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RESEARCH ARTICLE

Water quality evaluation and non-cariogenic risk assessment of exposure to nitrate in groundwater resources of Kamyaran, Iran: spatial distribution, Monte-Carlo simulation, and sensitivity analysis

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Abstract
Water is exceptionally vital for all living beings and socio-economic development. This study aimed to investigate the groundwater suitability for drinking in rural areas of Kamyaran city, Kurdistan province, Iran, by using the water quality index (WQI) and evaluating the non-carcinogenic health risk caused by nitrate from the drinking route. Forty-five groundwater samples were collected (2019) from operated 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 the calculation of WQI. Hazard Quotient (HQ) and sensitivity analysis (SA) using the Monte-Carlo Simulation technique with 10,000 iterations were employed to determine the non-carcinogenic effects of Nitrate in different exposed groups (Infant, children, teenagers, and adults). The results of WQI showed that 74% of groundwater samples fall within the excellent water quality class, and 26% of rural areas fall in the category of good water type. The nitrate concentration in drinking water ranged from 22.42 ± 11.44 mg/L. The HQ mean for infants, children, teenagers, and adults were 0.5606, 0.7288, 0.5606, and 0.438, respectively. Probability estimation showed the HQ values for the 5th, and 95th percentile in infants, children, teenagers, and adult groups were (0.25–1.81), (0.13–1.08), (0.13–0.97), and (0.07–0.51), respectively. The SA showed that the most significant parameter of non-carcinogenic risk in all exposed populations was nitrate concentration. Generally, nitrate concentration in the study area was relatively high, and remarkably in agriculture and fertilizer management required more attention.

Keywords Water quality index · Nitrate · Health risk assessment · Monte-Carlo simulation · Sensitivity analysis · Kamyaran

Introduction

Water is exceptionally vital for all living beings, socio-economic development, and healthy ecosystems. Access to usable water is one of the most significant problems of all countries [1–3]. In many regions of the world, specifically in arid and semi-arid regions, groundwater resources are the most important resources for domestic, industrial, irrigation, and agricultural uses [4–7]. Unfortunately, over the recent decades, rapid population growth, dumping of domestic waste, and uncontrolled industrial and commercial developments have deteriorated contamination of ground and surface water resources [8–10]. So, monitoring and controlling the groundwater resources and using the approaches to health risk

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assessment of water contaminants are necessary to health promotion programs. In recent years, groundwater studies have experienced extended growth. One of the simple techniques that can recount the qualitative conditions of groundwater is water quality indices [11, 12]. Water quality indices are procedures that minimize the data volume to a large extent and clarify water quality status. Several techniques have been developed worldwide for analyzing water quality data, such as the Oregon Water Quality Index (OWQI), US National Sanitation Foundation Water Quality Index (NSFWQI) [13, 14], of which the Water Quality Index (WQI) has received more attention from researchers [15].

WQI is the most effective tool for communicating water quality information and an essential indicator for groundwater assessment and management [16, 17]. WQI is the practical way to assess water quality information and a key indicator for groundwater evaluation and management. Employing mathematical functions, this index converts large amounts of water quality data into a single number that indicates the water quality level [18, 19]. Soleimani et al. (2018) conducted a study to evaluate the water quality index for groundwater in the Qorveh&Dwhgolan region of Kurdistan province in Iran. In this study, the parameters of pH, EC, TDS, SO_4, HCO_3, K, Cl, Na, Mg were used to calculate WQI [20]. Also, another study investigated the groundwater's WQI in Tumkur Taluk, India. studied parameters including pH, total hardness, Ca^{2+}, Mg^{2+}, bicarbonate, Cl^{-}, No_3^{-}, So_4^{2-}, total dissolved solids, Fe^{2+}, Mn^{2+}, and F^{-}. Results confirmed that the WQI was within 89–660 and high values due to water hardness, TDS, and bicarbonate .

Groundwater resources may contain chemical contaminants such as NO_3^{-} as the prevalent contaminant in the before-mentioned resources. This element can quickly penetrate from soil to the water tables and cause pollution [21]. Constant water consumption containing high nitrate levels may lead to adverse health effects, including a blue baby syndrome (especially in infants under six months of age), various cancer types, miscarriage, ovarian cancer, coronary cardiac diseases, and thyroid malfunction [22].

Excessive use of nitrogenous fertilizers, irrigation with untreated wastewater, industrial wastewater discharges [23], defective septic-system, decomposition of animal and plant residues in soil, use of absorbent wells for wastewater disposal, and abandoned landfills [24] are important factors contributing to nitrate contamination in surface and groundwater [25]. In the rural areas of Kurdistan (Iran), drinking water's chemical elements and nitrate variations were assessed. In most samples, nitrate concentrations in the wet season were more than in the dry season. Also, the lowest and highest nitrate concentrations were 0.526 and 113.65 mg/l, respectively [26]. In another research, nitrate levels of drinking water wells in Indonesia were examined. The results were applied to estimate the health risks for the local community by applying probabilistic methods. Nitrate in Drinking water was 0.01–84 mg/l [27].

Risk assessment procedures can determine the adverse effects of human exposure to environmental contaminants. These procedures are a systematic approach that helps identify significant risks and decide about the control measures to diminish exposure levels and achieve an acceptable risk range. Because of the environmental data's imprecision and insufficiency, two factors should be considered in risk assessment studies: data uncertainty and uncertainty measurement. Uncertainty can be quantified, evaluated, and modeled using various technical methods [28]. One such technique is the Monte-Carlo Simulation (MCS). MCS (what-if analysis), as one of the most widely used techniques for presumptive و risk assessment (PRA).

Moreover, it can assess the variability, heterogeneity, and uncertainty in the human health risk assessment. The present research intended to investigate the nitrate concentration in 45 groundwater wells supplying drinking water during 2019 in Kamyaran rural areas, Kurdistan Province, Iran. The probabilistic risk assessment, sensitivity analysis (SA), and uncertainty were evaluated by Crystall ball software. Besides, the water quality index (WQI) was applied for assessing groundwater quality. Moreover, the spatial distribution of nitrate concentration and WQI was performed using the inverse distance weighted (IDW) method in the ArcGIS software. Generally, the finding provided by this study helps researchers to know whether a particular water source is desirable for population consumption. Also, these results could be helpful for future planning of water resources and public knowledge about health problems related to high nitrate concentrations.

