The University of Tehran Press

Pollution

https://jpoll.ut.ac.ir/

Print ISSN: 2383-451X
Online ISSN: 2383-4501

Hydrogeochemistry and Health Risk Assessment of Nitrate and Fluoride in Groundwater of Gorgan and Kordkuy, Iran

Mojtaba Ghareh Mahmoodlu[1]✉ | **Ali Radkani**[2]

1. Water and Watershed Engineering Department, Agriculture and Natural Resources Faculty, Gonbad Kavous University, Gonbad Kavous, Iran
2. Watershed Management Department, Rangeland and Watershed Management Faculty, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran

Article Info

Article type:
Research Article

Article history:
Received: 15 July 2024
Revised: 5 November 2024
Accepted: 16 January 2025

Keywords:
Drinking Water
Salinity
Hazard Quotient
Environmental Contaminants

ABSTRACT

This study was conducted to assess hydrogeochemistry together with the non-carcinogenic health risk of nitrate and fluoride in groundwater of Gorgan and Kordkuy cities in the north of Alborz mountain belt. For this purpose, drinking water sources of these two cities were analyzed for hydrochemical characteristics including major ions, nitrate and fluoride. Results revealed that an increase in salinity of Kordkuy groundwater caused the various mixed and saline hydrochemical facies. Result of HFD and Gibbs diagrams revealed that rock-water interaction is chief contributing factor for release of ions into Gorgan groundwater. While, Kordkuy groundwater is more influenced by saline water that is originated from the subsurface layers. Human activities are the primary source of nitrate concentration in the Gorgan groundwater. In contrast, nitrate concentration of Kordkuy groundwater is more influenced by saline water. Results revealed that the hazard quotient (HQ) values of Gorgan drinking water samples for children are considerably higher than the permissible limit (HQ=1). In contrast, all HQ values of Kordkuy drinking water samples are below permissible limit and they don't cause adverse non-carcinogenic health risks for all age groups. Only three well in Kordkuy that their HQ of F- values are larger than the permissible limit for children. For the rest of drinking water samples, the HQ values of F- in both cities are less than permissible limit for all three groups.

Cite this article: Ghareh Mahmoodlu, M., & Radkani, A. (2025). Hydrogeochemistry and Health Risk Assessment of Nitrate and Fluoride in Groundwater of Gorgan and Kordkuy, Iran. *Pollution*, 11(2), 411-424.
https://doi.org/10.22059/poll.2024.379439.2466

DOI: https://doi.org/10.22059/poll.2024.379439.2466

INTRODUCTION

Human life is highly dependent on natural resources. Groundwater is a valuable and the most common water source of drinking, agricultural, and industrial in semi-arid and arid regions like Iran. About one third of the world's population, especially in semi-arid and arid countries, depend on groundwater for drinking purposes due to the lack of precipitation and surface water (Muralidhara Reddy & Sunitha, 2020; Duvva at al., 2022; Kom et al., 2022).

Nowadays, the groundwater contamination is a serious concern for those in charge of drinking water supply. Rapid population growth, the excessive development of agriculture, various industrial activities, and the infiltration of raw and untreated domestic and agricultural sewage into the ground and finally groundwater sources are constantly exposed to contamination by all kinds of chemical, physical, and microbial pollutants. Based on the geographical location of Iran (situated in Eurasian desert belt) and the significant decrease in rainfall as well as the increase in excessive use of groundwater, the quality of these resources has decreased

---

*Corresponding Author Email: *m.g.mahmoodlu@gmail.com*

considerably (Piraste et al., 2018).

Currently, nitrate is the most widespread contaminant in surface water and groundwater (WHO, 2016; Craswell et al., 2021), and its increased concentration leads to restrictions on use of water resources. Based on the World Health Organization (WHO) standards for the drinking water quality, the nitrate limit is 50 mg/liter (WHO, 2016). Nitrate is very soluble and is not chemically bound to soil particles. Hence, it is susceptible to leach through the soil and into groundwater and thus deteriorate both surface and groundwater quality. Over the last few decades, the overconsumption of N fertilizers has caused in groundwater contamination which has become a main environmental concern (Haghbin et al., 2021) and that N fertilizer amount applied in the agriculture section is strongly associated to high nitrate concentrations in groundwater.

Previous literature has revealed that agriculture activities contribute about to 60% of groundwater nitrate contamination globally (Shukla & Saxena, 2018; Rawat et al., 2022). Moreover, in the urban area, nitrate sources comprise leaky underground tunnel or pipe system which is used for transferring sewage from commercial buildings and houses, industrial spills, leaching from landfills, runoff from roads, use of fertilizer for lawns in parks, infiltration from the polluted river, septic tanks, and sewage disposal (Yifru et al., 2022). The nitrate surplus in drinking water and continuous consumption of nitrate leads to a variety of adverse health effects on newborn (like methemoglobinemia or blue baby syndrome) and also different ages of peoples (Rawat et al., 2022).

Fluoride is one of the less discussed and most electronegative elements in groundwater. The source of fluoride adulteration in water sources is mainly geogenic however, in some instances anthropogenic sources like industrial inputs may cause a health threat (Xiao et al., 2022; Gharekhani et al., 2023). Since fluoride concentration is mainly influenced by geological formations containing fluorite, apatite, amphibole, and micas minerals, its concentration within groundwater is greater than surface waters (Aghapour et al., 2018). The existence of fluoride in drinking water can cause many complications in consumers. It is an essential micronutrient for the body that has significant effects on human health (e.g., tooth and bone growth), especially through drinking water (Ghosh et al., 2013; Rehman et al., 2022). The fluoride concentration in drinking water is like a double-edged sword, its deficiency and/or increase in the long term leads to the spread of oral and dental diseases, and bone disorders. Fluoride at low concentration (0.5-1.2 mg/L) is a vital anion for dental health (Horowitz, 2000). However, the fluoride concentration in groundwater in many countries is more than permissible limit (1.2 mg/L), which poses a health threat to millions of people around the world. Literature shows that around 200 million people from among 25 countries are suffering from fluorosis as a result of fluoride-rich drinking water consumption (Ayoob & Gupta, 2006; Yousefi at al., 2019). In Iran, the existence of this disease has been reported in cities such as Maku, Bazargan, Poldasht, Bushehr, Borazjan, Bandar Abbas, Damghan, Kerman and some parts of central Iran (Mohseni Sajadi et al., 2011; Mahmoodlu et al., 2023).

A human health risk assessment is generally a process to evaluate the feasibility and nature of adverse human health impacts who may possibly be exposed to substances in contaminated environmental media, now or in the future. Basically, risk assessment is a four-steps procedure containing (1) hazard identification, (2) dose-respond, (3) exposure analysis, and (4) risk characterization. Non-carcinogenic risk assessments are generally based on the use of the hazard quotient (HQ) which estimates as a ratio of the measured dose of a contaminant to the reference dose (Aghapour et al., 2018; Peng et al., 2022). Assessing non-carcinogenic health risks because of drinking fluoride and/or nitrate-contaminated groundwater is important to ensure a safe drinking water supply (Giri et al., 2021; Bazeli et al., 2022; Duvva et al., 2022). Over the last decades, several countries tackled the topic of the non-carcinogenic health risk assessment of fluoride and nitrate-contaminated groundwater (Aghapour et al., 2018; Giri et al., 2021; Bazeli et al., 2022; Duvva et al., 2022; Kom et al., 2022; Igibah et al., 2022).

