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Spatiotemporal Analysis and Health Risk Assessment of Nitrate in Kan River Basin, Tehran: Application of IRWQI and Monte Carlo Simulation

Negin Rezaeiarshad [1], *Mohammad Rafiee* [1,2], *Mojtaba Sayyadi* [3], *Akbar Eslami* [1,2*]

[1] Department of Environmental Health Engineering, School of Public Health and Safety, Shahid Beheshti University of Medical Sciences, Tehran, Iran.
[2] Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran.
[3] Water and Wastewater Company of Tehran Province, Tehran, Iran.

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Corresponding Author:
Akbar Eslami

Email:
aeslami@sbmu.ac.ir

Tel:
+98 2122432040

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ABSTRACT

Introduction: Monitoring and controlling water resources and using health risk assessment approaches for water pollutants are essential for health promotion programs. This study aims to determine the water quality status and its spatiotemporal variation across the Kan River Basin, explore the interrelationship between surface and groundwater quality indices, and assess the nitrate health risk in drinking water.

Materials and Methods: The water quality index (WQI) was calculated based on the guideline of the Iran Environmental Protection Organization, and spatiotemporal distribution maps were prepared using ArcGIS in 2020. To determine the correlation between $IRWQI_{SC}$ and $IRWQI_{GC}$ indices, Spearman's non-parametric test was applied. Furthermore, Hazard Quotient (HQ), Excess Lifetime Cancer Risk (ELCR), and Monte-Carlo Simulation techniques were used to determine the carcinogenic and non-carcinogenic risks of nitrate in three age groups.

Results: The water resources were classified into three groups of medium quality, relatively good, and good during the study period. All parameters complied with the Iranian water quality standards. Furthermore, the statistical analysis revealed no significant relationship between the surface and groundwater quality indices. The calculated HQ values for infants, children, and adults were 0.661, 0.620, and 0.236, respectively. The ELCR values for infants, children, and adults were 1.06×10^{-4}, 0.99×10^{-4}, and 0.38×10^{-4}, respectively, which, for the infants' group was higher than the guideline limit of the United States Environmental Protection Agency (USEPA) (10^{-4}).

Conclusion: The water resources are suitable for drinking purposes. However, more attention is needed to prevent water contamination in the coming years.

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Introduction

Today, due to the population growth, increasing living standards in the communities, and consequently, the increasing extraction rate of surface and groundwater resources and decreasing rainfall, the problem of water scarcity has arisen in most parts of the world [1, 2]. Located in the arid and semi-arid region, Iran is one of the critical countries in the world in terms of water per capita and water supplies. In recent decades, mainly due to increased water consumption and overexploitation of water resources, especially

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groundwater resources, as well as lack of management and optimal use of available water, the phenomenon of water scarcity has emerged in the country. Insufficient rainfall and inappropriate time and place distribution have also exacerbated the water scarcity issue [3]. Also, due to the growing population and human demand for food and other livelihoods, humans have made changes in the environment to meet their needs. Factories, roads, increased use of surface and groundwater resources, mining, and development have caused various pollutants to enter the environment. Today, some of these pollutants have entered the food cycle while polluting the environment. Some have polluted the waters, which directly threatens human health and causes several diseases [4].

Nitrate is one of these pollutants that pose potential risks to human health. The high solubility of nitrate in aqueous media makes drinking water one of the main ways of exposure to nitrate [5]. Constant consumption of water containing high amounts of nitrate may lead to adverse health effects, such as blue baby syndrome, various types of cancer, miscarriage, coronary cardiac disease, and thyroid malfunction [6].

Supply of safe drinking water in cities and villages is one of the concerns of government officials and residents of the countries, and proper management of water resources and awareness of their status and quality is one of the most important goals of organizations and those in charge of water supply [3].

The water quality index (WQI) method has been widely used in water quality assessments of groundwater and surface resources, particularly rivers, and it has played an essential role in managing water resources [7]. The WQI is a mathematical approach for converting large amounts of water quality data into a single number used to describe water quality to relevant citizens and policymakers. This ranking index, which shows the effect of combining different parameters on the quality of water bodies, was initially developed by Horton; by selecting the 10 most commonly used water quality parameters, such as Dissolved Oxygen (DO), pH, coliforms, specific conductance, alkalinity, and chloride [8, 9].

Nowadays, the advent of technologies such as satellites and Geographic Information System (GIS) has made it much easier to survey the area under test; therefore, such tools have been widely used in determining water quality [8].

Jamshidi et al. conducted a study to evaluate water quality, and non-carcinogenic risk assessment of exposure to nitrate in groundwater resources of Kamyaran, Iran. The results of WQI showed that 74% and 26% of the groundwater samples were in the excellent and good water quality categories, respectively. The concentration of nitrate in the drinking water ranged from 22.42 ± 11.44 mg/L and the HQ mean scores for infants, children, teenagers, and adults were 0.5606, 0.7288, 0.5606, and 0.438, respectively [6].

In another study by Raja et al., an evaluation of groundwater quality, and health risk assessment of fluoride and nitrate was done in India. The results of the WQI indicated that 19%, 33%, 36%, and 10% of the analyzed samples were excellent, good, poor, and very poor, respectively, and the remaining 2% were considered unsuitable for drinking purposes. The mean calculated non-carcinogenic risk of fluoride and nitrate was 1.8. A total of 63% of the samples exceeded the non-carcinogenicity limit recommended by the USEPA [10].

Fallahzadeh et al. studied the mean annual nitrate level in 18 wells around Abarkouh. The results indicated that the mean concentration of nitrate was 27.57 ± 6.80 mg/L. Therefore, it was below the maximum permissible concentration (50 mg/L) by the World Health Organization (WHO). HQ values for children and adults were > 1 and < 1, respectively. As a result, children's health was highly at risk in these areas [11].

The primary objectives of this study were (1) to determine the water quality status and its spatiotemporal variation across the Kan River Basin, (2) to explore the interrelationship between surface and groundwater quality indices, and (3) to assess the nitrate carcinogenic and non-carcinogenic health risk associated with drinking water consumption.

The results of this study can help water supply authorities to manage the water resources properly, and increase public awareness of the quality of potable water used.

Materials and Methods

Study area

The Kan River basin is located in the north of Tehran city, between the latitudes of 35º 46' to 35º 58' north and the longitudes of 51º 10' to 51º 23' east, in an area of approximately 216 square kilometers. According to metrological data, the annual rainfall is about 662 mm, and about 70% of the total rainfall occurs in spring and winter. Due to the high altitude and low temperature of the basin, most of the rainfall in spring and winter is in the form of snow. The Kan River, 33 kilometers in length, originates from the Tochal Mountain Range located in the south of Alborz, and is the most watery river entering Tehran province. The average discharge of this river is equal to 2.2 m^3/s [12, 13].

Data collection

The results of previous years' analysis (Table 1) and land use information (Figure 1) were gathered from the Water and Wastewater Company of Tehran Province and the Soil and Water Research Institute of Iran, respectively. The geographical coordinates of surface and groundwater sampling points were also recorded using Global Positioning System (GPS).