Material and method

Study area

Kamyaran, with an area of about 1852 Km^2, is located in southern Kurdistan Province with coordinates 34° 47′ 44″ N, 46° 56′ 8″ E and an altitude of 1464 m above the sea level. Due to the proper weather circumstances and relatively high annual rainfall (average precipitation = 517 mm/year), Kurdistan province is one of the important agricultural regions of Iran. It is one of the principal centers of the wheat culture of this province. Over 80% of the residents in this area mainly rely on agriculture activities for their living. Consequently, various kinds of nitrogen fertilizers and other agrochemicals are used in agriculture to enhance farm yields [29].

In terms of climate, this area has a cold temperate with long winters and relatively mild spring and summer and is considered one of Iran's cold and snowy areas. The mean annual temperature and precipitation of the studied area have been estimated to be 5 °C and 572, 27 mm. Figure 1 shows the position of Kurdistan province, Kamyaran city, and groundwater sampling locations.

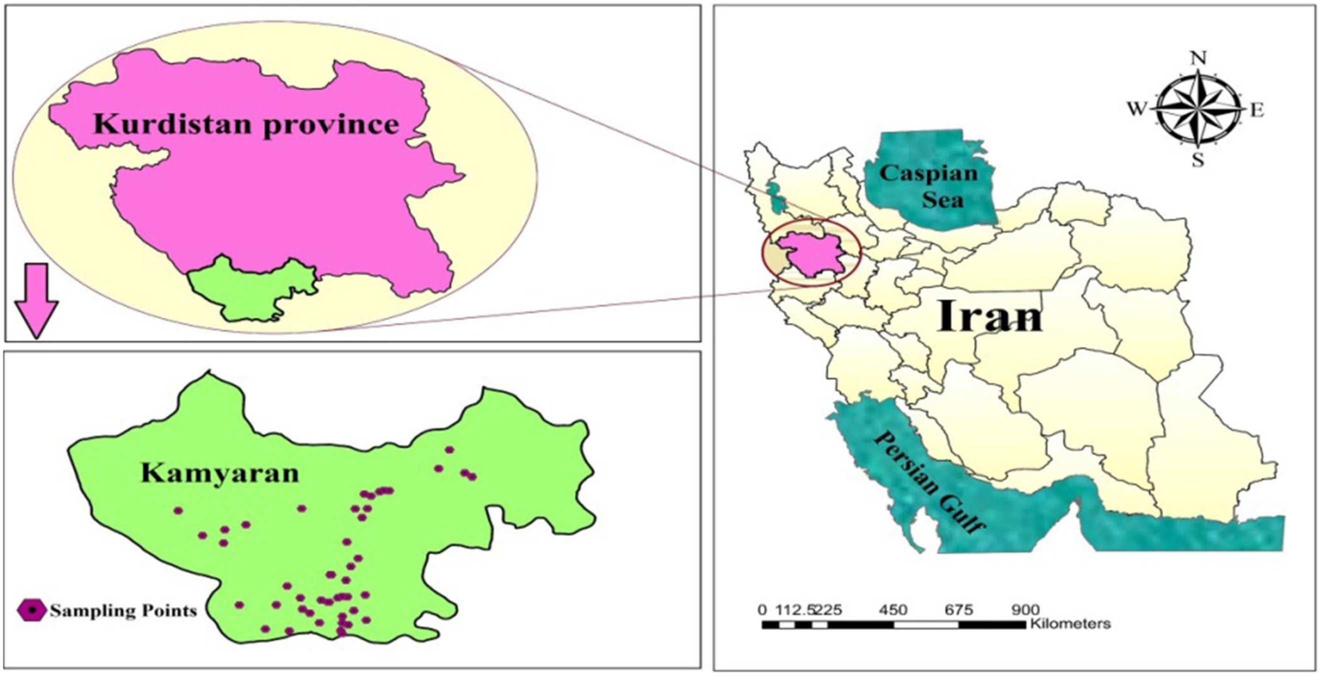


Fig. 1 Location of the study area in Kurdistan province

Sampling procedure

A total of 45 drinking groundwater were gathered in the Kamyaran area, Kurdistan province (2019). All water samples have been examined according to the Standard Methods for Examination of Water and Wastewater [30]. Sampling points were selected, considering standard criteria such as collecting the representative samples, noticing the contaminants, gathering proper and enough quality control samples, and sufficiently distributing (in space and time) [31]. Groundwater samples were collected from 45 operated dug wells situated in Kamyaran rural areas within the two-time repetition period.

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 min to abolish stagnant water's influence. After sampling, the groundwater samples were labeled, stored at four °C, and transported to the laboratory for chemical analysis.

Laboratory analysis

According to guidelines, delivery time was approximately 5–6 h from sample collection to lab receipt and analytical tests [31]. Groundwater samples were examined to determine 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^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-).

The parameters including TH, Mg^{2+}, Ca^{2+}, $HCO3^-$, and Cl^- were measured by the titrimetric method. The metals (Na^+ and K^+) were measured by the flame photometric method; EC and pH by pH meter (model 7020. E.I.L., Kent). Also, NO_3^- and SO_4^{2-} concentrations were determined by spectrophotometer UV (HACH DR/5000) in the wavelength of 220 and 420 nm [32, 33].

Data Analysis & Spatial Analysis

All data have been analyzed using the statistical package IBM SPSS Version 16.00 (SPSS Inc., Chicago, IL, USA) [34]. The geographic information system (GIS) was used for investigating the spatial distribution of groundwater samples in the study area. Arc GIS 10.3 software (ESRI, Redlands, CA, USA) was utilized. 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 [35].

Water quality index method

WQI describes a reliable picture of surface and groundwater quality for most domestic usages. WQI is usually used for evaluating drinking water quality throughout the world. This index Was introduced by Horton et al. [36] and then was expanded and revised by Brown et al. [37]. So far, it has been used in many studies all over the world. To measuring the

WQI, physicochemical parameters including pH, TDS, TH, EC,cations (K^+, Na^+, Mg^{2+}, Ca^{2+}), anions (Cl^-, SO_4^{2-}, and NO_3^-) are used [38].

