results and discussion

3.1. Physico-chemical parameters

One of the main goals of this research was to investigate the drinking water quality index in rural areas of Divandarreh County which is the important area of wheat cultivation of the Kurdistan province.The findings of the chemical analysis are presented in Table 5. This table indicates the mean, maximum, minimum, and standard deviation (SD) of determined parameters in groundwater samples of the study area.

According to Table 5, the pH of groundwater samples ranges within 7.2–8.15 with a mean of 7.81, which indicates that the dissolved carbonates are mainly in the HCO_3^- form [63]. Overall, it can be said that the underground water samples are weakly alkaline, and the pH amounts of all of the rural study areas are in the range of guideline value of world health organisation (2011) for drinking-water quality (6.5–8.5) [41]. The pH value of less than 6.5 is

Table 5. Descriptive statics and WHO standard for determined groundwater parameters.

Parameter	Unit	Mean	Max	Min	SD*	WHO Standard [41]
pH	-	7.81	8.15	7.2	0.19	6.5–8.5
EC	µmhos/cm	972.95	2872	434	628.78	1000
TDS	mg/L	638.87	1924	278	424.96	600
TH	mg/L as $CaCO_3$	363.50	950	167	186.63	500
Ca^{2+}	mg/L	116.80	14.2	2.65	53.10	75
Mg^{2+}	mg/L	17.34	59.29	4.84	13.45	75
Na^+	mg/L	70.03	304.98	6.67	82.88	200
K^+	mg/L	1.74	10.92	0.39	2.52	12
SO_4^{2-}	mg/L	180.22	724.8	11.04	210.61	250
HCO_3^-	mg/L	201.98	297.92	156.8	32.80	500
Cl^-	mg/L	65.58	394.76	6.39	97.93	200
NO_3^-	mg/L	36.06	62	6.2	14.32	50

*. Standard Deviation

corrosive and value 8.5 and above indicates the carbonated water. The higher pH values in drinking water resources have no direct health effect on human bodies. Still, it alters the various other water quality parameters which have an indirectimpact onhuman health as well as on our environment [30]. However, all groundwater samples of the present study were within acceptable limits (Table 4).

Electrical conductivity (EC) shows the amount of dissolved solids in water, and this study ranged from 434 to 2872 µmhos/cm and with a meanof 972.95 µmhos/cm. Magnesium (Mg^{2+}), potassium (K^+), and bicarbonate (HCO_3^-) values are less than the guideline values of 75, 12, and 500 mg/L, respectively (Table 4). TDS is the amount of the inorganic salts and small amounts of the organic matter present in water. The TDS values ranged from 278 to 1924 mg/L, with an average of 638.87 mg/L. These values show that water in the studied rural regions has a great potential to dissolve salts and minerals.The total hardness (TH) of water is due to the availability of the calcium and magnesium cations that are naturally available in the water resources. The TH was in the range 167–950 mg/L, with an average of 363.5 as $CaCO_3$. The hardness value of 16% of the samples exceeded the limit of 500 mg/L as CaCO3.

The concentrations of sodium (Na^+) and chloride (Cl) ranged from 6.67 to 304.98 (Mean: 70.3) and 0.18 to 11.12 mg/L (Mean: 1.84 mg/L), respectively. Na^+ and Cl^- have a vital role in the human body. Both of them affect the metabolism and also physiological and process. The higher concentration of these ionsmay cause high blood pressure [30]. The range of calcium, magnesium and sulphate concentrations were 2.65 to 14.2 mg/L (Mean: 5.84), 0.4 to 4.9 mg/L (Mean: 0.4), and 0.23 to 15.1 mg/L (Mean: 3.75), respectively. Potassium (K) is an important mineral for living organisms. It is also necessary for plants, humans and animals. In this study, the concentration of K^+ ranged from 0.39 to 10.92 mg/L (Mean: 1.74) that it can be said all groundwater samples of the present study were lower than acceptable limits of WHO (12 mg/L). The Potassium amounts in the human body are 110 to140 g. Potassium deficiency in the human body may affect heartbeat disorder and muscleweakness, whereas a high amount may affect thehomeostatic mechanism [64]. The survey of nitrate concentration in the study area and adverse health effects related to it has been described in part 3.3.

3.2. Water quality index

Water Quality Index is created by using the determination of some essential physico-chemical parameters of underground water resources. WQI was calculated to assess overall water quality in this area. The weight considered for each water parameter (wi) and relative weight (Wi) to the calculation of WQI is given in Table 1. The Wi calculations adopted here were based on the drinking water guidelines of WHO and also the result of similar studies about the WQI evaluation [40]. The range of WQI values varied from 29.6 to 127.16. Figure 2 indicates the spatial distribution of WQI in the study area.