The average consumption of N fertilizer in the agriculture section for Golestan province is higher than the average of Iran. Hence, nitrate contamination in groundwater which has become a main environmental concern in this province. Moreover, previous study by Mahmoodlu et al. ,(2023) revealed that fluoride concentration in groundwater is associated with spatial distribution of loess formation in Golestan province.

So far, nitrate and fluoride health risk assessment have been extensively performed in some part of in Iran (Azhdarpoor et al., 2019; Yousefi et al., 2019; Golaki et al., 2022; Bazeli et al., 2022; Qasemi et al., 2022). However, literature currently lacks information on nitrate and fluoride health risk assessment in Golestan province. Therefore, the present study was conducted to determine and compare nitrate and fluoride health risk assessment in two major cities of Gorgan and Kordkuy in Golestan province by applying an effectual probabilistic technique (USEPA, 1989) and various hydrogeochemical methods.

MATERIALS AND METHODS

Study of area

In this research, two major cities of Gorgan and Kordkuy were selected as study regions. Gorgan with an approximate area of 1615 square kilometers and a population of nearly half a million people is as a capital city of Golestan Province (Fig. 1). Goran lies about 30 km away from the Caspian Sea and 400 km to the north east of Tehran. It is situated on alluvial fan that is mostly influenced by sedimentation of Ziarat River. Second city, Kordkuy, with a population of around 71,000 people is placed in the SE of Caspian Sea and the west of Gorgan City (Fig. 1). Similar to Gorgan City, it is located on alluvial fan that is influenced by sedimentation of Ghazi Mahalleh River, so that the altitude diminishes from south to north (Ghezelsofloo et al., 2021).

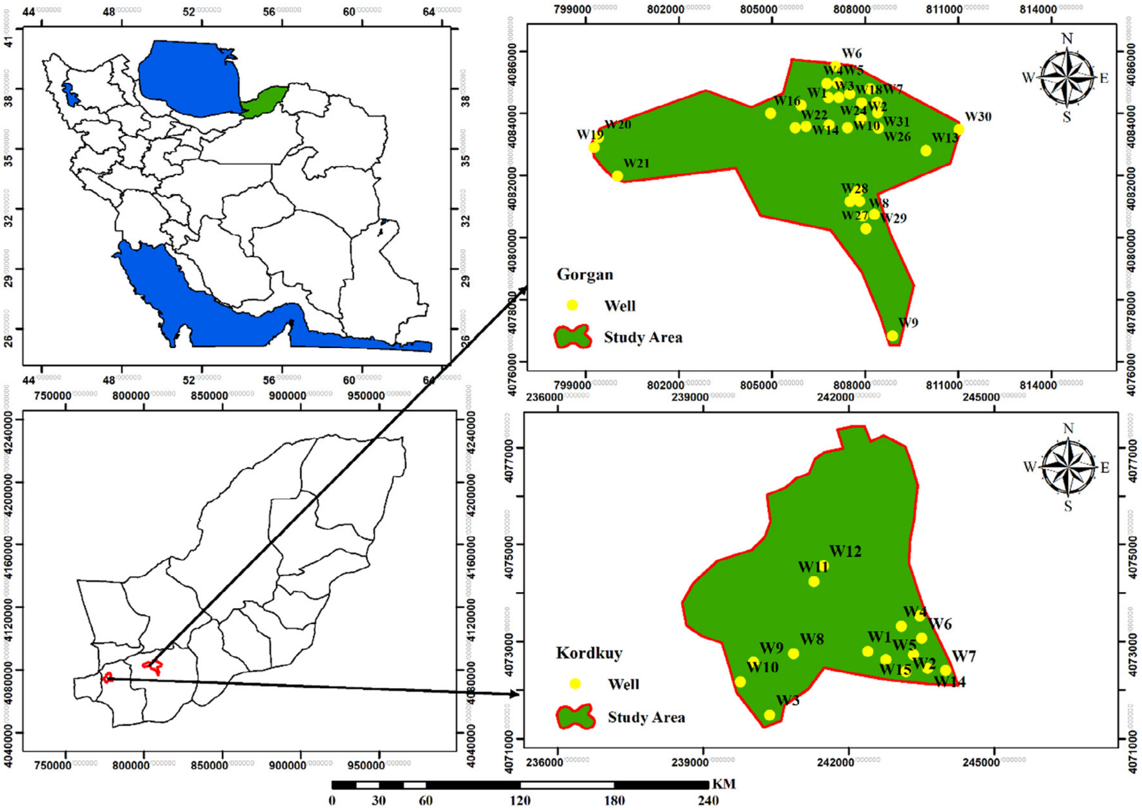

Fig. 1. Study area location in Golestan Province and Iran

From a geological perspective, both cities situated in East Alborz mountain and Gorgan-Rasht zone. Geological formations of study areas from the oldest to youngest comprise the green schist of Gorgan (Ordovician), Lar Formation contains limestone and brownish dolomite (upper Jurassic), alluvial sediments consist of sand, silt and peat with Quaternary age, and loess deposits contains silt-sized sediment with Quaternary that is mainly distributed in Gorgan City (Ghezelsofloo et al., 2021).

Chemical analysis

For hydrogeochemistry and nitrate and fluoride health risk assessment, 15 and 31 drinking water samples of Kordkuy and Gorgan cities, respectively, were collected using sterile-polyethylene bottles. The sampling bottles were kept at 4°C and transported to the Water and Wastewater Laboratory of Golestan Province for further laboratory analysis. The drinking water samples are analyzed using American Public Health Association procedure (APHA, 2012) and proposed precautions are taken to avoid pollution from any other sources (Muralidhara Reddy & Sunitha 2020; Ghezelsofloo et al., 2021).

A number of parameters such as temperature (T), pH value, total dissolved solids (TDS), and electrical conductivity (EC) were determined in the field using a calibrated portable multi-parameter digital meter (HQ30d, HACH). The water samples were analyzed for bicarbonate (HCO_3^-) using acid titration method with methyl orange as indicator; chloride (Cl^-) using titration with silver nitrate ($AgNO_3$) as titrant. The concentration of NO_3^- and SO_4^{2-} was estimated by spectrophotometer method (HACH, DR5000). F^- concentration in water samples was measured by ion chromatograph (Metrohm 861 advanced compact) using an appropriate column. Two major cation of Ca^{2+} and Mg^{2+} were estimated using the titration method. Flame photometer was used to analyze Na^+ and K^+ (Muralidhara Reddy & Sunitha, 2020; Ghezelsofloo et al., 2021).