To computing the WQI, the relative weight (wi) has been assigned. These assigned weights depend on the importance of the parameters on human health. Parameters with severe adverse health effects are attributed to higher relative weights and vice versa. The maximum relative weight has been considered for nitrate and total dissolved solids because generally, these two parameters affect the quality of groundwater resources often. The weights were adopted from several investigations and determined according to the study area's groundwater condition [20, 39]. Eq. (1) was used in the calculation of the relative weight [40]:

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

Wi: the weight of each parameter; n: the number of parameters; and Wi: the relative weight. Table 1 indicates the weight (wi) and relative weight (Wi) of each chemical parameter calculated based on the standard values reported by the World Health Organization (WHO, 2011) [22].

After that, the quality rating scale was measured for each parameter by dividing its amount in any water specimen to its standards (World Health Organization 2011) [22] and multiplying the results by 100 [41].

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

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) [22].

Then, the sum of Si values calculated for the WQI of any sample according to Eqs. (3 and 4) [41].

$$SI_i = W_i \times Q_i \tag{3}$$

$$WQI = \sum_{i=1}^{n} SI_i \tag{4}$$

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 [42].

WQI is generally classified into five categories, shown in Table 2 [43].

Risk assessment methodology

Deterministic approach

The risk assessment was done to determine the adverse effects of nitrate exposure in groundwater sources of the Kamyaran city. 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 into four groups: infant (<2 years), children (2–6 years), teenager (6–16 years), and adult (>16 years) and were surveyed regarding non-carcinogenic risk [19]. For the non-carcinogenic risk to be determined, the Reference Dose (RFD) is of great significance. RFD is an exposure that, if

Table 1 Weight (wi) and relative weight (Wi) of each chemical parameter

S. No	Parameter	Unit	WHO Standard [22]	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**

Table 2 General classifications Water Quality Index

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

contacted by a human population (including sensitive groups) daily, is likely to cause no significant risk of harmful effects throughout life [9, 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 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 [1].

Non-carcinogenic risk is indicated by HQ, which is calculated by eq. 5 [46]:

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

Where;

HQ Hazard Quotient.
CDI chronic daily intake and.
RFD Oral reference dose (mg/Kg.day).

The chronic daily intake (CDI) values of nitrate via oral pathway were calculated using eq. (6) [41]:

$$CDI_{oral} = (C_W \times IR \times EF \times ED)/(BW \times AT) \quad (6)$$

Where;

HQ Hazard Quotient.
Cw Average contamination concentration in water (mg/L).
IR Ingestion rate of water (L/d).
Efr Exposure frequency (d/year).
ED exposure duration (year).
BW Average body weight (kg).
AT Averaging time (day) = (ED × 350).

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

According to the values given in Table 3, the HQ point value was estimated using the above formula. Then the uncertainty analysis was done using the MCS method by 10,000 repetitions in Oracle Crystal Ball®.

The probabilistic approach by Monte Carlo simulation & sensitivity analysis

MCS (what-if analysis), being one of the several widely adopted probabilistic risk assessment (PRA) models, is a strategy that can evaluate the variability and uncertainty in the various parameters of human health risk assessment. In the current study, the variability and SA of the risk assessment predictions model were done using the Monte-Carlo simulation. An uncomplicated approach to perform MCS is to create the model without uncertainty in Microsoft Excel software, subsequent use the spreadsheet-based application, as Crystal Ball® software [48].

The Monte Carlo Simulation (MCS) was used for sensitivity analysis (SA)with 10,000 repetitions by using Oracle Crystal Ball® software (version 11.1.34190). MCS modeling keeps the parameters Amounts from their fitted distribution to input data and consequently calculates both point value and exposure and risk dispersion. Risk analysis using Crystal Ball relies on developing a mathematical model in Excel representing the situation of interest [49]. Table 4 indicates the parameters for determining SA by the MCS technique. The probability distribution functions used in the Monte Carlo simulation and SA are obtained from the US Environmental Protection Agency.

Table 3 Values of parameters used in health risk assessment method

Parameters	Unit	Infant	Children	Teenager	Adults	References
IR	L/day	0.4	0.78	2	2.5	[47]
E_{fr}	Day/year	350	350	350	350	
ED	Year	1.5	4	13	40	
Rfd	mg/kg.day	1.6				[17]
BW	Kg	10	15	50	80	
AT	Day	525	1400	4550	14,000	

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	Lognormal	[50]
Nitrate concentration	Location=0.00, Mean=22.64, Std. Dev.=12.64				Lognormal	This study
Bodyweight (kg)	7.98±1.02*	16.41±3.78*	39.83±10.16*	77.45±13.6*	Lognormal	[51]
Exposure Duration (year)	1.5	4	13	40	–	[47]
Exposure Frequency (day/year)	350	350	350	350	–	[52]
Averaging Time (day*365)	1.5*350	4*350	13*350	40*350	–	
RfD (mg/kg.day)	1.6				–	[17]

*. Mean ± S.D

Results and discussion

Physico-chemical parameters

WQI in rural areas of Kamyaran, which is the vital area of wheat cultivation of the Kurdistan province, was investigated in the current study. The results of the chemical analysis are shown in Table 5. This table indicates the mean, maximum, minimum, and standard deviation (SD) of determining parameters in groundwater samples of the study area.

According to Table 5, groundwater samples' pH ranges within 7.3–8.3 with an average of 7.81. The pH values in this study indicate that the dissolved carbonates are mainly in the HCO_3^- form. 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 the world health organization (2011) for drinking-water quality (6.5–8.5) [22].

The pH value of less than 6.5 is corrosive, and values 8.5 and above indicate the carbonated water. The higher pH values in drinking water resources have no direct health effect on humans, but it is an operational severe water quality parameter. Water with lower-than-standard pH levels is corrosive and tends to react with pipes and mains, which in turn have an adverse effect on the water quality. In other words, the direct impact of pH is the reaction with pipes in the distribution [53]. However, all groundwater samples of the present study were within acceptable limits (Table 5).

EC parameter indicates the number of dissolved solids in water, and this study ranged from 380 to 960 μmhos/cm and with a mean of 620.53 μmhos/cm. HCO_3^- values were less than the guideline values of 500 mg/L (Table 5). TDS is the amount of inorganic salts and small amounts of organic matter present in water. The TDS values ranged from 276 to 614 mg/L, with an average of 415.33 mg/L. These values show that water in the studied rural regions has a great potential to dissolve salts and minerals. TH is due to the availability of calcium and magnesium cations in the water resources. In this area, TH was in the range of 130–412 mg/L, with an average of 254.48 as $CaCO_3$.