Water quality index using a quality rating scale to evaluate the suitability of water for drinking purposes shows that 61.66% of groundwater samples fall within the class of excellent water quality. The calculated water quality index indicates that 31.66% of rural areas fall in the category of good water type for drinking purposes. However, 6.66 and 0% of the rural regions fall in the category of poor and very poor water quality, respectively. Table 6 shows the WQI values of sampling areas.

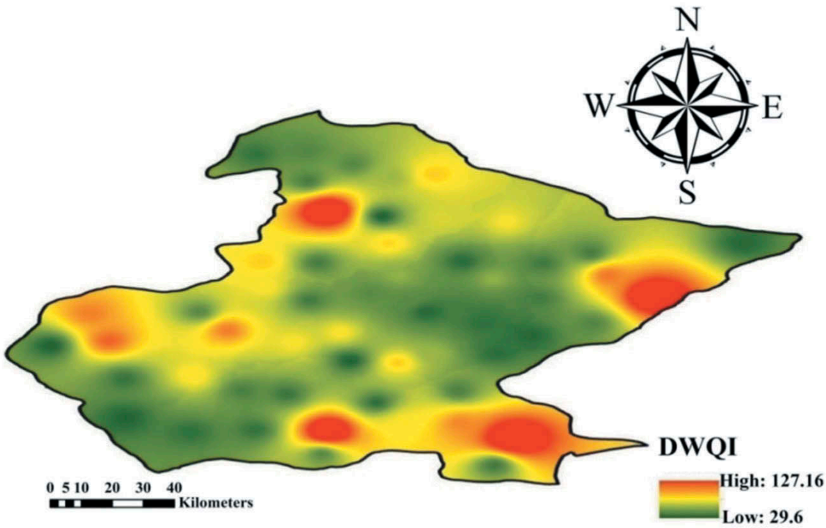

Figure 2. Spatial distribution of DWQI in the study area.

Table 6. The percentage of each WQI categorisation in the study area.

WQI Range	Type of Groundwater	Number of samples	Percentage of samples (%)
<50	Excellent water	37	61.66
50–99.99	Good water	19	31.66
100–199.99	Poor Water	4	6.66
200–299.99	Very poor water	0	0
≥300	Unsuitable for drinking/Irrigation purpose	0	0

In a study, groundwater quality was assessed using water quality index (WQI) in Qorveh&Dehgolan, Kurdistan province, Iran. Twelve water quality parameters have been considered for the calculation ow WQI. Based on the study, from 50 groundwater samples, about 64% of the studied area falls under the Good water class, and the rest are in Excellent water as per the WQI classification [13]. In another research, the WQI was evaluated for drinking purposes in Chabahr city, Sistan and Baluchistan province in Iran. According to the results, 25% of the samples showed the excellent watercategory, and50% of the samples were classified as good water category. Also, the spatial analysis of water quality indicated that water quality was poor in 25% of the entire studied area [39].

3.3. Non-carcinogenic risk assessment

3.3.1. Survey of nitrate concentration in the area

According to the results of Table 5, the nitrate concentration in drinking water ranged from 6.2 to 62 mg/L, with an average of 36.06 mg/L. The nitrate concentration was higher than 50 mg/L (WHO Standard) in 6% of the drinking groundwater samples. Naturally, groundwater resources contain a low level of NO_3^-, and it is supposed that groundwater resources with nitrate higher than ten mg/L are affected by external parameters such as anthropogenic activities. The difference in concentration of nitrate in different wells can be due to factors such as geological structure, land use and leakage of contaminantsfrom various sources. Higher NO_3^- concentration can cause the Methemoglobinemia (MetHb) disorder which is commonly named as Blue baby syndrome [30], whereas the low concentration may lead to the inadequate working of tissues, muscles, and bones [64].

In rural regions, there is ordinarily no facilities for sewage collection. In such areas, absorbing wells are usually the primary means for sewage collection. The presence of absorbing wells in an area can increase the likelihood of groundwater contamination. The maximum concentration of nitrate obtained in this research was 62 mg/L, which was higher than the WHO guidelines (50 mg/l) and Iran Standards (50 mg/L) [65].