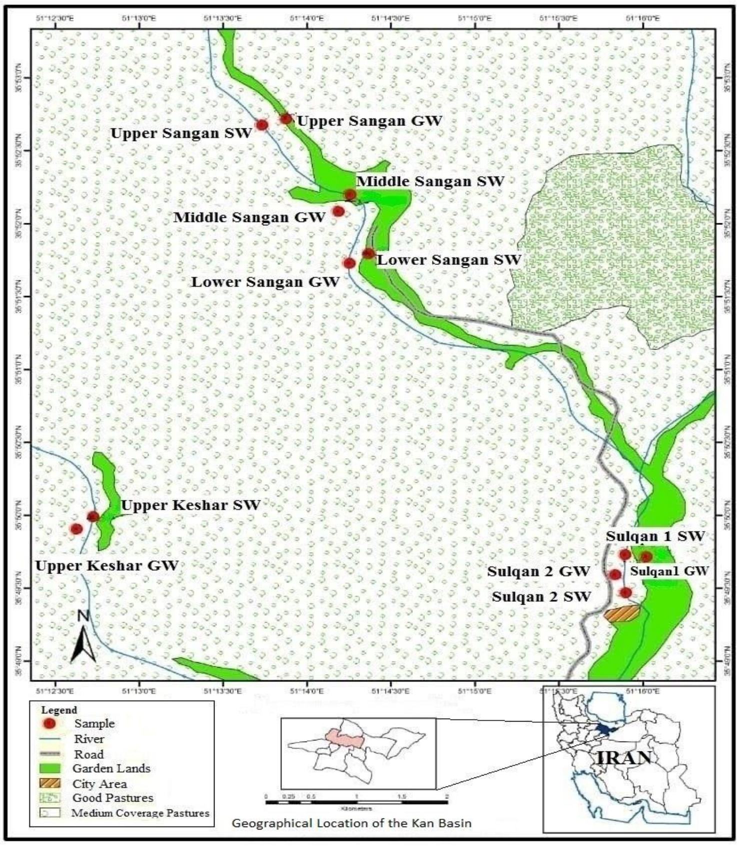

Figure 1: Land use map of the study area in the Kan River basin, Tehran

Table 1: The water quality parameters of the drinking water wells, measured by the Water and Wastewater Company of Tehran Province

Well name	Sampling Date	Turbidity (NTU)	EC (ms/cm)	TDS (mg/L)	pH	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	No_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	F^{-} (mg/L)	Total Hardness (mg/L $CaCO_3$)	Total Alkalinity (mg/L $CaCO_3$)
Upper Sangan	May-2012	1.00	0.31	186.00	7.29	9.00	39.00	10.00	0.10	5.00	30.00	5.00	-*	132	114
	Oct-2015	0.40	0.33	170.88	7.98	3.55	53.04	7.72	0.15	1.62	17.98	2.71	0.12	147	140
	Oct-2018	0.84	0.35	182.82	7.40	3.00	56.80	8.80	0.20	1.50	22.30	6.40	0.24	154	139
Lower Sangan	June-2012	1.00	0.33	198.00	7.65	14.00	39.00	5.00	0.20	11.00	36.00	12.00	-	155	124
	July-2015	0.20	0.41	230.46	7.62	4.49	67.38	8.05	0.43	12.66	51.03	9.45	0.16	187	128
Sulqan 1	Feb-2016	0.45	0.45	248.30	7.55	5.16	68.74	12.55	0.46	15.18	51.45	15.36	0.20	193	132
	Oct-2018	0.35	0.46	252.70	6.85	5.00	70.00	14.80	0.40	11.00	48.00	17.20	0.33	195	143
Sulqan 2	Dec-2014	0.80	0.40	224.51	7.30	4.92	62.50	11.10	0.53	12.93	43.50	10.82	0.20	176	130
	Feb-2016	0.15	0.54	314.81	7.84	6.36	83.38	16.44	0.42	20.43	86.80	16.76	0.22	235	140
	Aug-2016	3.10	0.55	311.51	7.40	6.33	84.65	15.32	1.27	21.18	69.50	21.78	0.27	238	152
Upper Keshar	June-2012	1.00	0.36	216.00	7.70	15.00	39.00	10.00	0.10	11.00	39.00	10.00	-	157	118
	Oct-2015	4.00	0.43	223.77	8.05	6.00	63.80	13.23	1.04	3.63	23.21	4.73	0.34	184	180

*Data not available.

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Sample collection and laboratory analysis

In this study, 144 samples from six drinking water wells and six monitoring stations in the tributaries of the Kan River were collected to analyze the quality of groundwater and surface water resources. The studied villages include Upper Sangan, Middle Sangan, Lower Sangan, Sulqan (with two wells), and Upper Keshar. Sampling of the target points was performed twice a month, during wet (spring 2020) and dry (summer 2020) seasons. Based on the EPA instructions, the samples were collected in polyethylene bottles for physical and chemical analysis, and special sterile containers for microbial analysis, then transferred to the laboratory of the Faculty of Health and Safety of Shahid Beheshti University of Medical Sciences in the cool box [14, 15]. Field parameters such as DO and pH were measured using portable oxygen meter, Martini Mi605, and Merck pH paper at the sampling site. In the laboratory, by performing the relevant analysis according to the book "Standard Methods for the Examination of Water and Wastewater", the amounts of desired parameters were determined [16]. Employed Instrument to determine the concentrations of NO_3^-, PO_4^{3-}, and NH_4^+ was spectrophotometer, DR5000, Hach. Electrical Conductivity (EC) was determined using the conductivity/TDS meter, Hach. The chemicals weights were observed by electronic weighing balance Sartorius, BL 210S. The solutions were mixed using a magnetic stirrer (IKA, C-MAG HS7). HACH turbidity meter model 2100AN was used to determine the turbidity, and the amount of sodium was measured using Jenway, PFP7 flame photometer. All chemicals used in this study were purchased from Merck, Sigma-Aldrich, and Samchun brands with suitable purity for laboratory analysis.

IRWQI calculation and spatiotemporal distribution

An effective monitoring tool that provides valuable information on water from various sources is WQI, which often incorporates several water quality parameters to describe the state of the water resources and their potential application for drinking purposes [17]. Iran Water Quality Index (IRWQI) has been developed to provide an index appropriate to natural conditions and issues of water resources in Iran. After determining the test results, the values of $IRWQI_{GC}$ and $IRWQI_{SC}$ were calculated based on the method introduced by the Environmental Protection Organization of Iran [18]. The index proposed in the present study consists of eleven parameters for the surface water and ten parameters for the groundwater that are shown in Table 2. Each environmental parameter was assigned a weight based on its perceived effect on primary health.

Surface and groundwater quality indices were calculated using Equation 1:

Equation 1: $IRWQI = [\prod_{i=1}^{n} Ii^{Wi}]^{1/Ɣ}$

Equation 2: $Ɣ = \sum_{i=1}^{n} Wi$

Where, W_i is the weight of the i parameter, n is the number of parameters, I_i is the index value for the i parameter of the ranking curves provided in the guideline, and Ɣ is obtained from the Equation 2.

The IRWQI ranges from 0 to 100, with high values representing good water quality conditions. Table 3 shows the range of the IRWQI specified for drinking water.

Table 2: The IRWQI parameters and their relative weights

Parameter		Relative weight	Unit
Fecal coliform	Surface Water	0.140	MPN/100ml
	Ground Water	0.134	
BOD_5	Surface Water	0.117	mg/L
	Ground Water	0.088	
Nitrate	Surface Water	0.108	mg/L
	Ground Water	0.151	
DO	Surface Water	0.097	Saturation percentage
	Ground Water	0.067	
EC	Surface Water	0.096	µs/cm
	Ground Water	0.129	
COD	Surface Water	0.093	mg/L
	Ground Water	0.08	
Ammonium	Surface Water	0.090	Total Ammonium
	Ground Water	-	
Phosphate	Surface Water	0.087	mg/L
	Ground Water	0.085	
Turbidity	Surface Water	0.062	NTU
	Ground Water	-	
Total hardness	Surface Water	0.059	mg/L $CaCO_3$
	Ground Water	0.103	
pH	Surface Water	0.051	-
	Ground Water	0.074	
SAR	Surface Water	0.089	-
	Ground Water	-	

Table 3: The water quality classification based on the IRWQI value

IRWQI range	Water quality
< 15	Very bad
15-29.9	Bad
30-44.9	Relatively bad
45-55	Medium
55.1-70	Relatively good
70.1-85	Good
85	Very good

To determine the relationship between surface and groundwater resources in the study region, in addition to the spatial distribution maps, R statistical software (v.3.6.1) was used. Initially, the normal distribution of data was evaluated with the Kolmogorov–Smirnov test, then the Spearman test was implemented to determine the correlation of the surface and groundwater quality indices.