Health risk assessment (HRA)

As explained above a HRA is a process used to assess the probability and nature of the adverse health effects in humans caused by exposure to environmental contaminants in a variety of media (USEPA, 2022; Zhang et al., 2022). In this study, the concentration of NO_3^- and F^- in drinking water samples of Kordkuy and Gorgan cities were selected as the parameters for investigation of human HRA (HHRA). Based on USEPA (1989) classification, toxic substances are classified in two groups of carcinogenic and non-carcinogenic, whereas NO_3^- and F^- are listed under the non-carcinogen group. Literature shows the oral ingestion of NO_3^- and F^- is the critical exposure path. Hence, current study evaluated the HHRA that is posed by NO_3^- and F^- via oral pathway (drinking contaminated water) for three different age groups: children (2-16 years), men and women (≥16 years). Average daily dosage (ADD) of NO_3^- and F^- ingested through drinking of water in the study area was estimated by the below equation (Kom et al. 2022; Muralidhara Reddy & Sunitha, 2020):

$$\mathrm{ADD} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{F} \times \mathrm{ED}}{\mathrm{ABW} \times \mathrm{AET}} \tag{1}$$

where C represents the concentration of NO_3^- and F^- in groundwater (drinking water) in mg/L, IR denotes the ingestion rate (0.3 L/day for infants, 0.78 L/day for children, 2.5 L/day for adults), F indicates the exposure frequency (365 days/year for adults, children, and infants), ED denotes the exposure duration (<1 year for infants, 12 years for children, and 64 years for adults), ABW represents the average body weight (16.9 kg for infants, 18.7 kg for children, and 57.5 kg for adults), and AET denotes the average exposure time (23,360 days for adults, 4380 days for children's and 365 days for infants).

The hazard quotient (HQ) of NO_3^- and F^- via oral intake can be estimated as follows (USEPA, 1989; Su et al., 2021; Kom et al., 2022)

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \tag{2}$$

where RfD referred as exposure dosage of NO_3^- and F- that is equal to 1.6 and 0.06 mg/kg/day, respectively (USEPA, 1989; Su et al., 2021; Kom et al., 2022).

RESULTS AND DISCUSSION

Physicochemical parameters of groundwater

The statistical data of physicochemical parameters of groundwater are given in Table 1. Results revealed that, the pH of drinking water sources ranges from 7.1-7.8 and 7.5- 7.9 for Gorgan and Kordkuy cites, respectively, representing slightly alkaline nature. As given in Table 1, Total Hardness (TH) in drinking water sources ranges 220.5- 528.5 mg/L and 220.5-839 mg/L for Gorgan and Kordkuy cites, respectively representing hard (150-300 mg/L) to very hard (>300 mg/L) waters. Moreover, mean value of TH for both cities is less than permissible limit (500 mg/L)

EC varies from 507 to 1876 µmho/cm and 512 and 2642 µmho/cm for Gorgan and Kordkuy cites, respectively. Hence, salt concentration in both cities varies between low to a medium (Subba Rao et al., 2016; Muralidhara Reddy & Sunitha, 2020). However, salt concentration in Kordkuy drinking water sources due to saline water intrusion is slightly larger than for Gorgan City (Ghezelsofloo et al., 2021). Spatial variation of EC showed that the EC value increases in the direction of the groundwater flow of Gorgan Aquifer and towards the north of the region (Fig. 2). In contrast with Gorgan Aquifer, the amount of EC has increased significantly in the southeastern part of the region where there are more water wells (Fig. 2).

TDS range 292 to 1090 mg/L and 285 to 1506 mg/L for Gorgan and Kordkuy cites, respectively. Expect one sample for Kordkuy City, all the samples are below the permissible limit of TDS. Na^+ concentration in groundwater of both cities ranges between 13 to 220 mg/L. While maximum value of K^+ concentration in Gorgan groundwater (7.3 mg/L) is almost two time larger than Kordkuy City (3.6 mg/L). Results reveal also that a mean value of Ca^{2+} concentration in Kordkuy groundwater is larger than Gorgan groundwater. In contract, Mg^{2+}

Table 1. Descriptive statistics of physicochemical parameters of groundwater together with guideline values of WHO (2011) and ISIRI 1053 in the study regions.

City	Statistical Parameters	K	Na	Mg	Ca	HCO_3	SO_4	Cl	NO_3	F	TDS	EC	TH	pH
Gorgan	Mean	3.4	51.2	39.2	96.9	328.2	92.1	87.4	37.1	0.21	602	1039	406.6	7.3
	Minimum	1.2	13.3	19.7	55.4	210.0	49.4	16.6	4.2	0.08	292	507	220.5	7.1
	Maximum	7.3	221.5	54.8	123	430	128.6	388.5	72.5	0.38	1090	1876	528.5	7.8
	Sample Variance	2.2	1279	83.4	360	3589	454	3909	349	0.003	22651	68713	6339	0.03
Kordkuy	Mean	1.9	81.3	28.8	108.5	251.5	17.2	236.9	5.28	0.34	638.9	1143	387.8	7.7
	Minimum	0.9	13.8	15	63.2	210	14.9	21.8	1.76	0.12	285.5	512	220.5	7.5
	Maximum	3.6	227.7	61	234.7	272	18.6	806	13.7	0.55	1506	2642	839	7. 9
	Sample Variance	0.58	3693	202.7	2367	287	1.7	44763	15.2	0.019	110283	350618	32163	0.01
	WHO (MPL)	200	50-200	50-150	75-200	30-150	150-400	200-600	50	0.6-1.5	500-1500	500-1500	500	6.5-8.5
	ISIRI 1053 accept limit		200	-	-	-	400	400	50	1.5	1500	1500	500	6.5-9.0

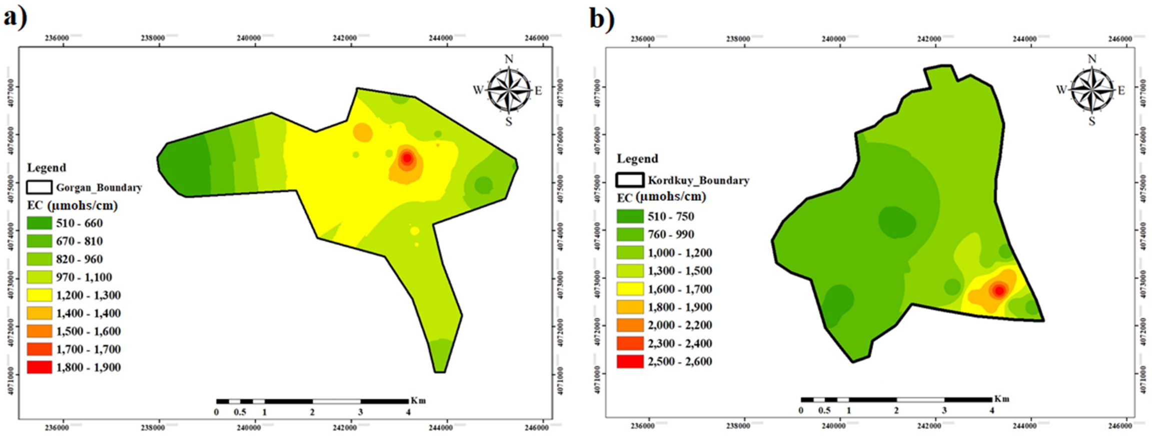

Fig. 2. Spatial variation of EC in Gorgan (a) and Kordkuy (b) aquifers

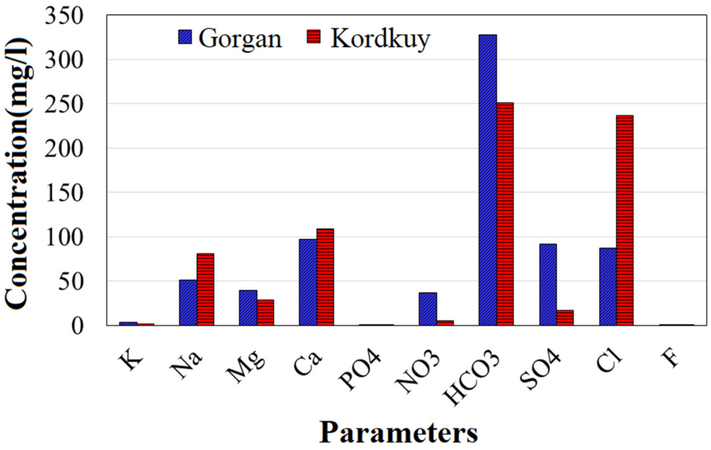

Fig. 3. Variations of chemical parameters in groundwater of Gorgan and Kordkuy cities.