Table 5 Descriptive statics and WHO standard for determining groundwater parameters

Parameter	Unit	Max	Min	Mean	SD*	WHO Standard [22]
PH	–	8.3	7.30	7.87	0.225	6.5–8.5
EC	μmhos/cm	960	380	620.53	157.67	1000
TDS	mg/L	614	276	415.33	97.65	600
TH	mg/L as $CaCO_3$	412	130	254.48	82.97	500
Ca^{2+}	mg/L	55.7	50.34	53.51	1.51	75
Mg^{2+}	mg/L	22.69	20.41	21.41	0.71	75
Na^+	mg/L	26	7.5	14.98	5.65	200
K^+	mg/L	19.5	0.5	3.01	4.23	12
SO_4^{2-}	mg/L	0.69	0.08	0.28	0.13	250
HCO_3^-	mg/L	6.96	2.24	4.51	1.37	500
Cl^-	mg/L	0.67	0.05	0.27	0.18	200
NO_3^-	mg/L	55.8	6.20	22.42	11.44	50

*SD: Standard Deviation

The concentrations of sodium (Na^+) and chloride (Cl^-) ranged from 7.5–26 (Mean: 14.98) and 20.41 to 22.69 mg/L (Mean: 21.41), 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 ions may cause high blood pressure [53]. In our study area, no worrisome concentration of Na^+ and Cl^- was found, so no health hazard is predicted. The range of calcium, magnesium were 50.34 to 55.7 mg/L (Mean: 53.51), and 0.23 to 15.1 mg/L (Mean: 3.75), respectively. One of the effects of Ca^{2+} and Mg^{2+} is an increase in the water's hardness [54].

The concentration of Potassium (K^+) in most groundwater samples was lower than levels that can pose any danger to human health. K^+ concentration was found in the range of 0.5–19.5 mg/L with a mean of 3.01 mg/L. With 12 mg/L sets as the potassium threshold value, 6% of the sampled water exceeded the limit. The Potassium-contaminated water consumers in some areas are likely exposed to the risk of hyperkalemia and the disease associated with excessive intake of potassium. Potassium deficiency in the human body may affect heartbeat disorder and muscle weakness, whereas a high amount may affect the homeostatic mechanism [54].

The sulfate (SO_4^{2-}) concentration was in the range of 0.64 to 11.92 mg/L with an average of 3.67 mg/L (Table 5). According to the sulfate standard limit, all the samples are considered safe. The concentration level of SO_4^{2-} in the groundwater raises no adverse health concerns. The adverse effects of sulfate contamination are distaste (depending on the combining cation) and discomforting bowel activity [22].

Nitrate concentration in the study area

According to the results of Table 5, the nitrate concentration in drinking water ranged from 6.2 to 55.8 mg/L, with an average of 22.42 mg/L. Figure 2 shows the spatial distribution of nitrate in the study area.

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. Nitrate concentration difference in various wells can be due to geological structure, land use, and contaminants leakage from various sources. Nitrate presence in groundwater resources may lead to cyanosis and asphyxia in babies. Higher NO3- concentration can cause Methemoglobinemia disorder which is commonly named Blue baby syndrome [53]. Whereas the low concentration may lead to the inadequate working of tissues, muscles, and bones [54].

In rural regions, there are 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 55.8 mg/L, which was higher than the WHO guidelines (50 mg/l) and Iran Standards (50 mg/L) [55].

Nitrogen fertilizers usage can be another notable source of nitrate pollution in rural areas. According to the result of the study by Maleki et al., it was found that there is a significant distinction between the nitrate ions concentration in samples taken in the two low water and high water seasons ($P < 0.01$). It is due to expanded agricultural activities in the high-water

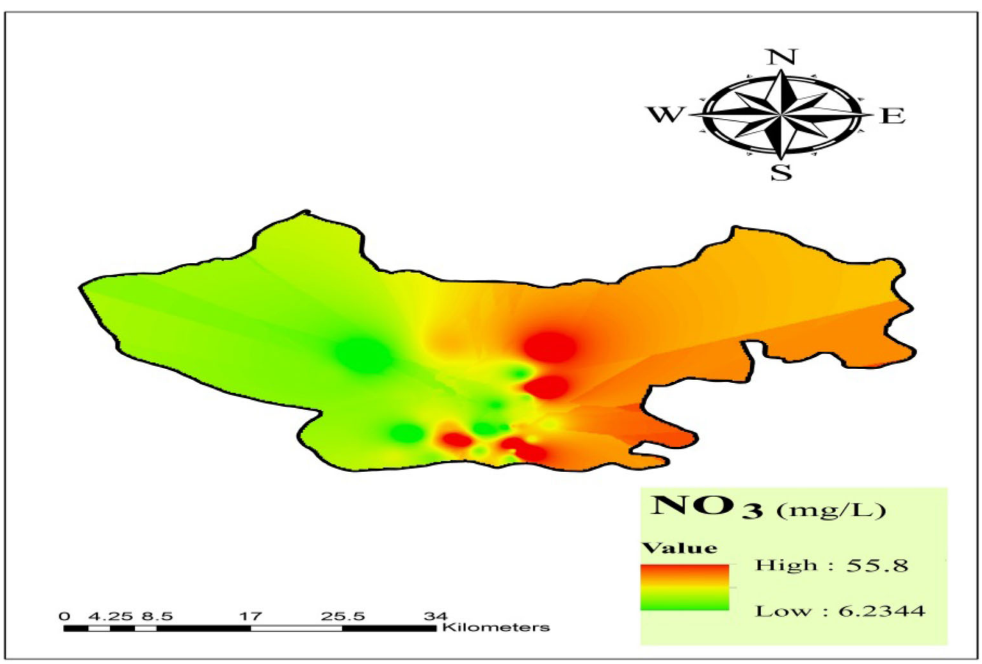


Fig. 2 Spatial distribution of nitrate concentration

season following increased consumption of fertilizers and pesticides, which results in a high concentration of nitrate in groundwater supplies [55]. Over 80% of the inhabitants in Kamyaran rural areas mainly rely on agriculture for their livelihood. Consequently, various kinds of nitrogen fertilizers and agrochemicals are utilized in farming practices to improve farm yields. Therefore, monitoring of agricultural practices and fertilizer use is necessary for this area.