Spatiotemporal distribution maps were prepared for nitrate and the indices in spring and summer, using ArcGIS 10.2 software (ESRI, Redlands, CA, USA). The kriging interpolation method is considered the most basic geostatistical technique, which provides the best linear unbiased estimation for the spatial distribution modeling of a random variable [19]. After examining the standard error rate of kriging with various semi-variograms, a spherical semi-variogram was employed to prepare the maps.

Human health risk assessment

Human health risk assessment is the process of estimating the nature and probability of adverse health effects in humans who may be exposed to chemicals in various contaminated environments, such as air, water, and soil, now or in the future. This process includes four steps, including hazard identification, dose-response assessment, exposure assessment, and risk characterization [20, 21]. There are three main exposure routes to the pollutants, including oral, dermal, and inhalation. In general, ingestion is the primary route of nitrate exposure [6]. Therefore, in the present study, only this route was considered. The exposed population was classified into three groups, including infants, children, and adults. The non-carcinogenic health risk due to groundwater contamination by nitrate was estimated using Equation 3.

Equation 3: $HQ = \frac{CDI}{RFD}$

Where, HQ, CDI, and RFD represent hazard quotient, chronic daily intake, and oral reference dose, respectively.

Equation 4: $CDI_{ingestion} = \frac{C \times DI \times EF \times ED}{BW \times AT}$

Where, C is the mean concentration of contaminant in water (mg/L), DI is ingestion rate of water (L/d), EF is exposure frequency (d/year), ED is the exposure duration (year), BW is average body weight (kg), and AT indicates average life expectancy (days) = (ED × 350).

The nitrate carcinogenic health risk via the ingestion pathway was computed by Equation 5:

Equation 5: $ELCR = CDI \times CSF$

Where, CSF is the cancer slope factor (mg/kg.day).

The values of DI, EF, ED, BW, AT, RFD, and CSF are shown in Table 4.

Monte Carlo simulation and uncertainty analysis

When we use single-point values to assess the health risk of a population, there is a significant level of uncertainty. To minimize the uncertainty, the Monte Carlo simulation can be used in research [24]. Monte Carlo simulation is a method that can estimate the variability and uncertainty in the different parameters of human health risk assessment. Recently, it has been widely used in the assessment of environmental health and safety risks [6, 25]. In the present study, a Monte Carlo simulation with a 95% confidence interval and 10,000 iterations was performed to compute health risks, using Oracle Crystal Ball software (v.11.1.2.4.850).

Table 4: Values of parameters used in the health risk assessment equation [22, 23]

Parameter	Infants	Children	Adults
DI (L/day)	0.8	1.5	2
EF (Day/year)	365	365	365
ED (Year)	1	10	40
RFD (mg/kg.day)	1.6	1.6	1.6
BW (Kg)	10	20	70
AT (Day)	365	3650	14600
CSF (mg/Kg.day)	10^{-5}	10^{-5}	10^{-5}

Ethical issue

This study was conducted with the approval of Shahid Beheshti University of Medical Sciences, School of Public Health and Safety. Medical Ethics Committee Code: IR.SBMU.PHNS.REC.1399.174

Results

Physicochemical characteristics

The mean values and standard deviations of physical and chemical parameters in the spring and summer are presented in Tables 5 and 6, respectively. The number of fecal coliforms in all the samples was < 3, and the concentration of NH_4^+ in the surface water resources was below the detection limit.

Table 5: Water quality parameters summarized as the mean and standard deviation in spring, 2020

Parameter	Standard	Upper Sangan		Middle Sangan		Lower Sangan		Upper Keshar		Sulqan 1		Sulqan 2	
		*GW	*SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW
EC (ms/cm)	-	0.2 ± 0.05	0.17 ± 0.02	0.34 ± 0.13	0.24 ± 0.06	0.22 ± 0.01	0.24 ± 0.06	0.28 ± 0.14	0.37 ± 0.11	0.42 ± 0.02	0.25 ± 0.06	0.3 ± 0.01	0.31 ± 0.06
BOD_5 (mg/L)	-	7.33 ± 0.6	3.86 ± 1.97	3.1 ± 0.28	4.46 ± 0.36	4.01 ± 1.97	7.42 ± 2.43	3.43 ± 1.32	4.35 ± 0.11	3.2 ± 0.57	3.79 ± 1.61	3.25 ± 1.5	3.82 ± 0.48
Nitrate (mg/L)	50	5.17 ± 1.09	6.06 ± 0.29	16.75 ± 0.92	6.05 ± 0.35	10.21 ± 0.4	5.24 ± 0.46	13.4 ± 3.22	17.99 ± 4.41	18.11 ± 4.74	5.32 ± 3.23	11.14 ± 4.56	9.81 ± 0.59
DO (Saturated %)	-	82.9 ± 5.09	92.8 ± 5.37	84.9 ± 10.89	84.8 ± 0.57	82.65 ± 7.1	85.25 ± 1.06	77.3 ± 2.4	72.65 ± 1.34	66.95 ± 3.18	61.85 ± 16.47	46.4 ± 14.1	78.1 ± 4.81
COD (mg/L)	-	15.56 ± 1.08	7.45 ± 4.31	4.5 ± 0.85	10.24 ± 0.01	9.33 ± 5.66	14.76 ± 0.91	6.8 ± 1.98	9.31 ± 1.15	4.55 ± 0.92	7.05 ± 3.75	7.05 ± 3.89	9.35 ± 1.27
Phosphate (mg/L)	-	0.01 ± 0	0.02 ± 0	0.015 ± 0.01	0.02 ± 0	0.01 ± 0	0.02 ± 0	0.01 ± 0	0.015 ± 0.01	0.025 ± 0.01	0.03 ± 0	0.01 ± 0	0.03 ± 0
Turbidity (NTU)	5	-	3 ± 2.55	-	4.35 ± 3.99	-	4.16 ± 3.56	-	2.14 ± 1.08	-	2.7 ± 1.46	-	2.26 ± 0.76
Total Hardness (mg/L $CaCO_3$)	500	132.5 ± 10.6	112.5 ± 17.68	205 ± 7.07	125 ± 21.21	125 ± 35.35	135 ± 14.14	155 ± 21.21	179 ± 41.01	212.5 ± 17.68	132.5 ± 17.68	151.5 ± 2.12	167.5 ± 3.54
SAR	-	1.01 ± 0.53	-	1.49 ± 0.35	-	1.44 ± 0.4	-	1.7 ± 0.23	-	1.84 ± 0.14	-	1.72 ± 0.21	-
pH	6.5 - 9	7 ± 0	7 ± 0	7 ± 0	7 ± 0	7 ± 0	7 ± 0	7 ± 0	6.75 ± 0.35	7 ± 0	6.75 ± 0.35	7 ± 0	7 ± 0

* SW represents the surface water resources and GW represents the groundwater resources.