The use of nitrogen fertilisers can be another significant source of nitrate contamination in rural areas [66]. According to the result of the study performed by Maleki et al., it was found that there is a significant difference between the nitrate ions concentration in samples taken in the two seasons of high and low water ($P < 0.01$). It is due to increased agricultural activities in the high-water season following increased consumption of fertilisers and pesticides, which results in ahigh concentration of nitrate in groundwater resources [65]. Over 80% of the inhabitants in Divandarreh rural areas mainly rely on agriculture for their livelihood. Consequently, various kinds of nitrogen fertilisers and agrochemicals are utilised in farming practices to improve farm yields. Therefore, monitoring of agricultural practices and fertiliser use is necessary for this area.

Nitrate concentration in several parts of Iran has been surveyed in some studies. In this context, Table 7 indicates the result of several studies.

Although 94% of the groundwater samples of this study were less than the WHO standard for nitrate (50 mg/L), comparison of the values of Table 7 with the mean nitrate concentration in the present study (36.06 mg/L) show that the nitrate concentration was relatively high and required more attention by the authorities, especially in agriculture and management of the use of fertilisers.

3.3.2. Deterministic approach for nitrate risk assessment

Risk assessment is a systematic approach to identify significant risks and decide about the control measures to reduce exposure levels [16].In the presentresearch, health risk assessment was done to determine the effects of non-carcinogenic ofnitrate on the health of residents in rural areas of Divandarreh county, Kurdistan province, Iran. To assess the potential hazard level of the selected contaminants in drinking water, the Hazard Quotient (HQ (Eq.5)) values were calculated for infants, children, teenagers, and adult

Table 7. Compare the concentration of Nitrate in drinking water in several parts of Iran.

Study area	Range of NO_3^-concentration(mg/L)	Mean (mg/L)	Refernce
The rural area of Qorveh	22.6 ± 12.3*	-	[65]
Shiraz city	4–74	31.65	[67]
The rural area of Sonqor	3.09–88.5	18.75	[50]
The rural area of Chabahar	2-8705	12.39	[39]
The Rural area of Saravan	1-76.12	14.34	[68]
The rural area of Khash	6-35	16.08	[43]
Rural area of Bajestan	5.5–84.3	-	[69]
Present study	6.2-62	36.06	-

*Mean±SD

Table 8. A deterministic approach to the calculation of HQ.

Deterministic approach				
Parameter	Infant	Children	Teenager	Adult
Mean	0.90158	1.17205	0.90158	0.70436
*SD	0.35813	0.46557	0.35813	0.27979
*P5%	0.16275	0.21157	0.16275	0.12714
P95%	1.395	1.8135	1.395	1.08984
The percentage of HQ > 1	45%	70%	45%	6%

***SD**: Standard Deviation **P**: Percentile

groups.The statistical findings of HQ for the non-carcinogenic human health riskassessment (HRA)of nitrate in groundwaterresources areshown in Table 8.

According to the United States Environmental Protection Agency (US. EPA), HQ values larger than one mean unacceptable exposure conditions with high chronic non-cancer risks for the target organs in the human body [70].The results of the deterministic approach ofthe HQ index (Table 7) showall studied exposed(Infant, Children, Teenager, and Adult) arehigher than one.The non-carcinogenic hazard quotients (HQ) values of 45% of infants, 70% children, 45% of children, and 6% of adults were higher than thesafety level (i.e., HQ>1), suggesting adverse health effectsfor exposed population.However, the HQvalues for the 95th percentile in the adult agegroup were slightly higher than one in only some areas that indicates this age group was somewhat at the risk of non-carcinogenic effects due to nitrate intake from drinking water in these areas.

The range of HQ for infants, children, teenagers, and adults in the studied area was 0.16275–1.395 (Mean: 0.90158), 0.21157–1.8135 (Mean: 1.17205), 0.16275–1.395 (Mean: 0.90158), and 0.12714–1.08984 (Mean: 0.70436), respectively.

The non-carcinogenic risks (HQ level) of nitrate for the four exposed peoples varied in order: children > infant = teenagers > adults. Consequently, the children, infants, and teenagers can be considered as hypersensitive populations and children had a higher adverse health effect through drinking water consumption (HQ mean: 1.17205) (Table 7).

Dispersion, Spatial Distribution, and Zoning maps of nitrate by inversedistance weighting (IDW) method in four exposed groups: infants, children, teenagers, and adults is shown in Figure 3.

The health risk assessment of nitrate in drinking water of rural residents living in the Bardaskan city, Iran, was conducted in a study. According to their results, the lowest and highest value of nitrate concentrations was in the rangeof 0.0–77.2. Also, HQs of nitrate for children, teenagers, and adults in 3, 1, 2 villages were higher than one [71].