Water quality index (WQI)

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 34.06 to 68.43. Figure 3 indicates the spatial distribution of WQI in the study area.

WQI showed that 74% of groundwater samples were within the excellent water quality class, and 26% of rural areas were in the category of good water type for drinking purposes. Table 6 shows the WQI of sampling areas.

In the study of Sadat Noori [56], the WQI was assessed in the Saveh-Nobaran aquifer, Iran. In this study, > 65% of water samples were in poor, very poor, and unsuitable range for drinking. High levels of TDS and TH of water samples had a significant impression on the area's water quality. In a study, groundwater quality was assessed using a WQI in Qorveh&Dehgolan, Kurdistan, Iran.

The number of twelve water quality parameters have been considered for WQI estimation. 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 base on WQI classification [20]. In another investigation, WQI was evaluated for drinking purposes in Anna Nagar, India. Based on obtained results, most groundwater samples varied from excellent to good and suitable for drinking purposes [57].

Health risk assessment of nitrate

Deterministic approach

Risk assessment is a systematic procedure to recognize risk factors and decide about the risk control to reduce exposure levels [58]. In this study, a health risk assessment was carried out to determine the effects of non-carcinogenic risk of nitrate on the health of inhabitants of rural areas of Kamyaran County, Kurdistan province, Iran. To assess the potential hazard level of the considered contaminants, the Hazard Quotient (HQ (Eq.5)) was calculated for infants, children, teenagers, and adult population groups. The statistical results of nitrate HQ are shown in Table 7.

According to the United States Environmental Protection Agency (US. EPA), hazard quotients (HQ) values larger than one mean unacceptable exposure conditions with high chronic non-cancer risks for the target organs in the human body [9]. The non-carcinogenic HQ values of 11% of infants, 26% of

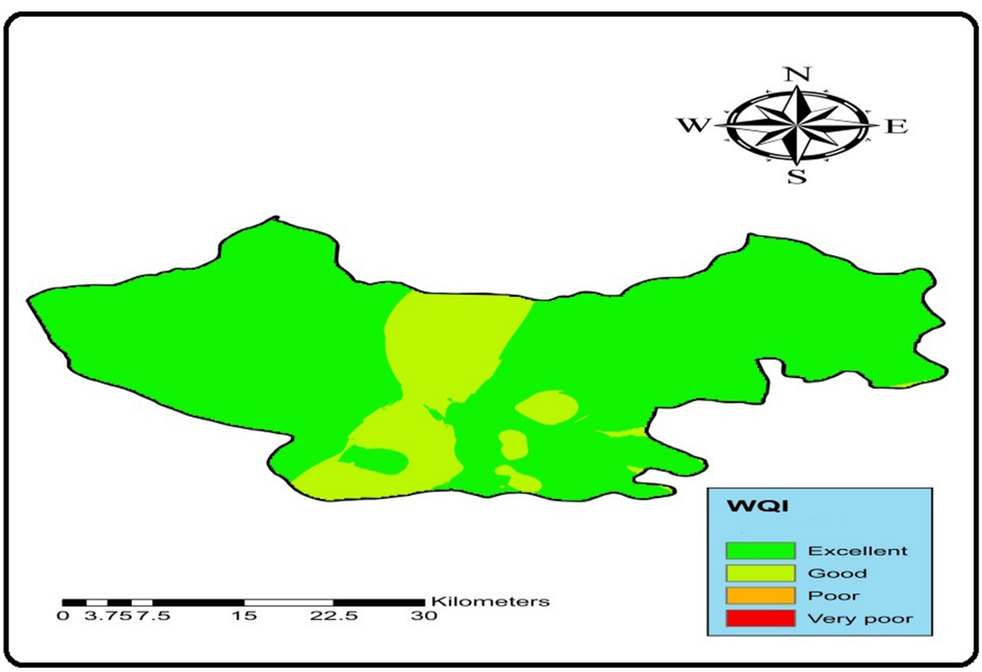


Fig. 3 Spatial distribution of Water Quality Index in the study area

Table 6 The rating of WQI in sampling points

NO. S	WQI	Water quality rating	NO. S	WQI	Water quality rating	NO. S	WQI	Water quality rating
1	68.43	Good Water	16	35.17	Excellent Water	31	35.42	Excellent Water
2	44.17	Excellent Water	17	42.75	Excellent Water	32	36.72	Excellent Water
3	52.81	Good Water	18	48.05	Excellent Water	33	54.55	Good Water
4	40.42	Excellent Water	19	44.35	Excellent Water	34	53.33	Good Water
5	34.22	Excellent Water	20	34.91	Excellent Water	35	44.49	Excellent Water
6	42.13	Excellent Water	21	38.82	Excellent Water	36	59.84	Good Water
7	48.81	Excellent Water	22	55.34	Good Water	37	43.80	Excellent Water
8	47.31	Excellent Water	23	57.43	Good Water	38	35.28	Excellent Water
9	34.06	Excellent Water	24	44.69	Excellent Water	39	44.69	Excellent Water
10	40.57	Excellent Water	25	58.99	Good Water	40	54.92	Good Water
11	47.98	Excellent Water	26	41.95	Excellent Water	41	46.27	Excellent Water
12	54.97	Excellent Water	27	36.25	Excellent Water	42	40.36	Excellent Water
13	43.13	Excellent Water	28	44.44	Excellent Water	43	53.33	Good Water
14	56.06	Excellent Water	29	44.04	Excellent Water	44	49.51	Excellent Water
15	40.43	Excellent Water	30	47.05	Excellent Water	45	51.49	Good Water

children, 11% of children, and 0.2% of adults were higher than the safety level (i.e., HQ > 1), suggesting adverse health effects for the exposed population. However, the HQ values for the 95th percentile in the adult age group 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 0.155–1.395 (Mean: 0.5606), 0.2015–1.8135 (Mean: 0.7288), 0.155–1.395 (Mean: 0.560), and 0.12714–1.08984 (Mean: 0.43802), respectively.

The non-carcinogenic risks (HQ level) of nitrate for the four exposed peoples varied in order: children > infant = teenagers > adults. Consequently, infants, children, and teenagers can be considered hypersensitive populations, and children had a higher adverse health effect through ingestion of drinking groundwater (HQ mean: 0.7288) (Table 7). Dispersion and Spatial Distribution of nitrate by inverse distance weighting (IDW) method in four exposed are indicated in Fig. 4.