Table 6: Water quality parameters summarized as the mean and standard deviation in summer, 2020

Parameter	Standard	Upper Sangan		Middle Sangan		Lower Sangan		Upper Keshar		Sulqan 1		Sulqan 2	
		*GW	*SW	GW	SW	GW	SW	GW	SW	GW	SW	GW	SW
EC (ms/cm)	-	0.28 ± 0.01	0.28 ± 0.03	0.48 ± 0.01	0.43 ± 0.01	0.31 ± 0.11	0.44 ± 0.03	0.33 ± 0.02	0.53 ± 0.01	0.45 ± 0.01	0.35 ± 0.04	0.32 ± 0.01	0.41 ± 0
BOD_5 (mg/L)	-	7.52 ± 0.54	4.37 ± 1.03	6.86 ± 3.56	4.83 ± 1.34	6 ± 1.7	8.07 ± 0.55	4.43 ± 1.06	7.03 ± 1.1	6.39 ± 1.82	4.26 ± 0.42	8.03 ± 0.31	5.48 ± 0.39
Nitrate (mg/L)	50	3.5 ± 1.12	6.48 ± 1.75	19.95 ± 2.96	15.35 ± 0.21	14.12 ± 3.21	20.65 ± 0.62	13.13 ± 0.45	28.06 ± 2.86	21.1 ± 0.52	14.84 ± 4.2	12.03 ± 0.17	19.11 ± 0.12
DO (Saturated %)	-	71.25 ± 8.84	93.75 ± 3.89	83.05 ± 3.32	80.75 ± 1.06	75.6 ± 21.78	76.6 ± 1.98	84.55 ± 14.21	93.55 ± 1.34	72.25 ± 12.8	95.1 ± 0.28	71.85 ± 14.92	82.8 ± 7.07
COD (mg/L)	-	16.35 ± 0.57	7.4 ± 1.27	13.25 ± 5.37	9.88 ± 0.88	9.75 ± 1.48	13.45 ± 0.92	6.64 ± 1.9	13.82 ± 1.8	12.18 ± 4.36	6.42 ± 1.3	15.6 ± 2.33	10.28 ± 0.25
Phosphate (mg/L)	-	0.01 ± 0	0.025 ± 0.01	0.025 ± 0.01	0.025 ± 0.01	0.025 ± 0.01	0.03 ± 0.01	0.015 ± 0.01	0.035 ± 0.01	0.025 ± 0.02	0.04 ± 0.01	0.02 ± 0.01	0.06 ± 0.04
Turbidity (NTU)	5	-	0.19 ± 0.07	-	0.18 ± 0.06	-	0.16 ± 0.06	-	0.33 ± 0.02	-	8.91 ± 2.2	-	6.42 ± 0.66
Total Hardness (mg/L $CaCO_3$)	500	144.8 ± 2.47	155 ± 0	230 ± 0	189.5 ± 0.71	154 ± 48.08	205.8 ± 1.06	146.5 ± 9.19	240.8 ± 8.13	206.5 ± 2.12	166.5 ± 16.26	149 ± 3.54	207.2 ± 6.01
SAR	-	1.19 ± 0.02	-	1.51 ± 0	-	1.78 ± 0.56	-	1.78 ± 0.11	-	2.12 ± 0.02	-	1.75 ± 0.05	-
pH	6.5 - 9	7.5 ± 0	7.25 ± 0.35	7.25 ± 0.35	7.25 ± 0.35	7 ± 0	7.5 ± 0	7 ± 0	7 ± 0	7 ± 0	7.25 ± 0.35	7 ± 0	7 ± 0

* SW represents the surface water resources and GW represents the groundwater resources.

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Based on the obtained results, the EC of groundwater of the Kan River basin varied from 0.2 ms/cm to 0.48 ms/cm. The highest and lowest values for EC were observed in Middle Sangan and Upper Sangan, respectively. The EC of surface water was 0.17-0.53 ms/cm, with the highest amount in the upper Keshar and the lowest in the Upper Sangan. Groundwater BOD_5 was in the range of 3.1 mg/L to 8.03 mg/L, most of which was related to Sulqan 2 in summer. The BOD_5 of surface water was between 3.79 mg/L in Upper Sangan, and 8.07 mg/L in Lower Sangan. Variations in nitrate concentrations were from 3.5 mg/L to 21.1 mg/L in the groundwater, and 5.24 mg/L to 28.06 in the surface water. The highest DO level of groundwater was related to Middle Sangan with 84.9%, and the lowest was related to Sulqan 2 with 46.4%. The DO of surface water was between 61.85% and 95.1%, the highest value of which was related to Sulqan 1 station, in summer. The COD amounts of groundwater varied from 4.5 mg/L to 16.35 mg/L, and in the surface water, varied from 6.42 mg/L to 14.76 mg/L. The phosphate concentration ranged from a minimum of 0.01 mg/L to a maximum of 0.025 mg/L in the groundwater and 0.02 mg/L to 0.06 mg/L in the surface water. The surface water turbidity was in the range of 0.16 NTU in the Lower Sangan to 8.91 in Sulqan 1. The total hardness varied from 125 mg/L $CaCO_3$ to 230 mg/L $CaCO_3$ in the groundwater and 112.5 mg/L $CaCO_3$ to 240.8 mg/L $CaCO_3$ in the surface water. The highest level of groundwater hardness belonged to Middle Sangan and the highest level of hardness in surface water belonged to Upper Keshar. The lowest SAR index was related to Upper Sangan well in spring with a value of 1.01, and the highest was related to the Sulqan 1 well in summer with a value of 2.12. The pH of groundwater varied between 7 and 7.5. The highest pH was observed in the Upper Sangan in summer. The pH of surface water was between 6.75 and 7.5, most of which was related to Lower Sangan.

Surface and groundwater quality indices

The computed values of IRWQI are presented in Table 7. The results indicated that the mean values of $IRWQI_{GC}$ ranged from 55.95 to 70.8, and $IRWQI_{SC}$ varied from 47.75 to 71.5. The highest $IRWQI_{SC}$ value was observed in Upper Sangan in spring (71.5), and the lowest one was related to Upper Keshar in summer (47.75). Among groundwater resources, the Lower Sangan well had the highest index in spring (70.8), and the Sulqan 1 well had the lowest index in summer (55.95).

Table 7: IRWQI values as the mean and standard deviation in spring and summer, 2020

	Spring				Summer			
Sampling point	**$IRWQI_{GC}$**	**Water Quality**	**$IRWQI_{SC}$**	**Water Quality**	**$IRWQI_{GC}$**	**Water Quality**	**$IRWQI_{SC}$**	**Water Quality**
Upper Sangan	67.6 ± 1.27	Relatively Good	71.5 ± 3.67	Good	67.35 ± 0.49	Relatively Good	70.8 ± 3.25	Good
Middle Sangan	69.9 ± 2.26	Relatively Good	69.2 ± 0.28	Relatively Good	59.45 ± 4.31	Relatively Good	55.3 ± 0.42	Relatively Good
Lower Sangan	70.8 ± 7.64	Good	67.25 ± 3.88	Relatively Good	62.95 ± 0.49	Relatively Good	48.45 ± 0.91	Medium
Upper Keshar	70.1 ± 2.97	Good	52.9 ± 3.53	Medium	68.05 ± 0.95	Relatively Good	47.75 ± 1.9	Medium
Sulqan 1	64.95 ± 2.33	Relatively Good	67.6 ± 6.92	Relatively Good	55.95 ± 0.07	Relatively Good	57.9 ± 4.52	Relatively Good
Sulqan 2	67.5 ± 4.38	Relatively Good	60.4 ± 0.98	Relatively Good	59.05 ± 1.48	Relatively Good	49.35 ± 1.9	Medium

Data analysis

Spearman's non-parametric test was applied to determine the correlation between surface and groundwater quality indices, the results of which are given in Table 8. This test showed that due to the higher p-value of 0.05, there was no significant correlation between $IRWQI_{SC}$ and $IRWQI_{GC}$ indices in the sampled points.