In another study, the amount of nitrate in drinking water of 77 rural and urban areas of Nagpur and Bhandara in India was 45.69 ± 2.08 and 22.53 ± 1.97, respectively [72]. The average amount of nitrate in 71 mineral water brands in Iran was 10.55. Also, the results of exposure to nitrates in the exposed groups (as in the following study) in infants, children, teenagers, and adults were 0.0497, 0.3520, 0.2485, and 0.1991, respectively. It was reported that children were the most sensitive group of nitrates, which is similar to the results of this study [73].Chen et al. in a study in China, found that infant groups were the most vulnerable group to nitrate. In their research, 72% of infants and 60% of childrenwere exposed to the detrimental effects of nitrate which is similar tothe findings of the present study [1].

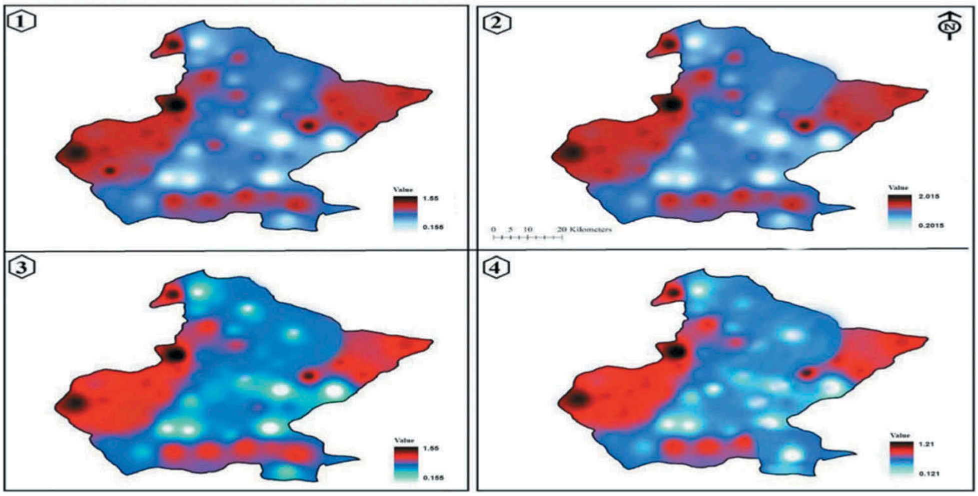

Figure 3. Spatial variation of hazard quotient for different exposed groups 1) infant, 2)children, 3) teenager and 4)adult for the study area.

3.3.3. A probabilistic approach for nitrate risk assessment

In addition to point estimation of hazard quietens using Equation (5), the Monte-Carlo simulation (MCS) approach by 10,000 repetitions was run via Oracle Crystal ball software (version 11.1.34190) to estimate HQ variances [54]. The probabilistic approach for nitrate in the four exposed groups, taking into account the proper distribution of parameters including the nitrate concentration, ingestion rate (IR), and body weight (BW), were performed and the statistical results have been indicated in Table 9 for infant, children, teenager, and adults.

Also, histograms for simulating HQ results in four exposed groups are displayed in Figure 4(a–d).

HQ values larger than one means unacceptable exposure conditions with high chronic non-cancer risks for the target organs in thehuman body [55]. The results of probability estimation indicate that HQ levels were in the order of infant > children > teenagers > adults. According to Figure 4 and Table 9, the HQ values for the 5th and 95th percentile in infants, children, teenagers, and adults groups were (0.52–2.53), (0.27 − 1.54), (0.25–1.40), and (0.15 − 0.71), respectively, which indicates a non-carcinogenic risk for first three groups.

The highest 95th percentile of the calculated HQ in the study areas was 2.53 for infants, shows a higher non-carcinogenic risk in this group. High-risk levels in infants can be due to their low body weight compared to other age groups [74]. According to Figure 4(a), the result with 55.81% certainty shows that the HQ values will be between 1–2.53 (Blue part of histogram). Also, uncertainty analysis results showed that the HQ levelin children group was between1 and 1.54 with 15.18% certainty. Similarly, in the teenager group, the HQ level was between 1–1.40 with 9.35% confidence. It means that the likelihood of being an HQ value of at least one is 9.35%.