Table 7 A deterministic approach to the calculation of HQ

Deterministic approach				
Parameter	Infant	Children	Teenager	Adult
Mean	0.56066	0.72886	0.56066	0.43802
*SD	0.28616	0.372008	0.28616012	0.223563
*P5th	0.155	0.2015	0.155	0.121094
P95th	1.16425	1.513525	1.16425	0.90957
The percentage of HQ>1	11%	26%	11%	2%

*__SD:__ Standard Deviation __P:__ Percentile

Ross Sadler et al. [27] evaluated the nitrate concentration in 52 active drinking water wells in rural Central Java, Indonesia. They evaluated the amount of nitrate concentrations exposure throughout drinking water in congenital disabilities and nitrate in infants below three months. The results revealed a low risk of infant methemoglobinemia and a high risk for birth defects, especially for the more susceptible inhabitants. Another study [59] assessed the health risk related to an agricultural district in the northeast of China. In this region near the sewage irrigation canals and agricultural areas, groundwater nitrate risk was > in urban areas. Besides, children's health risks were more notable than those of adults.

The results of D.Karunanidhi et al. [60] showed that children are more vulnerable than adults (men) for health risk in the Shanmuganadhi basin. Soleimani et al. studied the estimation of the non-carcinogenic health risk induced by nitrate due to the drinking route in rural areas of Divandarreh County, Kurdistan province, Iran [41]. In their study, the probability estimation results indicate that HQ levels were in the order of infant > children > teenagers > adults. They stated that high-risk levels in the infant group should be due to their low body weight compared to other exposed groups.

The probabilistic approach by Monte-Carlo simulation (MCS)

In addition to point estimation of HQ using eq. (5), the MCS technique by 10,000 repetitions was run via Oracle Crystal ball software (version 11.1.34190) to estimate HQ variances [61]. The probabilistic approach for nitrate in the four exposed groups, taking into account

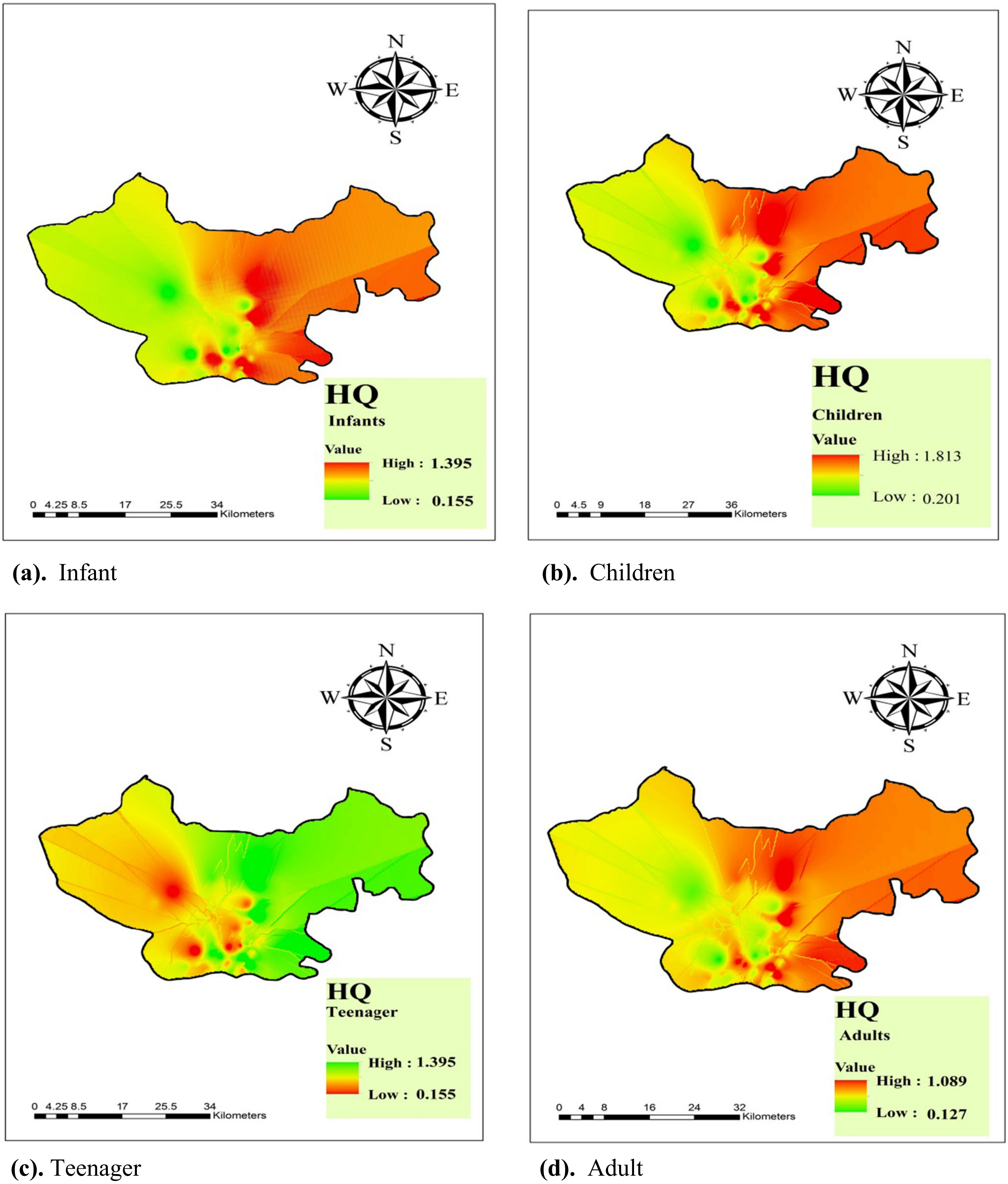


Fig. 4 Spatial distribution of HQ in different exposed groups **a)** Infant, **b)** Children, **c)** Teenager and **d)** Adult in the studied area

the proper distribution of parameters including the nitrate concentration, ingestion rate (IR), and body weight (BW), was performed, and the statistical results have been indicated in Table 8 for four exposed groups.