Table 8: Spearman test results to determine the correlation between $IRWQI_{SC}$ and $IRWQI_{GC}$

Sampling point	p-value	rho	Result
Upper Sangan	0.33	0.8	The connection is not meaningful
Middle Sangan	0.42	0.6	The connection is not meaningful
Lower Sangan	0.33	0.8	The connection is not meaningful
Upper Keshar	0.75	0.4	The connection is not meaningful
Sulqan 1	0.33	0.8	The connection is not meaningful
Sulqan 2	0.33	0.8	The connection is not meaningful

Spatiotemporal analysis

Spatiotemporal distribution maps of nitrate and IRWQI are shown in Figures 2-4. As can be seen from the maps of the surface and groundwater quality indices (Figures 2, 3), in Upper Sangan, which was the source of the river, the value of the index was higher than the other points, and as a result, it had better quality. Among ground water resources, the water of the Upper Keshar well had a better quality than the other.

Nitrate concentration variations

In this study, variations of nitrate concentration as a critical contaminant in drinking water resources was investigated in recent years. Table 1 reveals that the nitrate concentration of the Upper Sangan well was in the range of 1.5-5, Lower Sangan, 11-12.66, Sulqan 1, 11-15.18, Sulqan 2, 12.93-21.18, and Upper Keshar, 11-11.63. The results of the Middle Sangan well were not available at the time of the study. Nitrate concentrations measured in this study were also in the range of 3.5-5.17 in Upper Sangan, 16.75-19.95 in Middle Sangan, 10.21-14.12 in Lower Sangan, 13.4-13.13 in Upper Keshar, 18.11-21.1 in Sulqan 1, and 11.14-12.03 in Sulqan 2.

Nitrate health risk assessment

In the current study, a health risk assessment was carried out to determine the effects of carcinogenic and non-carcinogenic risks of nitrate on the health of inhabitants of the Kan River Basin, Tehran province.

The HQ and ELCR were calculated for infants, children, and adults groups. According to the USEPA, HQ $\geq$ 1 shows the presence of non-carcinogenic health risk, and HQ < 1 represents an ignorable hazard. Moreover, ELCR > 1×10^{-4}, 1×10^{-6} < ELCR < 1×10^{-4}, and ELCR < 1×10^{-6} were considered 'not acceptable', 'acceptable', and 'ignorable' carcinogenic health risk, respectively [26].

The results of nitrate HQ and ELCR are shown in Table 9. The range of HQ for infants, children, and adults in the studied area was 0.175–1.055 (Mean: 0.661), 0.164–0.989 (Mean: 0.620), and 0.063–0.377 (Mean: 0.236), respectively.

The mean ELCR ranged from 0.000028 to 0.000169 (Mean: 0.000106) for the infants, 0.000026 to 0.000158 (Mean: 0.000099) for the children, and 0.000010 to 0.000060 (Mean: 0.000038) for the adults.

Monte Carlo simulation and uncertainty analysis

The probable estimation of HQ and ELCR for nitrate with 95% confidence interval was evaluated using Oracle Crystal Ball with 10,000 trials (Figures 5, 6).

The results indicated that the lower and upper-bound intervals (5th and 95th percentiles) for HQs of infants, children, and adults were 0.29–1.06, 0.28–1.02, and 0.03–0.1, respectively.

The lower and upper-bound intervals (5th and 95th percentiles) for ELCRs of infants, children, and adults were 0.000048–0.000173, 0.000045–0.000161, and 0.000004–0.000015, respectively.

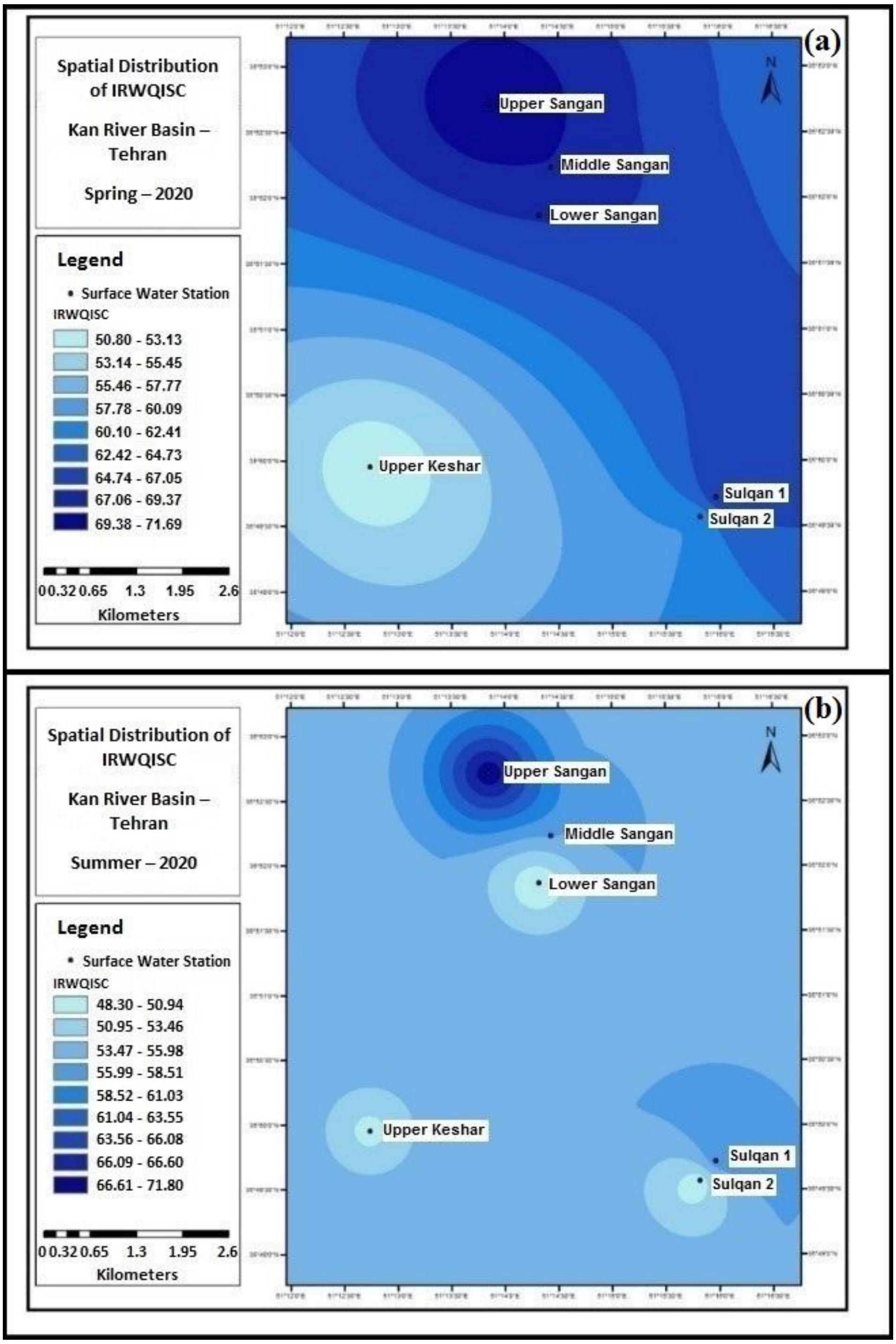

Figure 2: Spatiotemporal distribution of $IRWQI_{SC}$ based on the mean values in (a) spring, (b) summer