Also, the lowest 95th percentile belonged to the adult group (0.71)and the results of uncertainty analysis with 95% confidence showed that the HQ level in this group was less

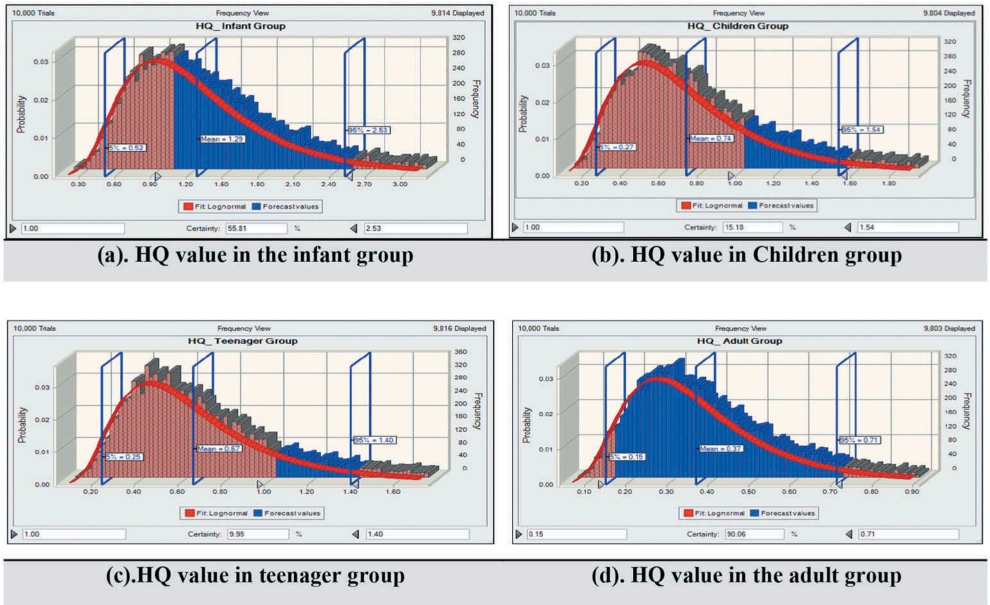

Figure 4. Histograms of the uncertainty analysis of nitrate HQ.

Table 9. The probabilistic approach to determine HQ.

Probabilistic approach				
Parameter	Infant	Children	Teenager	Adult
Mean	1.29	0.74	0.67	0.37
SD	0.66	0.41	0.38	0.19
P5%	0.52	0.27	0.25	0.15
P95%	2.53	1.54	1.40	0.71

***SD**: Standard Deviation **P**: Percentile

than0.71. The HQ valuesin this group were less than one, which shows long-term exposure to nitrate through drinking water consumption does not increase the likelihood of non-carcinogenic risk and the adverse health effects of water intake [54].

The amount of nitrate in 50 samples of drinking water in the semi-arid region of northwest China was investigated by Chen et al. in 2017. The samples were collected from well water and in the rural area. The average nitrate concentration was 2.66 ± 1.03 mg /L. Also, the results of the risk assessment showed that the infant groups are the most sensitive group in the community [1].This finding was also observed in Zhai, Y et al. [25].The results of research in India also showed that 100 percent of children group was at ahigh-risk level with an estimated daily gain of 13.2 to 2.56 of nitrate concentration [75].

3.3.3.1. Sensitivity analysis (SA).

Uncertainty can be described as a lack of knowledge regarding the true value of a parameter. Since many parameters are effective in creating health risk assessment, determining the most effective parameter can be helpful for better understanding and consequently, proper management drinking water resources. So, in