Table 8 The probabilistic approach to the calculation of HQ

Probabilistic approach				
Parameter	Infant	Children	Teenager	Adult
Mean	0.81	0.46	0.42	0.23
Median	0.68	0.38	0.35	0.19
*SD	0.54	0.33	0.3	0.15
*P5th	0.25	0.13	0.13	0.07
P95th	1.81	1.08	0.97	0.51

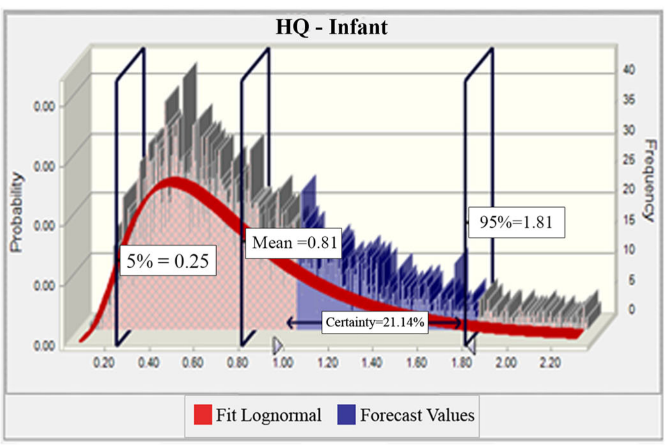
***SD:** Standard Deviation **P:** Percentile

Histograms for simulating HQ results in four exposed groups are displayed in Figs. 5 (a-d).

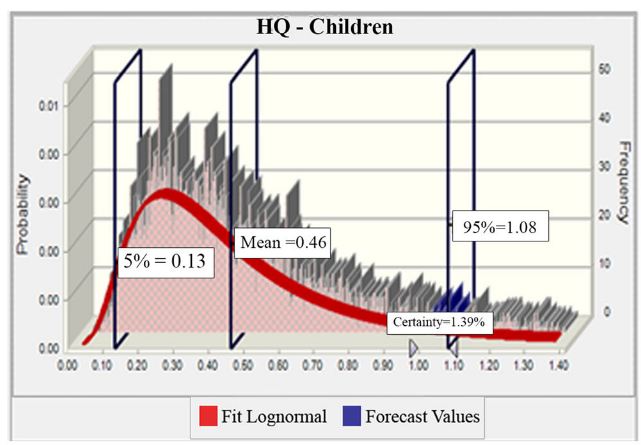
Table 4 shows the parameters and probability distribution functions derived from the US Environmental Protection Agency for Monte Carlo simulation.

Hazard quotient values larger than one means undesirable exposure conditions with high chronic non-cancer risks for the target organs in the exposed humans. The probability estimation results indicate that HQ levels were in the order of infant > children > teenagers > adults. According to fig. 5 and Table 8, the HQ values for the 5th and 95th percentile in infants, children, teenagers, and adults groups were (0.25–1.81), (0.13–1.08), (0.13–0.97), and (0.07–0.51), respectively, which indicates a non-carcinogenic risk for infant and children groups.

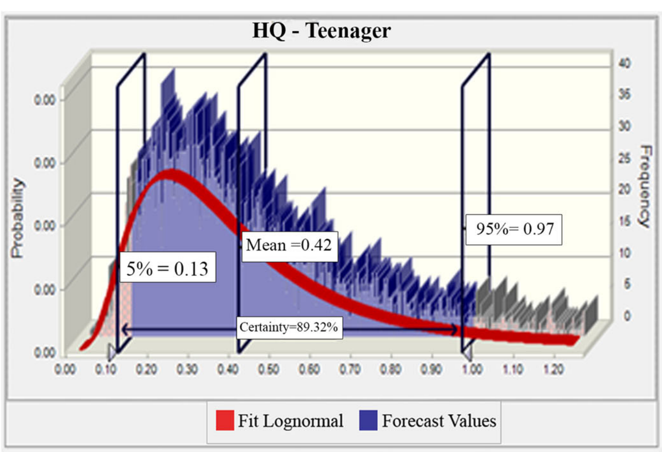
The highest 95th percentile of the calculated HQ in the study areas was 1.81 for infants, which shows a higher non-carcinogenic risk in this group. High-risk infants' levels can be due to their low body weight compared to other age groups [62]. According to fig. 4 (a), the result with 21.14% certainty shows that the HQ values will be between 1 and 1.81 (Blue part of histogram = certainty range). Also, uncertainty analysis results showed that the children group's HQ level was between 1 and 1.08 with 1.39% certainty. Similarly, in the teenager group, the HQ level was between 0.13–0.97 with 89.32%



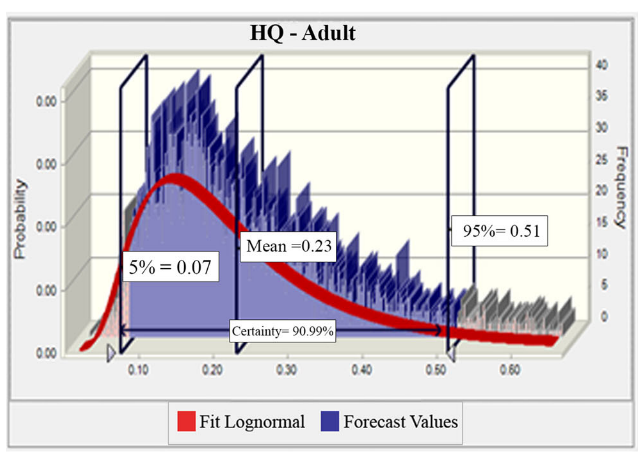
(a). HQ values in the infant group



(b). HQ values in children group



(c). HQ values in teenager group



(d). HQ values in the adult group

Fig. 5 Histograms of the uncertainty analysis of nitrate HQ. (a). HQ values in the infant group. (b). HQ values in children group. (c). HQ values in teenager group. (d). HQ values in the adult group confidence. It means that the likelihood of being HQ values between 0.13 and 0.97 is 89%. It can be inferred that because the values of percentile five and percentile 95 of HQ in this group are less than 1, exposure to nitrate from the drinking route does not pose a health risk to consumers [19].

The lowest 95th percentile belonged to the adult group (0.51), and the results of uncertainty analysis with 90.99% confidence showed that the HQ level in this group was less than 0.51. So, because the HQ values in this group were less than one, long-term exposure to nitrate does not increase the likelihood of non-carcinogenic risk and the adverse health effects of water intake [61].