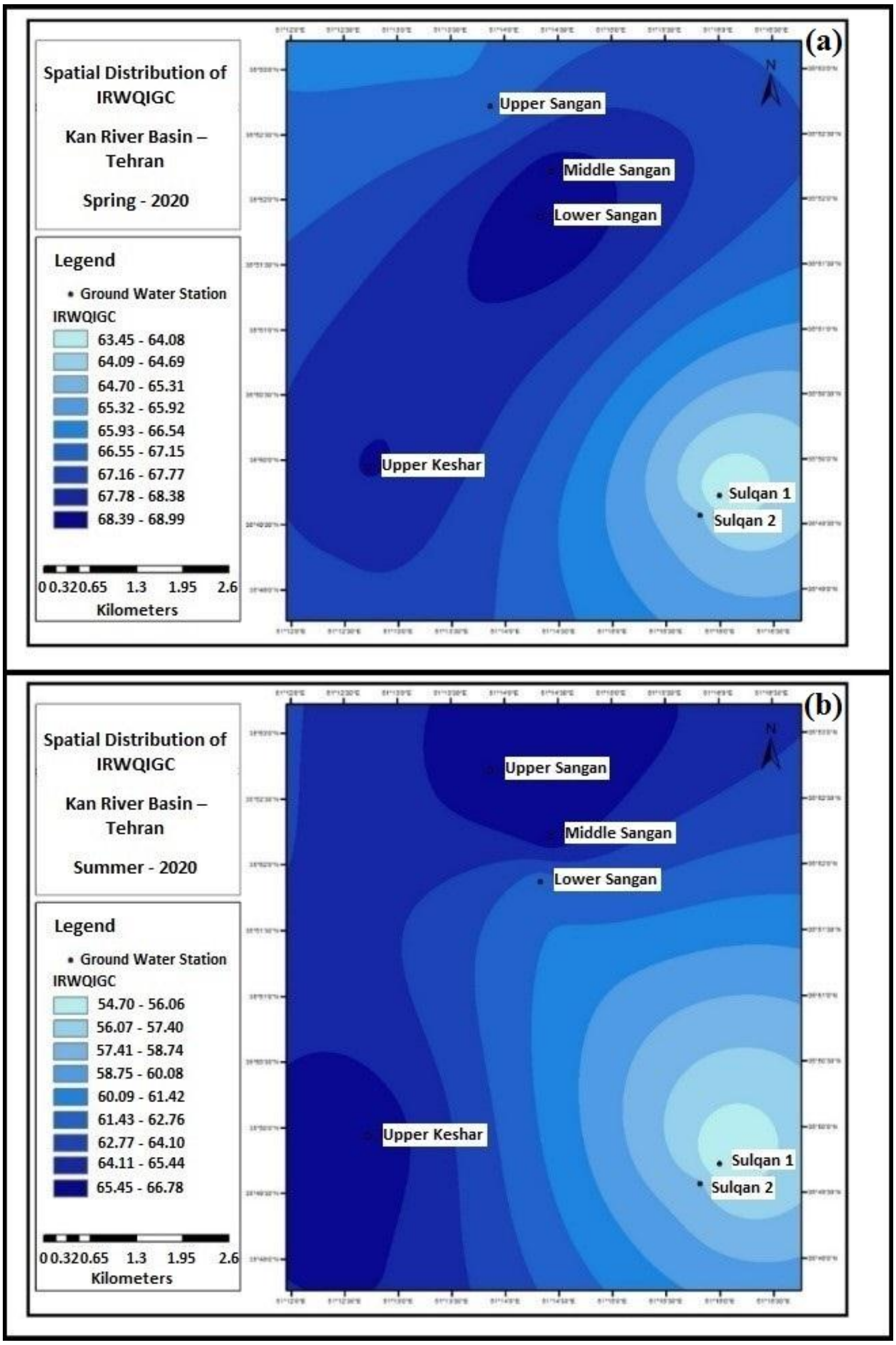

Figure 3: Spatiotemporal distribution of $IRWQI_{GC}$ based on the mean values in (a) spring, (b) summer

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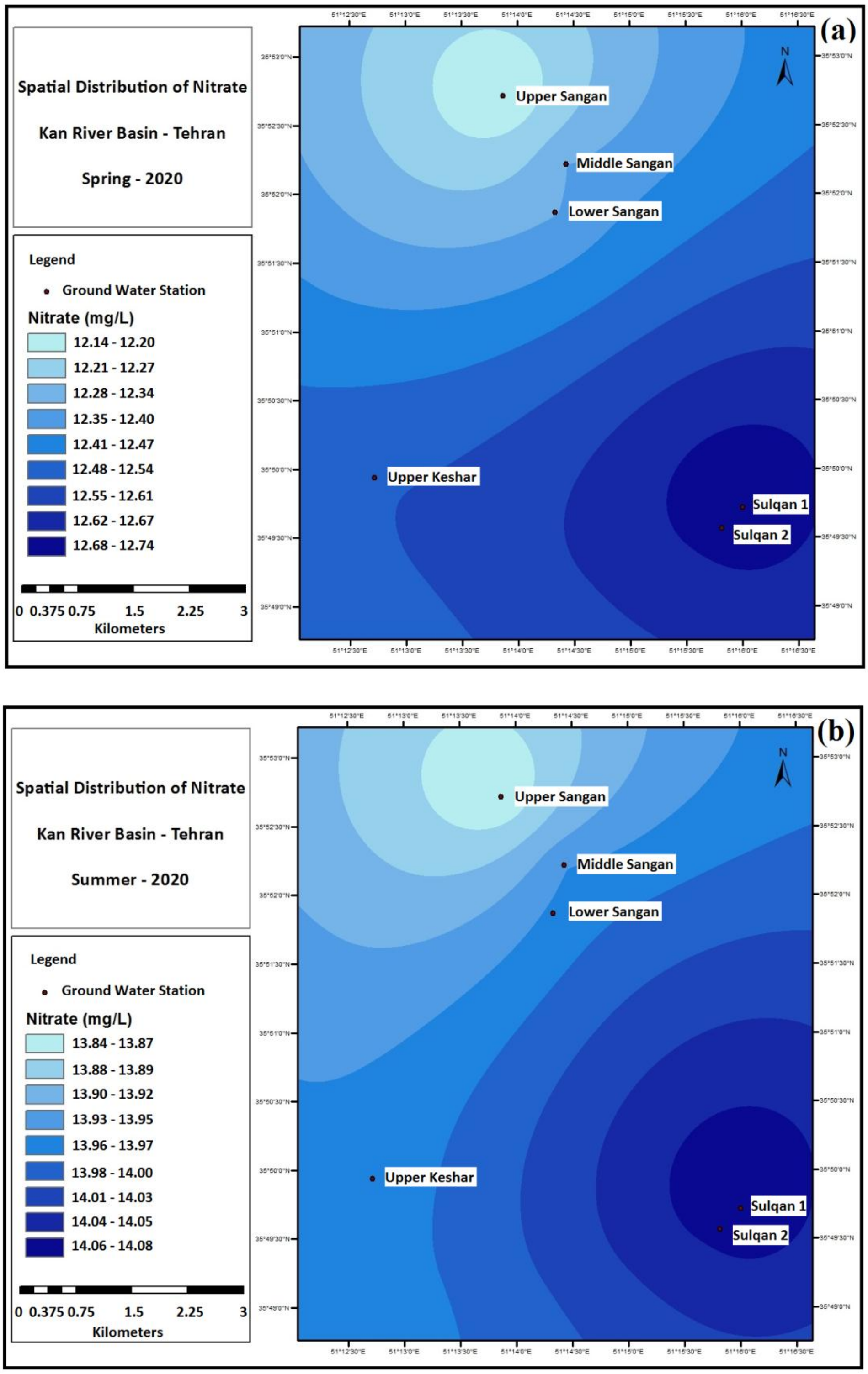