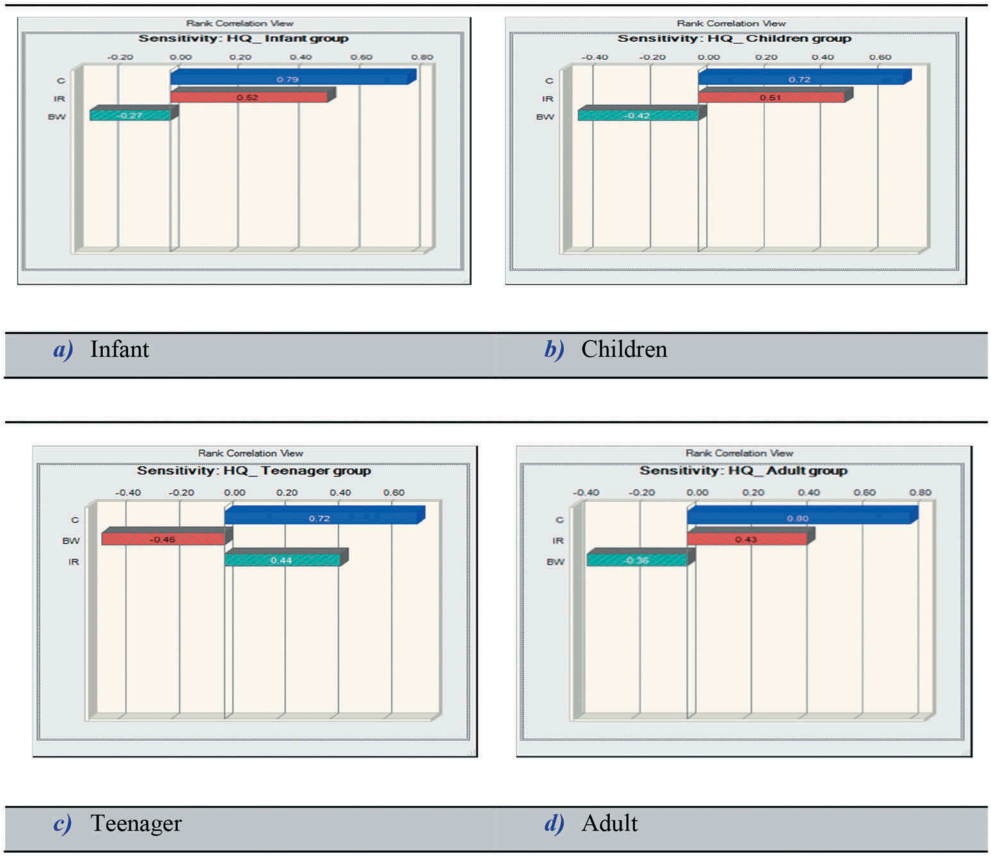

Figure 5. Sensitivity analysis of different age groups exposed to nitrate.

this research, the SA was used to determine which variables and pathways most strongly influence the risk estimate. SA shows how the variability of input variables affects the uncertainty of the final response. Figure 5(a-d) shows the sensitivity analysis of variables in calculating HQ for four exposed groups.

As shown in Figure 5, the most effective parameter in the non-carcinogenic riskin three exposed groups (i.e., infant, children, and adult) was NO_3^- concentration and the ingestion rate, which have anincreased effect on non-carcinogenic risk. Also, nitrate concentration and body weight had the most impact on the risk assessment in the teenage group. So, in all exposed groups, a decrease of nitrate concentration and ingestion rate can reduce the risk of health.

According to the results of sensitivity analysis, the body weight (BW) was inversely related to the sensitivity. These findings suggest that higher BW is associated with decreased sensitivity. Hence, these results could be a warning for decision-makers and also researchers to conduct more comprehensive investigations with more samples [76].

In a study conducted by Badeenezhad etal. in 2019, the nitrate concentration and the intestinal rate was reported as themost effective factor in the non-carcinogenic effect of nitrate in water wells [77]. These results are similar to our study.

4. Conclusion

Groundwater resources are the second abundant reservoir for fresh drinking water in the world, after glaciers. Nitrate is one of the critical contaminants that influence the quality of groundwater resources and pose a risk to public health.The present research was performed to evaluate the groundwater quality and its suitability for drinking purposes through GIS in rural areas of Divandarreh county, Kurdistan province in Iran. Also, the uncertainty analysis was performed using the Monte Carlo Simulation (MCS) method by 10,000 repetitions in Oracle Crystal Ball®.

The range of WQI values varied from 29.6 to 127.16, and the calculated WQI showed that 61.66, 31.66, and 6.66% of samples fall within the class of excellent, good, and poor quality, respectively.HQ values larger than one mean unacceptable exposure conditions with high chronic non-cancer risks for the target organs in thehuman body. The results of probability estimation indicate that HQ levels were in the order of infant> children > teenagers > adults.

Over 80% of the inhabitants in Divandarreh rural areas mainly rely on agriculture for their livelihood. Consequently, various kinds of nitrogen fertilisers and agrochemicals are utilised in farming practices to improve farm yields. Therefore, monitoring of agricultural practices and fertiliser use is necessary for this area. So, because of the high concentration of nitrate in some areas of this study, proper treatment, and governmental interventions for theappropriate provision of drinking water are recommended. Besides, the current evaluation of nitrate sources and associated health risks will assist policymakers in defining action plans to minimise nitrate exposure in Divandarreh and similar areas in the Middle East.

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No potential conflict of interest was reported by the author(s).

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