concentration

in Kordkuy groundwater less than Gorgan groundwater. Recharge of Gorgan aquifer by dolomitic formations can be main reason increasing Mg^{2+} concentration in Gorgan drinking water sources. HCO_3^- concentration in Gorgan and Kordkuy drinking water sources ranges from 210 to 430 mg/L and 210-430 mg/L, respectively. Variations of SO_4^{2-} and Cl^- concentrations, that are directly associated with salinity of water sources, are different in two regions. SO_4^{2-} concentration in Gorgan groundwater varies between 49.4 to 128.6 mg/L, while it ranges from 14.9 to 18.6 mg/L in Kordkuy groundwater. A mean value of Cl^- in Kordkuy groundwater is almost three times larger than Gorgan groundwater. This can be due to saline water (originated from lower layers) intrusion into aquifer. Nitrate concentration in Gorgan and Kordkuy drinking water sources ranges from 4.2 to 72.5 mg/L and 1.76 to 13.7 mg/L. In contrast, fluoride concentration ranges from.08-0.38 and 0.12-0.55 mg/L for Gorgan and Kordkuy cites, respectively.

A quick comparison of major ions in two cities of Gorgan and Kordkuy showed that salinity parameters of Cl and Na in Kordkuy city groundwater are larger than for Gorgan (Fig. 3). In contrast, HCO_3^- and NO_3^- in groundwater of Gorgan city is much higher than for Kordkuy.

Factors governing groundwater chemistry

Gibb's diagram was depicted to define the major factor controlling the chemistry of Gorgan

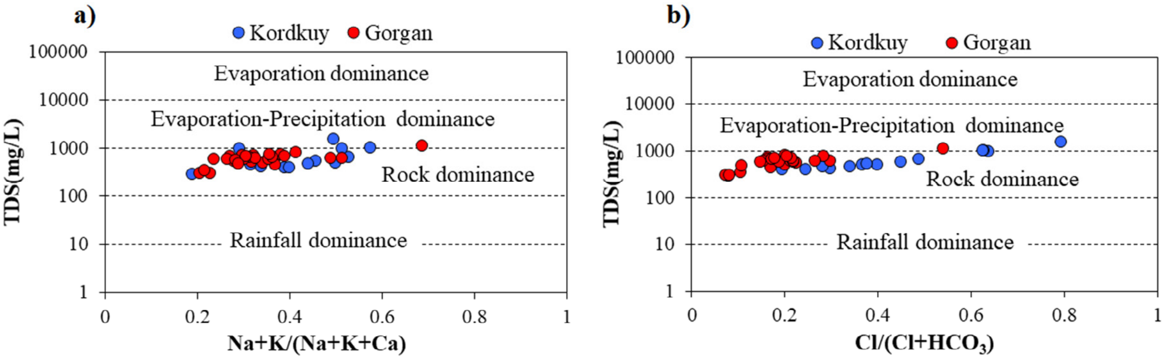

Fig. 4. Gibbs ratio for cations (a), and Gibbs ratio for anions (b) of water sources in study regions.

and Kordkuy groundwater (Fig. 4 b, c). Results based on the ratio for cations ($Na^+ + K^+/Na^+ + K^+ + Ca^{2+}$) and anion ($Cl^-/Cl^- + HCO_3^-$) revealed that almost all groundwater samples are distributed in rock dominance zone representing rock weathering and dissolution of minerals from the source rock are main contributing factors for release of ions into groundwater (Muralidhara Reddy & Sunitha, 2020).

In contrast with Gorgan water sources, rock dominance together with evaporation-precipitation dominance are two factors controlling water chemistry into Kordkuy groundwater. Results also showed that the mixing of saline and fresh waters has occurred in a number of drinking water wells. Furthermore, according to the distribution pattern of drinking water wells in Gibbs diagram (Fig. 4 b, c), that there is a tendency to alter the chemistry of groundwater and reach seawater composition (Ghezelsofloo et al., 2021).

Type and facies of groundwater

In current study, the Piper trilinear diagram was plotted to identify the hydrogeochemical facies and water types (Fig. 5a). As shown in the diamond part of piper, Gorgan water samples are distributed in three parts (facies) A, B, and C representing Ca-Mg-HCO_3, Ca-Mg-SO_4-Cl, and Na-Cl-SO_4, respectively. However, dominate facies of Gorgan groundwater is Ca-Mg-HCO_3. Contrary to Gorgan groundwater facies, Kordkuy water samples are divided into two groups (A and B). Results revealed that a large number of samples are distributed in zone B representing Ca-Mg-SO_4-Cl facies (mixed type). This is clearly shown in the triangular diagram of cations, where the most of the Kordkuy water samples are placed in the center of the triangle. Furthermore, based on triangular diagram of cations, Kordkuy water samples have tendency to reach seawater composition by an increase in Cl^- concentration.

The hydrochemical facies evolution diagram (HFE-Diagram) as a complex and an alternative graphical representation was used to identify the hydrochemical facies as well as the interpretation of saline water intrusion processes (Giménez-Forcada, 2010; Giménez-Forcada 2019; Moorthy et al., 2024). HFE-Diagram analysis of hydrochemical facies revealed that seven facies including Ca-HCO_3, Ca-Cl, MixCa-Cl, MixNa-Cl, Ca-MixHCO_3, MixCa-HCO_3, and MixCa-MixCl (Fig. 5b and c). Results also showed that in about 86.7% of the Kordkuy drinking water wells, saline water (originated from subsurface layers) intrusion has occurred and only 13.3% of drinking water wells still have fresh water. The diversity of hydrogeochemical facies in the water resources of Gorgan city is less than for Kordkuy city the water resources. So that, the number of hydrogeochemical facies in the groundwater of Gorgan city has diminished to five types of MixCa-HCO_3, Ca-HCO_3, Ca-MixHCO_3, Na-Cl, and MixCa-MixHCO_3. Furthermore, in the Gorgan drinking water wells, saline water has intruded up to 51%. However, this is about 35.7% less than for Kordkuy drinking water wells.