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 rural areas. The average nitrate concentration was 2.66 ± 1.03 mg /L. Also, the risk assessment results showed that the infant groups are the most sensitive group in the community [19]. This finding was also observed in Zhai, Y et al. [63]. The research results in India also showed that 100% of the children group was at a high-risk level with an estimated daily gain of 13.2 to 2.56 of nitrate concentration [64].

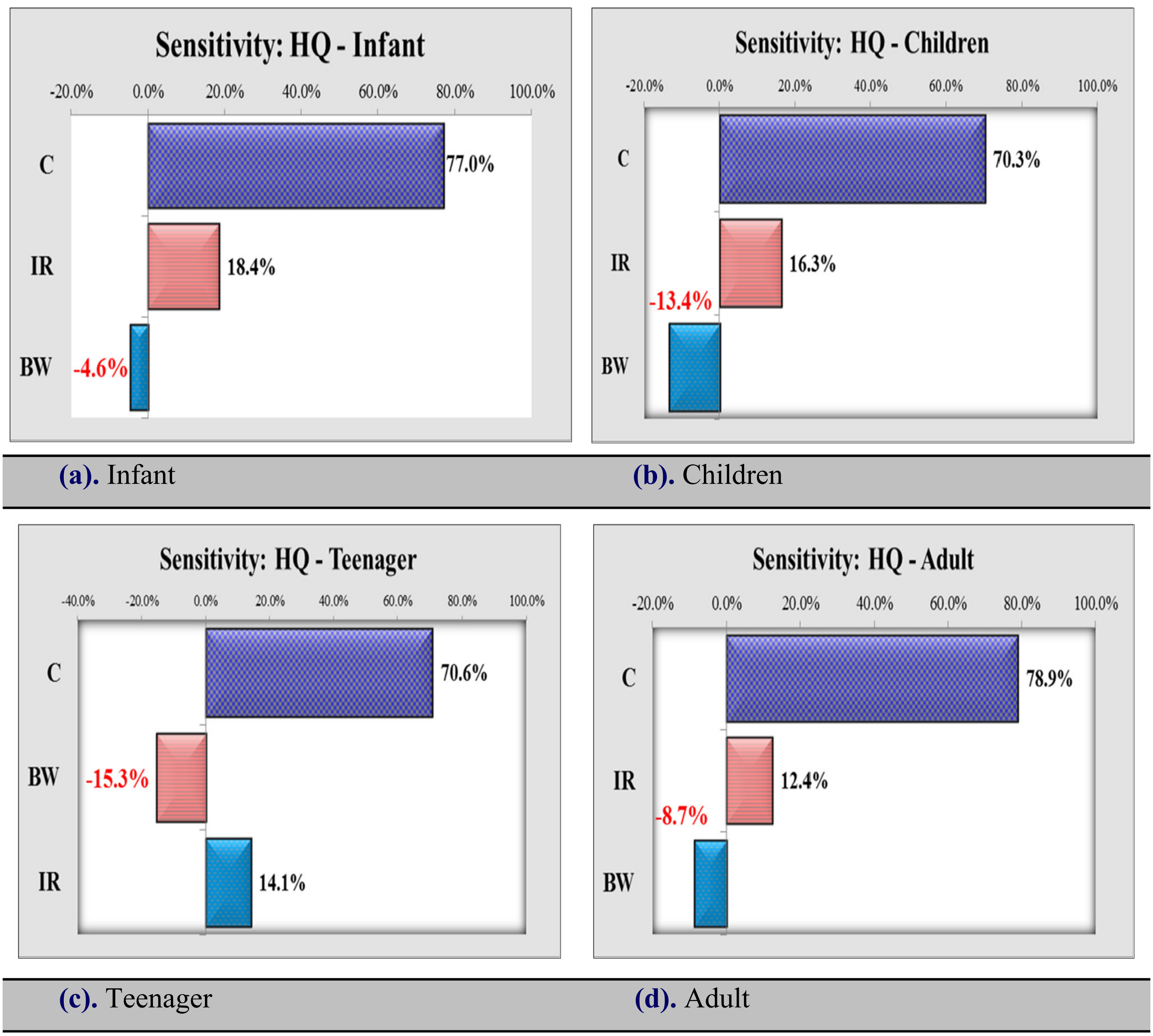


Fig. 6 Sensitivity analysis of different age groups exposed to nitrate. (a). Infant. **(b).** Children. (c). Teenager. **(d).** Adult

Sensitivity analysis

Uncertainty is a lack of knowledge about the actual value of a parameter. Since many parameters help create a health risk, determine the most effective one can help clear understanding and consequently, proper management of drinking water resources. In 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 6 (a-d) shows the SA of variables in calculating HQ for four exposed groups.

As shown in Fig. 6, the most influential parameter in the non-carcinogenic risk in three exposed groups (i.e., infant, children, and adult) is nitrate concentration and the ingestion rate, which increase the effect on non-carcinogenic risk. Also, nitrate concentration and body weight had the most impact on the teenage group's risk assessment. So, in all exposed groups, a decrease in nitrate concentration and ingestion rate can reduce the health risk.

According to the SA results, the body weight (BW) was inversely related to 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.

In the study by Badeenezhad et al., nitrate concentration and intestinal rate were reported as the most critical parameters in the non-carcinogenic impact of nitrate in drinking water wells [65]. Soleimani et al. studied the estimation of the non-carcinogenic health risk induced by nitrate due to the drinking route in rural areas of Divandarreh County, Kurdistan province, Iran. Similar to the present study results, they stated that the most influential parameter in the non-carcinogenic risk in three exposed groups was NO_3^- concentration and the ingestion rate [41].

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 groundwater resource quality and pose a risk to public health. The present investigation was aimed to assess the groundwater quality and its suitability for drinking purposes through GIS software in rural areas of Kamyaran, Kurdistan province of Iran.

Over 80% of the populations of Kamyarn in rural areas rely on agriculture activities for their livelihood. Consequently, various kinds of nitrogen fertilizers and agrochemicals are utilized in farming practices to improve farm yields. Therefore, monitoring agricultural practices and fertilizer 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 the appropriate drinking water provision are recommended. Additionally, the current nitrate source evaluation and related health risks will help policymakers define action strategies to minimize nitrate exposure in Kamyaran and similar Middle East areas.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest in considering or publishing this work.

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