Figure 4: Spatiotemporal distribution of nitrate based on the mean values in (a) spring, (b) summer

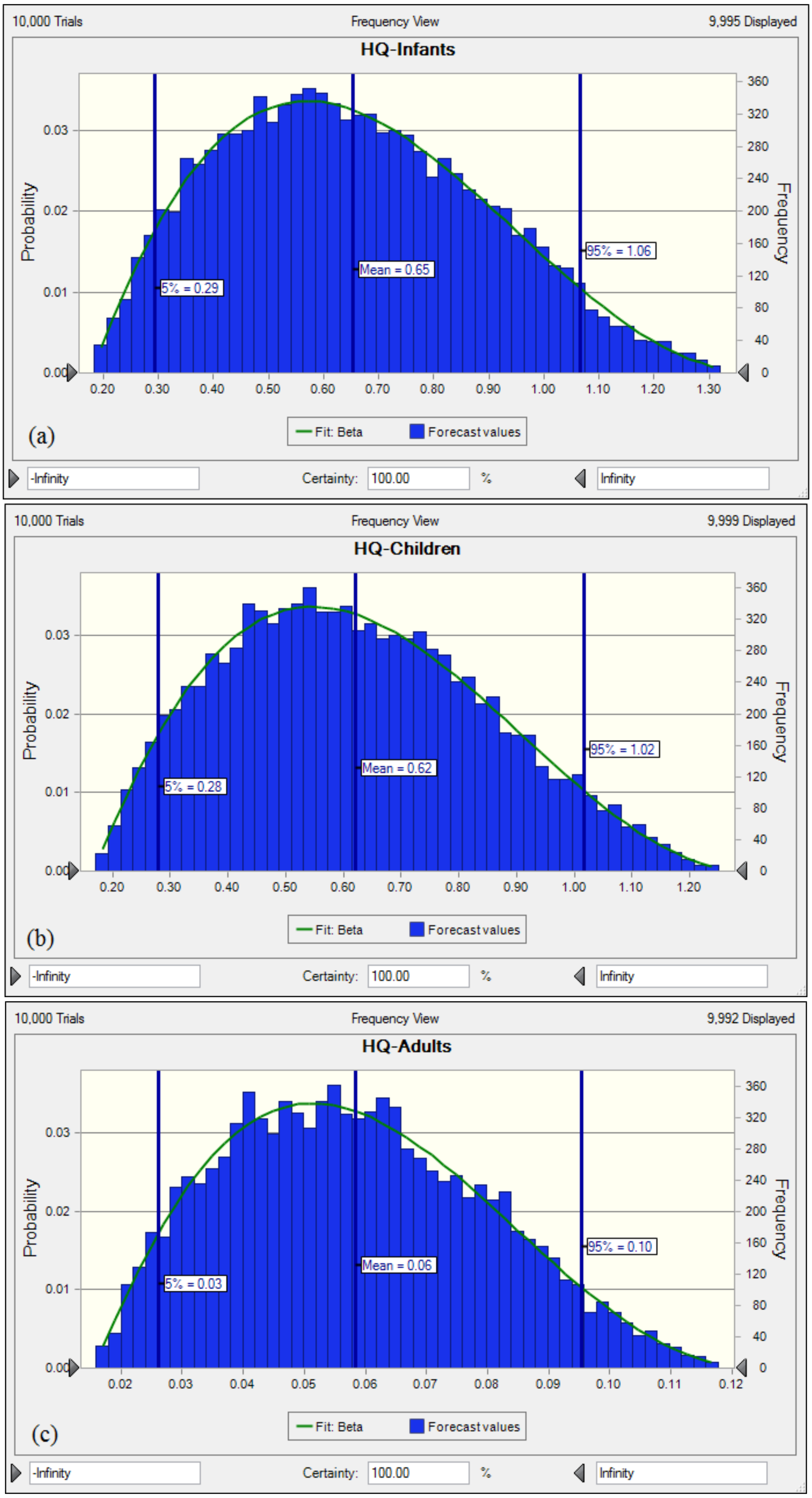

Figure 5: Histograms of the uncertainty analysis of nitrate HQ in (a) infants, (b) children, and (c) adults

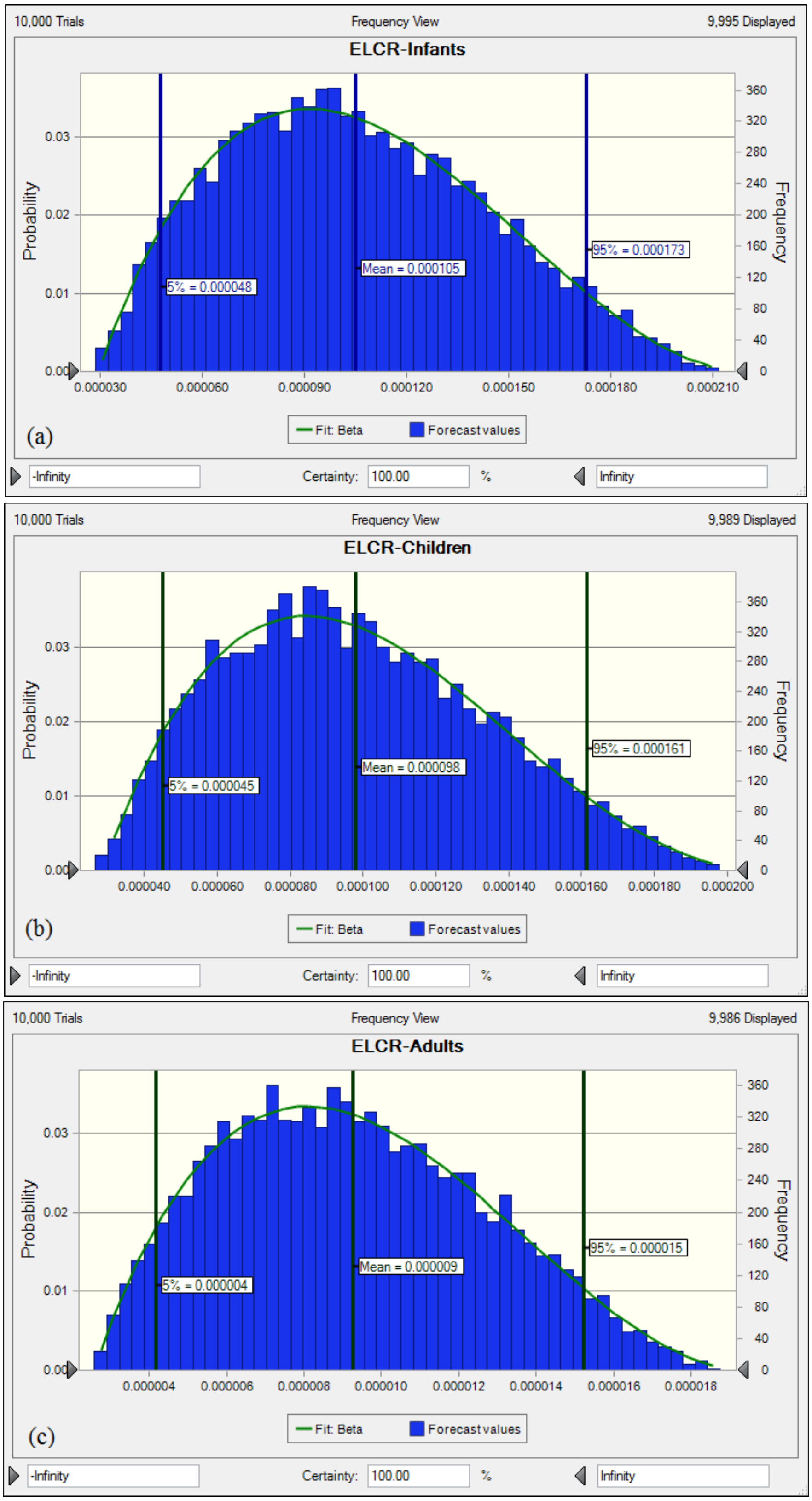

Figure 6: Histograms of the uncertainty analysis of nitrate ELCR in (a) infants, (b) children, and (c) adults