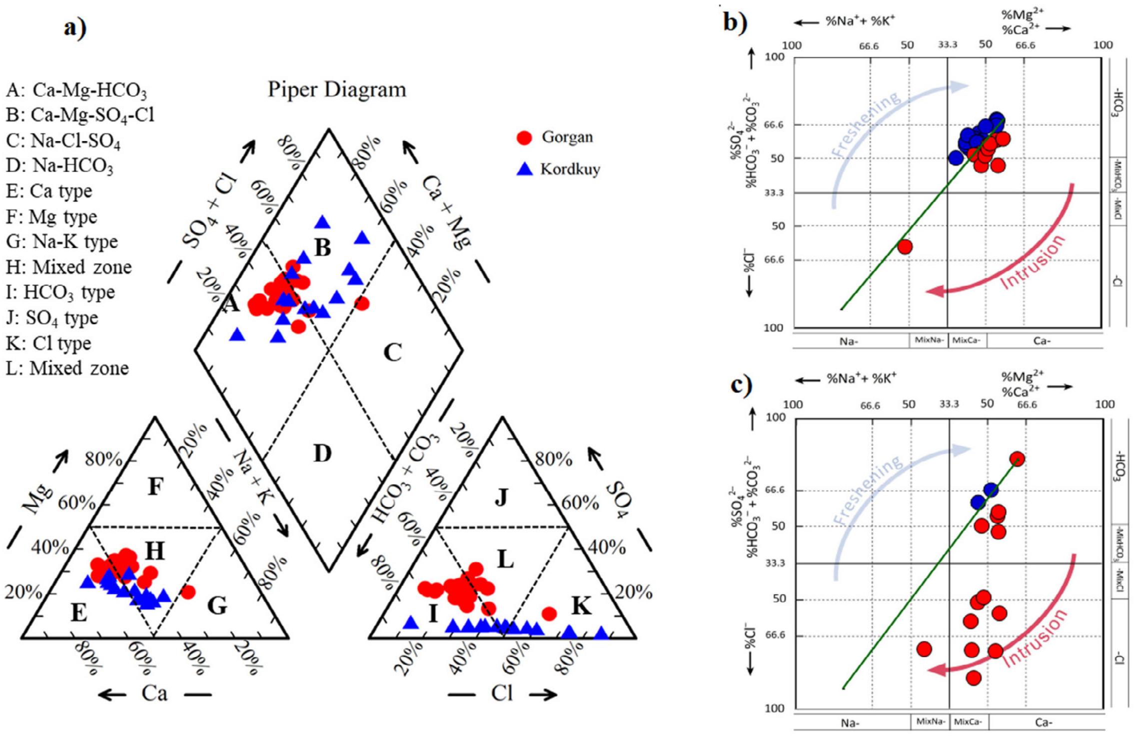

Fig. 5. Piper diagram (a), together with HFE diagram of groundwater of study regions; Gorgan (b) and Kordkoy (c).

Source contributions of dissolved solutes

As given in Table 1, NO_3^- concentration in the Gorgan drinking water samples vary in an extensive range from 4.2 to 72.5 mg/L than that in the Kordkuy groundwater (1.76 to 13.7 mg/L). Also, the average value of NO_3^- concentrations in Gorgan groundwater (37.1 mg/L) is much larger than that in Kordkuy groundwater (5.28 mg/L). To identify the source of NO_3^- concentration in the Gorgan and Kordkuy groundwater, the plot of the Cl^-/Na^+ molar ratios versus NO_3^-/Na^+ molar ratios was depicted. The relatively high NO_3^- concentration in the Gorgan drinking water samples is considered to be caused by human activities such as untreated or partly treated urban wastewater together with agricultural practices and septic tank leakage. While all Kordkuy drinking water samples influenced by seawater was suggested by Fig. 6. Several Gorgan groundwater wells also fell in seawater zone (Fig. 6). This is because of saline water intrusion originated from sediments containing saline water (tapped saline water and /or fossil) under the Gorgan freshwater aquifer.

Non-carcinogenic health risk of NO_3^- and F^-

In the current, to assess the non-carcinogenic health risk of NO_3^- and F^- for woman, men, and children the methodology proposed by United States Environment Protection Agency (USEPA) was used. Results showed that hazard quotient (HQ) of NO_3^- in the Gorgan City ranges between 0.081 and 1.393 (woman), 0.067 to 1.161 (men), and 0.181 to 3.123 (children). While, HQ values Kordkuy drinking water samples varies between 0.034 to 0.263 (woman), 0.028 to 0.220 (men), and 0.076 to 0.591 (children). Results revealed that the HQ values of Gorgan drinking water samples in some cases are greater than the permissible limit (HQ>1). Furthermore, in majority of drinking water wells (around 77.4%), the HQ values for children are considerably higher than the permissible limit (Fig. 7). This may cause adverse non-carcinogenic health risks. The results also showed that after children, women are more exposed to the health risks of drinking water with high nitrate content.

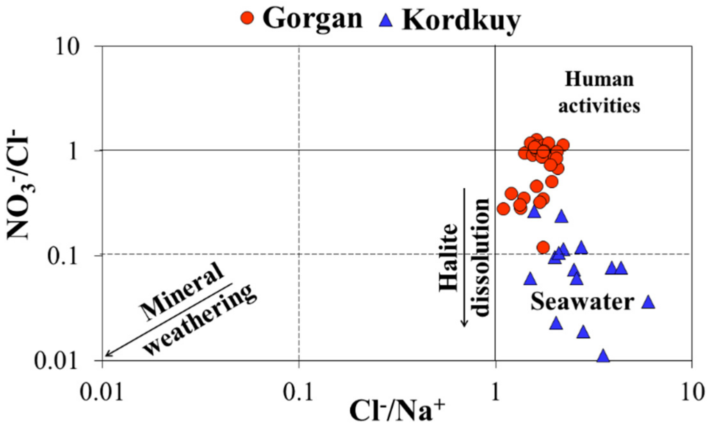

Fig. 6. Plot of the Cl^-/Na^+ molar ratios versus NO_3^-/Na^+ molar ratios for Gorgan (Red circle) and Kordkuy (blue triangle) drinking water samples

Table 2. Non-carcinogenic health risk assessment of NO_3^- in Gorgan and Kordkuy groundwater by Hazard Quotient (HQ)

Statistical Parameters	Gorgan HQ_{NO3}			Kordkuy HQ_{NO3}		
	Woman	Men	Children	Woman	Men	Children
Maximum	1.393	1.161	3.123	0.263	0.220	0.591
Minimum	0.081	0.067	0.181	0.034	0.028	0.076
Mean	0.714	0.595	1.601	0.102	0.085	0.228
Variance	0.129	0.089	0.648	0.006	0.004	0.028

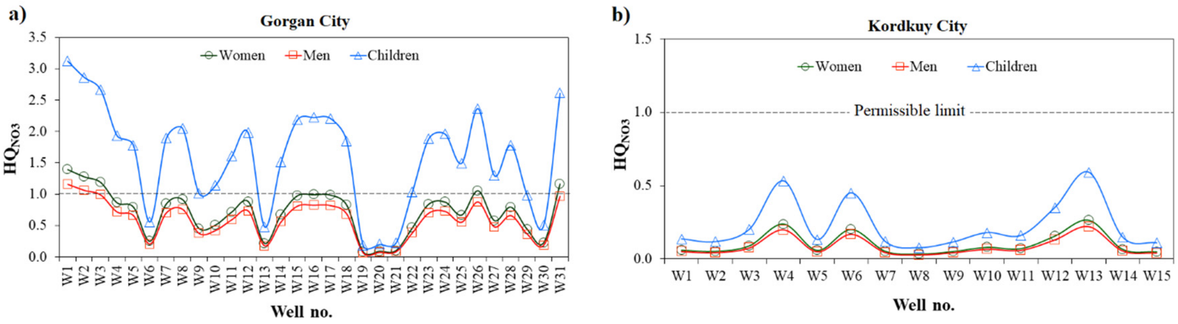

Fig. 7. Variation of hazard quotient (HQ) of NO_3^- for women, men, and children in the Gorgan and Kordkuy groundwater

In contrast, all HQ values of Kordkuy drinking water samples are below permissible limit (HQ <1) and they don't cause adverse non-carcinogenic health risks for any age groups (e.g., women, men, children). However, the HQ values for the children are much larger than for women and men.

Spatial variation of the HQ of NO_3^- in Gorgan aquifer (Fig. 8a, b, c) showed that the HQ of NO_3^- increases in the direction of the groundwater flow of Gorgan Aquifer and towards the north of the region which is consistent with the urban old texture, where the distribution of drinking water wells in this region is more than in other parts of the city. This results are consistent with the salinity (EC) variations in the Gorgan Aquifer. Spatial variation of the HQ of NO_3^- in Kordkuy Aquifer (Fig. 8e, f, g) revealed that the HQ of NO_3^- in the east region of aquifer is higher than other parts. An excessive pumping of groundwater and subsequently intrusion of saline water originated from sediments containing saline water together with the infiltration of domestic and/or municipal wastewater are two important factors in increasing the amount of

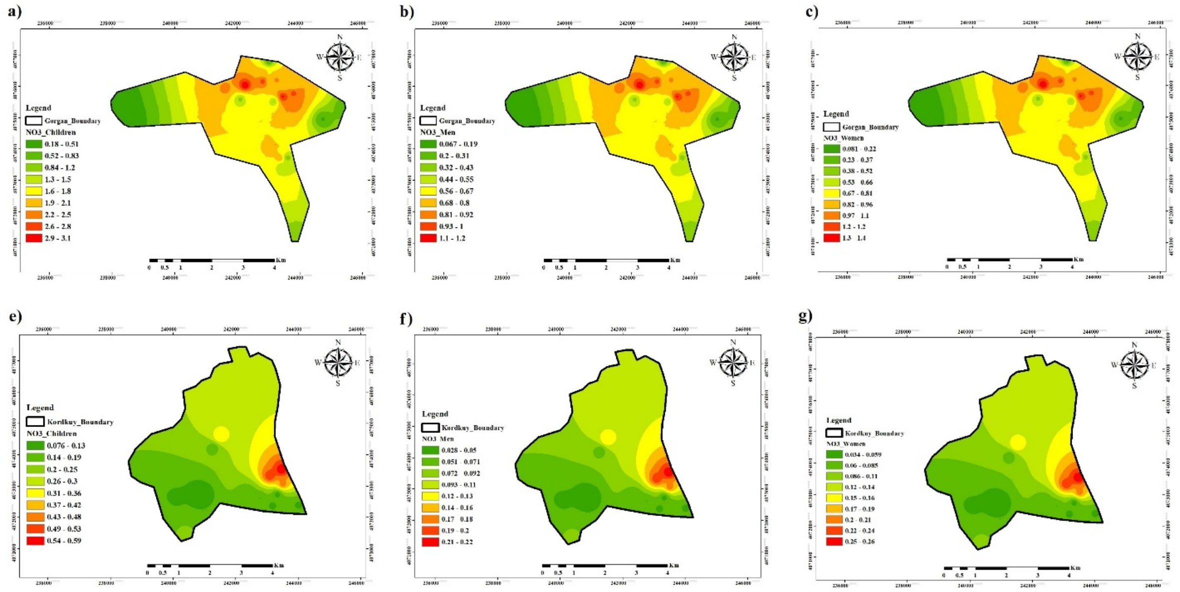

Fig. 8. Spatial variation of the HQ of NO_3^- in Gorgan (a, b, c) and Kordkuy (e, f, g) aquifers

Table 3. Non-carcinogenic health risk assessment of fluoride in Gorgan and Kordkuy groundwater by Hazard Quotient (HQ)

Statistical Parameters	Gorgan HQ_{F^-}			Kordkuy HQ_{F^-}		
	Woman	Men	Children	Woman	Men	Children
Max	0.193	0.160	0.432	0.282	0.235	0.632
Min	0.041	0.034	0.093	0.062	0.051	0.138
Mean	0.106	0.088	0.239	0.173	0.144	0.387
Variance	0.0007	0.0005	0.0036	0.0050	0.0034	0.0250

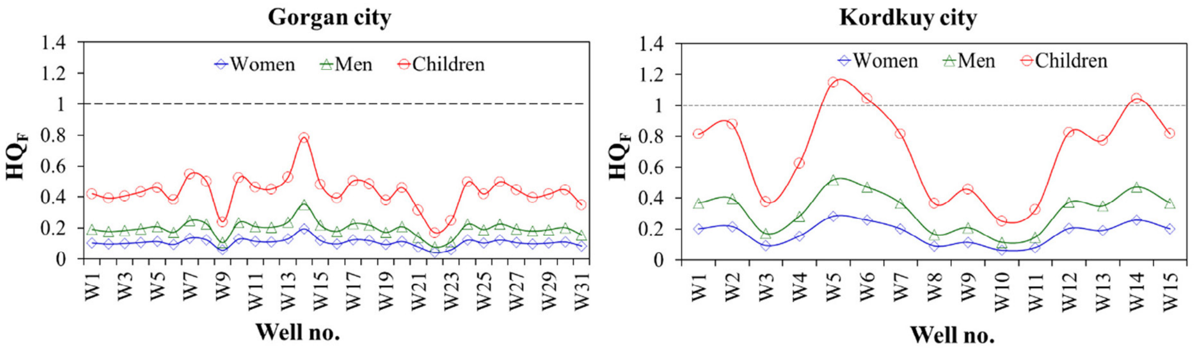

Fig. 9. Variation of hazard quotient (HQ) of F^- for women, men, and children in the Gorgan and Kordkuy groundwater

nitrates and subsequently increasing the hazard quotient (HQ), especially for children.

As given in Table 3, the HQ of F^- in the Gorgan City ranges between 0.041 and 0.193 (woman), 0.034 to 0.160 (men), and 0.093 to 0.432 (children). While, HQ of F^- values in Kordkuy drinking water samples varies between 0.062 to 0.282 (woman), 0.051 to 0.235 (men), and 0.138 to 0.632 (children). Only three well in Kordkuy that their HQ values are larger than the permissible limit (HQ>1) for children (Fig. 9). In the rest of drinking water samples, the HQ values of F^- in both cities are less than permissible limit (HQ<1) for all three groups. Hence, Gorgan and Kordkuy groundwater water samples are safe and they don't cause adverse non-