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Table 9: HQ and ELCR values for different age groups (infants, children, and adults)

Sampling point	Infants		Children		Adults	
	HQ	ELCR	HQ	ELCR	HQ	ELCR
Upper Sangan	0.217 ± 0.042	3.5E-05 ± 7E-06	0.203 ± 0.039	3.25E-05 ± 6.26E-06	0.077 ± 0.015	1.2E-05 ± 2.39E-06
Middle Sangan	0.918 ± 0.08	14.7E-05 ± 1.3E-05	0.860 ± 0.075	1.38E-04 ± 1.20E-05	0.328 ± 0.029	5.2E-05 ± 4.57E-06
Lower Sangan	0.608 ± 0.098	9.7E-05 ± 1.6E-05	0.570 ± 0.092	9.12E-05 ± 1.47E-05	0.217 ± 0.035	3.5E-05 ± 5.59E-06
Upper Keshar	0.663 ± 0.007	10.6E-05 ± 1E-06	0.622 ± 0.006	9.95E-05 ± 1.01E-06	0.237 ± 0.002	3.8E-05 ± 3.86E-07
Sulqan 1	0.980 ± 0.075	15.7E-05 ± 1.2E-05	0.919 ± 0.07	1.47E-04 ± 1.12E-05	0.350 ± 0.027	5.6E-05 ± 4.27E-06
Sulqan 2	0.579 ± 0.022	9.3E-05 ± 4E-06	0.543 ± 0.021	8.69E-05 ± 3.34E-06	0.207 ± 0.008	3.3E-05 ± 1.27E-06
Mean	0.661	10.6E-05	0.620	9.91E-05	0.236	3.8E-05

Discussion

The results of physicochemical parameters demonstrated that none of the parameters exceeded the permissible limits set in the guidelines for drinking water [27]. The results obtained in this study are similar to the study conducted by Farzin et al. [28] in the Kan River basin and the previous analysis of the Water and Wastewater Company of Tehran Province (Table 1).

According to the values of $IRWQI_{GC}$ and $IRWQI_{SC}$, most of the sampling sites in the Kan River basin were classified as having a "relatively good" water quality during the study period, and the rest were of medium or good quality. Furthermore, water quality status exhibited relatively minor seasonal variations; But generally, water quality from both surface and groundwater sources declined in summer. Decreasing the WQI and increasing the concentration of pollutants in summer in comparison with spring, may be due to reduced aquifer recharge and dilution of pollutants as a result of rising water temperature during summer. Alizadeh et al. examined the water quality of Kan and Karaj rivers based on three indicators: WQI, NSFWQI, and IRWQI. According to their findings, the water quality of the Kan and Karaj rivers according to NSFWQI index was in the range of poor and medium quality water, according to $IRWQI_{SC}$ index was in the range of very poor to relatively good quality water, and according to WQI index was in the range of good quality water. The results of the present study do not correspond to the study of Alizadeh et al. [29], since in this study, sampling was done from the tributaries of Kan River which have less pollution.

Due to the spearman's test results, the quality variations of the wells were not a function of the quality variations of the river. The findings of the current study are similar to those of Rostam Beik et al. who used the WQI to study the area of the Latian Dam in Tehran. The results of their research showed that there was no significant relationship between the surface and groundwater quality indices in the studied area [30]. However, the findings of this study are not in line with the results of the study by Givi et al. (2020). They used the WQI to investigate the relationship between surface and groundwater quality of the Jajrood River and concluded that there was a significant relationship between the surface and groundwater quality status [31].

Based on the spatial distribution maps, by moving in the direction of the slope to the south of the basin, the water quality decreases due to the accumulation of pollutants along the way. The water quality of the Upper Keshar has decreased due to the washing of loose surface soil and the increase of the surrounding gardens. Among groundwater resources, Sulqan 1 well was of lower quality, and the water of the Upper Keshar well was better than the others, which can be justified by the distance of the well from the residential areas and less accessibility. As a result, this area can be considered the most suitable place for digging future wells in the region.

Most of the inhabitants in the rural areas of Kan district rely mainly on agriculture for their livelihood. As a result, a variety of nitrogen fertilizers and agricultural chemicals are used in

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agricultural practices to improve farm yields. Nitrogen fertilizers can be a considerable source of nitrate pollution in rural areas. Moreover, in rural areas, there are usually no facilities for wastewater collection. In such areas, absorbing wells are usually the primary means of collecting wastewater which can lead to groundwater contamination [6]. Comparing the present study results with the previous results of the Water and Wastewater Company, it can be concluded that the concentration of nitrate in the groundwater resources of the study area has not changed considerably in the recent years and is still relatively far from the maximum allowed by the standards (50 mg/L). As a result, despite the existence of residential areas and gardens near the drinking water wells, anthropogenic activities, such as agricultural and domestic wastewater have not significantly affected the region's groundwater quality. However, it needs more attention to prevent water contamination in the coming years.

The results of the health risk assessment indicated that the carcinogenic and non-carcinogenic risks of nitrate for the three exposed groups varied in order: infants > children > adults.

The ELCR value for the infants was more than the recommended standard (10^{-4}). Hence, infants had a higher adverse health effect through ingestion of drinking water.

The Monte Carlo simulation for HQ indicated that the 95th percentile for infants and children was greater than 1, indicating potential adverse health effects for the infants and children. Furthermore, ELCR showed that the highest carcinogenic risks ($> 1 \times 10^{-4}$) were observed in the infants and children groups.

Vaiphei et al. evaluated the nitrate health risk assessment of groundwater in India. HQ values of nitrate for infants are 1.31E + 01, children 1.23E + 01, and adults 4.68E + 00, respectively. Consequently, 68.97% of infants and 72.41% of children are at risk of non-carcinogenic ingestion of nitrate contaminated groundwater [32].

Conclusion

In this case study, the IRWQI was implemented to investigate the Kan River basin surface and groundwater quality, and to assess the nitrate health risk of the drinking water wells. Based on the quality index, surface and groundwater resources of Sangan, Sulqan, and Upper Keshar were classified into three groups of medium quality, relatively good, and good, during the study period. Moreover, the water quality presented few seasonal variations, with the highest IRWQI values in spring. All of the physical, chemical, and microbial parameters complied with the Iran regulatory standards for drinking water, and as a result, the water of the wells was suitable for drinking purposes. Furthermore, according to the statistical and spatial analysis, the quality variations of wells in the study area were not a function of the quality variations of Kan River. Mean HQ results indicated that there was no non-carcinogenic risk for the exposed groups and based on mean ELCR values, there might be a risk of health effects for the infants, which require further studies.

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Conflict of interest

There is no conflict of interest to declare.

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