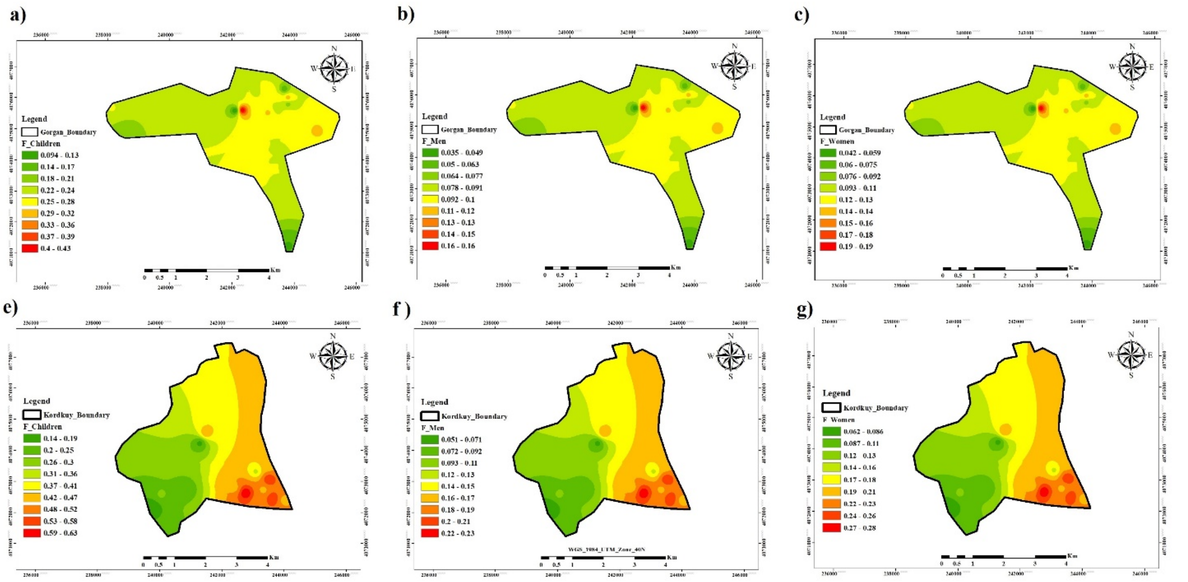

Fig. 10. Spatial variation of the HQ of F^- in Gorgan (a, b, c) and Kordkuy (e, f, g) aquifers

carcinogenic health risks for any age groups (Fig. 9).

Spatial variation of the HQ of F^- in Gorgan (Fig. 10 a, b, c) showed that the HQ of F^- in the urban old texture especially in well number 14 is higher than other place. But in the Kordkuy City, the highest value of the HQ of F^- is related to the southeast of the study area, where the highest amount of groundwater is extracted by drinking water wells. Previous study confirmed that intrusion of saline water into freshwater is the main reason for an increase in groundwater fluoride concentration and subsequently an increase in HQ of F^- in the southeast of the study area (Ghezelsofloo et al., 2021).

CONCLUSIONS

This study was conducted to assess hydrogeochemistry and health risk assessment of nitrate and fluoride in groundwater of Gorgan and Kordkuy, Iran. Hydrochemical characteristics of water samples revealed that there is a tendency to alter the groundwater chemistry and reach seawater composition for the Kordkuy water samples due to saline water intrusion. Also, human activities are responsible for the relatively high nitrate concentration in the Gorgan drinking water samples. While, saline water (tapped saline water and /or fossil) intrusion into groundwater is the main source of nitrate in Kordkuy aquifer.

In Gorgan Aquifer, the nitrate HQ increases in the of groundwater flow direction where is consistent with the urban old texture. The HQ values for children are significantly higher than the permissible limit (HQ=1) that may cause adverse non-carcinogenic health risks. Furthermore, women are more exposed to the health risks of drinking water with high nitrate content. In contrast, all HQ values of Kordkuy drinking water samples are below permissible limit. There are no adverse non-carcinogenic health risks for any age groups. Since the nitrate concentration in Gorgan city groundwater is on the threshold of the permissible limit; reducing the nitrate concentration using conventional methods (such as reverse osmosis and ion exchange) should be one of the priorities of Gorgan Water and Wastewater Company. Otherwise, the continuous consumption of Gorgan drinking water will increase the possibility of some blood problems especially in babies, digestive diseases, and even cancer in Gorgan city.

The HQ values of F revealed that except three wells in Kordkuy that their HQ values are larger than the permissible limit for children, the HQ values of F^- in both cities are less than permissible limit for all three groups. Hence, Gorgan and Kordkuy groundwater water samples are safe and they don't cause adverse non-carcinogenic health risks for any age groups. However, the amount of fluoride in drinking water in two cities was less than desirable and required fluorination.

AUTHORS' CONTRIBUTIONS

Mojtaba G. Mahmoodlu: supervision, writing the main draft, revising, editing the manuscript, conceptualization, chemical analyses, and interpretation. Ali Radkani: collecting the data, visualization, interpretation, chemical analyses, and conceptualization.

ACKNOWLEDGMENTS

The authors would like thank to Gonbad Kavous University and Golestan Province Water and Wastewater for supporting this research.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest in this manuscript.

LIFE SCIENCE REPORT

No life science threat was practiced in this research.

REFERENCES

Aghapour, S., Bina B., Tarrahi, M.J., Amiri, F., & Ebrahimi, A. (2018). Distribution and health risk assessment of natural fluoride of drinking groundwater resources of Isfahan, Iran, using GIS. Environ. Monit. Assess., 190; 1-13.

APHA, Standard Methods for the Examination of Water and Wastewater, 22nd ed. American Public Health Association, New York, 2012.

Ayoob, S., & Gupta, A.K. (2006). Fluoride in drinking water: a review on the status and stress effects. Critical Reviews in Environ. Sci. Technol., 36(6); 433-487.

Azhdarpoor, A., Radfard, M., Pakdel, M., Abbasnia, A., Badeenezhad, A., Mohammadi, A.A., & Yousefi, M. (2019). Assessing fluoride and nitrate contaminants in drinking water resources and their health risk assessment in a semiarid region of southwest Iran. Desalin. Water Treat., 149; 43-51.

Bazeli, J., Ghalehaskar, S., Morovati, M., Soleimani, H., Masoumi, S., Rahmani, Sani. A., Saghi M.H., & Rastegar, A. (2022). Health risk assessment techniques to evaluate non-carcinogenic human health risk due to fluoride, nitrite and nitrate using Monte Carlo simulation and sensitivity analysis in Groundwater of Khaf County, Iran. Int. J. Environ. Anal. Chem., 102(8); 1793-1813.

Craswell, E. (2021). Fertilizers and nitrate pollution of surface and ground water: an increasingly pervasive global problem. SN Appl. Sci., 3(4), 518.

Duvva, L.K., Panga, K.K., Dhakate, R., & Himabindu, V. (2022). Health risk assessment of nitrate and fluoride toxicity in groundwater contamination in the semi-arid area of Medchal, South India. Appl. Water Sci., 12(1); 11.

Gharekhani, M., Nadiri, A.A., Khatibi, R., Nikoo, M.R., Barzegar, R., Sadeghfam, S., &

Moghaddam, A.A. (2023). Quantifying the groundwater total contamination risk using an inclusive multi-level modelling strategy. J. Environ. Manage., 332; p117287.

Ghezelsofloo, E., Raghimi, M., Mahmoodlu, M.G., Rahimi-Chakdel, A., & Khademi, S.M.S. (2021). Saltwater intrusion in drinking water wells of Kordkuy, Iran: an integrated quantitative and graphical study. Environ. Earth Sci., 80(16); p.520.

Ghosh, A., Mukherjee, K., Ghosh, S.K., & Saha, B. (2013). Sources and toxicity of fluoride in the environment. Res. Chem. Intermed., 39; 2881-2915.

Giménez-Forcada, E. (2010). Dynamic of sea water interface using hydrochemical facies evolution diagram. Groundwater, 48(2); 212-216.

Giménez-Forcada, E. (2019). Use of the Hydrochemical facies diagram (HFE-D) for the evaluation of salinization by seawater intrusion in the coastal Oropesa Plain: comparative analysis with the coastal Vinaroz Plain, Spain. HydroResearch, 2, 76-84.

Giri, S., Mahato, M.K., Singh, P.K., & Singh, A.K. (2021). Non-carcinogenic health risk assessment for fluoride and nitrate in the groundwater of the mica belt of Jharkhand, India. Hum. Ecol. Risk Assess.: Int. J., 27(7); 1939-1953.

Golaki, M., Azhdarpoor, A., Mohamadpour, A., Derakhshan, Z., & Conti, G.O., (2022). Health risk assessment and spatial distribution of nitrate, nitrite, fluoride, and coliform contaminants in drinking water resources of Kazerun, Iran. Environ. Res., 203; 111850.

Haghbin, M., Sharafati, A., Dixon, B., & Kumar, V. (2021). Application of soft computing models for simulating nitrate contamination in groundwater: comprehensive review, assessment and future opportunities. Archives of Computational Methods in Engineering, 28; 3569-3591.

Horowitz, H.S. (2000). Decision-making for national programs of community fluoride use. Community Dent. Oral. Epidemiol., 28(5); 321-329.

Igibah, E.C., Amu, O.O., Agashua, L.O., & Adetayo, O.A. (2022). Hydro-geochemical autographs, attribute indicators and health threat evaluation of Fluoride and Ironic elements variability in ground water in Abuja North-central Nigeria. Fuel Commun., 10; p.100048.

Kom, K.P., Gurugnanam, B., & Bairavi, S. (2022). Non-carcinogenic health risk assessment of nitrate and fluoride contamination in the groundwater of Noyyal basin, India. Geodesy & Geodynamics, 13(6); 619-631.

Mahmoodlu, M.G., Raghimi, M., & Ramezani Mojaveri, M. (2023). Investigating the relationship between the fluoride concentration in groundwater and spatial distribution of loess deposits in the Gorgan Plain. Journal of Research in Environmental Health, 8(4); 378-391.(In Persian)

Mohseni, Sajadi, M., Afyuni, M., Khademi, H., Mohseni, Movahed, S.A., & Ayoubi, S. (2011). Spatial variability of fluoride in groundwater and soils in some areas of Arak Plain. Water & Soil, 25(5); 1033-1041. (In Persian)

Moorthy, P., Sundaramoorthy, S., Roy, P.D., Usha, T., Dash, S.K., Gowrappan, M., & Chokklingam, L. (2024). Evaluation of spatial and temporal dynamics of seawater intrusion in coastal aquifers of southeast India: insights from hydrochemical facies analysis. Environ. Monit. Assess., 196; 179.

Muralidhara Reddy, B., & Sunitha, V. (2020). Geochemical and health risk assessment of fluoride and nitrate toxicity in semi-arid region of Anantapur district, South India. Environ. Chem. Ecotoxicol., 2; 150-161.

Qasemi, M., Farhang, M., Morovati, M., Mahmoudi, M., Ebrahimi, S., Abedi, A., Bagheri, J., Zarei, A., Bazeli, J., Afsharnia, M., & Ghalehaskar, S. (2022). Investigation of potential human health risks from fluoride and nitrate via water consumption in Sabzevar, Iran. Int. J. Environ. Anal. Chem., 102(2); 307-318.

Peng, J.Y., Zhang, S., Han, Y., Bate, B., Ke, H., & Chen, Y. (2022). Soil heavy metal pollution of industrial legacies in China and health risk assessment. Sci. Total Environ., 816; p.151632.

Pirasteh, K., Bazrafshan, E., Ashrafi, S.D., Hosseini, A.R., Meshkininan, A., Kord Mostafapour F., & Kamani, H. (2019) Non-cancer Risk Assessment of Nitrate in Drinking Water of Urban and Rural areas of Zahedan City in 2018. Journal of Torbat Heydariyeh University of Medical Sciences, 7(3); 24-33. (In Persian)

Rawat, M., Sen, R., Onyekwelu, I., Wiederstein, T., & Sharda, V. (2022). Modeling of Groundwater Nitrate Contamination Due to Agricultural Activities-A Systematic Review. Water, 14(24); p. 4008.

Rehman, F., Siddique, J., Shahab, A., Azeem, T., Bangash, A.A., Naseem, A.A., Riaz, O., & ur

Rehman, Q. (2022). Hydrochemical appraisal of fluoride contamination in groundwater and human health risk assessment at Isa Khel, Punjab, Pakistan. Environ. Technol. Innovation., 27; p. 102445.

Su, H., Kang, W., Li, Y., & Li, Z. (2011). Fluoride and nitrate contamination of groundwater in the Loess Plateau, China: sources and related human health risks. Environ. Pollut., 286; p.117287.

Subba, Rao, N., Dinakar, A., Surya Rao, P., Rao, P.N., Madhnure, P., Prasad, K.M., & Sudarshan, G. (2016). Geochemical processes controlling fluoride-bearing groundwater in the granitic aquifer of a semi-arid region. J. Geol. Soc. India., 88; 350-356.

Shukla, S., & Saxena, A. (2018). Global status of nitrate contamination in groundwater: its occurrence, health impacts, and mitigation measures. Handbook of environmental materials management; 869-888.

USEPA (U.S. Environmental Protection Agency). (2022). Human Health Risk Assessment. https://www.epa.gov/risk/human-health-risk-assessment.

USEPA (U.S. Environmental Protection Agency) (1989) Risk Assessment Guidance for S uperfund, Volume I: Human Health Evaluation Manual (Part A), Office of Emergency and Remedial Response, Washington, DC.

WHO (World Health Organization).“World Water Day 2001: Oral Health.” Geneva: WHO. 2001. https://web.archive.org/web/20081007142428/https://www.who.int/water_sanitation_health/en/oralhealth.htm.

WHO (World Health Organization). Nitrate and nitrite in drinking-water. Background document for development of WHO Guidelines for drinking water quality. World Health Organization (WHO/SDE/FWC/16.52), Geneva. 2016.

Xiao, Y., Hao, Q., Zhang, Y., Zhu, Y., Yin, S., Qin, L., & Li, X. (2022). Investigating sources, driving forces and potential health risks of nitrate and fluoride in groundwater of a typical alluvial fan plain. Sci. Total Environ., 802; p.149909.

Yifru, B.A., Chung, I.M., Kim, M.G., & Chang, S.W. (2022). Assessing the effect of urbanization on regional-scale surface water-groundwater interaction and nitrate transport. Sci. Rep., 12(1); p. 12520.

Yousefi, M., Ghalehaskar, S., Asghari, F.B., Ghaderpoury, A., Dehghani, M.H., Ghaderpoori, M., and Mohammadi, A.A. (2019). Distribution of fluoride contamination in drinking water resources and health risk assessment using geographic information system, northwest Iran. Regul. Toxicol. Pharm., 107; p. 104408.

Zhang, S., Han, Y., Peng, J., Chen, Y., Zhan, L., & Li, J. (2022). Human Health Risk Assessment for Contaminated Sites: A Retrospective Review. Environ. Int., p.107700.