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# Comprehensive assessment of water quality and associated health risks in an arid region in south Iran

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## ABSTRACT

This study aims at investigating the quality of drinking water and evaluating the non-carcinogenic risk of fluoride and nitrate ions in drinking water, and fluoride in tea in Zarrin Dasht, Iran, We focus on tea since it is the most popular drink among Iranian people and in the study region. We collected and analyzed 23 drinking water samples and 23 tea samples from different locations in the study region. Based on the water quality index, the consumed drinking water does not have a good quality in most Zarrin Dasht areas. Accordingly, the water quality index (WQI) is poor and very poor in 70% and 13% of the water samples, respectively. The average fluoride concentration of the tea samples is 2.71 mg/L. The mean values of Fluoride Hazard Index (HIfuoride) are 3.77, 2.77, and 2.33 for children, teenagers, and adults, respectively, which are higher than the safe limit of 1. The Nitrate Hazard Index (HI<sub>nitrate</sub>) is higher than the safe limit of 1 in 8.7% of the samples. The results of the Monte Carlo simulation demonstrate that HI<sub>fluoride</sub> and HI<sub>nitrate</sub> are higher than 1 in all the groups, except for adults. According to the results of the sensitivity analysis, ingestion rate and body weight have a large effect on HI<sub>fluoride</sub> and HInitrate, but body weight is inversely associated with sensitivity. According to the Piper diagram, saline water is the predominant type in Zarrin Dasht. Besides, the results of the principal component analysis (PCA) show a high correlation between fluoride and pH, which could be related to the effect of pH on fluoride dissolution and ion exchange. Therefore, appropriate measures are recommended to be taken in order to reduce the amount of fluoride in the drinking water resources of this region. Reduction of tea consumption can also be considered an important factor in decreasing the amount of fluoride intake.

1. Introduction

Water is an essential element for the survival of living organisms and one of the most important natural resources in the world (He et al., 2022a). Providing safe drinking water is one of the important goals of human societies because consumption of contaminated water can lead to short term adverse health effects, and poses significant risk to health over a lifetime of consumption at different life stages (Dinka 2018; Kaur et al., 2020). Although mercury, lead, and arsenic are some of the most common carcinogenic inorganic contaminants in groundwater, in this study we focus on nitrate, nitrite, and fluoride, which are among the most common non-carcinogenic inorganic contaminants in groundwater (Chen et al., 2017; He et al., 2022b).

Nitrate concentration is naturally low in groundwater, but when effluents containing nitrate are discharged into the environment, nitrate transport from land surface through soil layers can lead to aquifer contamination (Elisante and Muzuka, 2017; Huno et al., 2018). There are restrictions on the consumption of nitrate-containing drinking water around the world. The World Health Organization (WHO), the European Union, and the Environmental Protection Organization of Iran have set

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Received 24 May 2022; Received in revised form 4 September 2022; Accepted 11 September 2022 Available online 21 September 2022 0273-2300/© 2022 Elsevier Inc. All rights reserved. the maximum permissible nitrate ion in drinking water to 50 mg/L, and the U.S. Environmental Protection Agency (US EPA) sets it to 45 mg/L (Radfard et al., 2018; Uzun and Debik, 2019; Regni et al., 2021).

Consumption of water with high concentrations of nitrate causes systemic problems in humans, especially in children and infants due to the higher ratio of water volume to their body weight. The most important side effects of drinking water with high nitrate concentrations include methemoglobinemia, thyroid dysfunction, infertility, incidence of various types of cancer, and death from asphyxia (Azhdarpoor et al., 2016; Ward et al., 2018; Duron, 2020).

Fluoride is an essential micronutrient that strengthens tooth enamel and prevents decay. Studies have shown that to prevent these problems, each person should receive 1-3 mg fluoride per day (Aggeborn and Öhman, 2021). Although fluoride can enter the body through food, inhalation, and skin absorption, 75% of the fluoride entering the body is through drinking water (Keramati et al., 2019). As fluoride is the 13th-most abundant element in Earth's crust, the presence of fluoride in groundwater is natural due to natural weathering and transport processes, and the contact of water with minerals such as fluorite (CaF<sub>2</sub>). Thus, the concentration of fluoride is expected to be higher in groundwater than in surface water. Nevertheless, municipal activities, discharge of effluents from industries such as aluminum and coal, and use of chemical fertilizers and fluoride-containing pesticides lead to the entrance of fluoride into water sources. The US EPA has set the maximum allowable fluoride concentrations in drinking water to 1.5 mg/L. Exposure to high concentrations of fluoride can cause dental and skeletal fluorosis, thyroid disorders, kidney, lung, and liver damages, infertility, cancer, osteoarthritis, and osteoporosis (Panda et al., 2015; Kheradpisheh et al., 2018; Poonia et al., 2021). In addition to drinking water as the main source of fluoride, tea is considered an important source of fluoride by selectively absorbing fluoride from the soil and storing it in its plant biomass (Wiseman et al., 1997). Tea is one of the most common beverages among people around the world, especially in Asian countries. When the consumption of drinking water and tea occurs at the same time, where both contain high amounts of fluoride, this can lead to a number of health issues associated with the excessive exposure to fluoride (Malinowska et al., 2008). Due to the widespread consumption of tea by Iranians and the significant amounts of fluoride in the tea consumed in Iran, various studies have revealed that tea can play an aggravating role in the occurrence of the complications of excess fluoride in the body (Mojarad and Khanlary, 2013; Miri et al., 2018; Karami et al., 2019).

A commonly used tools for calculating the quality of drinking water resources is the Water Quality Index (WQI). The WQI, which is used based on the allowable concentration of pollutants, reflects the combined effects of several water quality parameters, and displays different water quality parameters as a number (Li et al., 2019). WQI was used to assess water quality in several regions in Iran such as the Shiraz plain (Badeenezhad et al., 2020) and the Khaf city (Bazeli et al., 2022), and worldwide such as South Sikkim district, India(Dutta et al., 2022) and Kamiyaran city in Kurdistan province(Jamshidi et al., 2021). Furthermore, risk assessment is used to determine the potential risk and harmful health effects of the contaminants that humans are exposed to. Health risk assessment is a method that evaluates and describes the health risks of environmental pollution as well as the extent of their possible damages to human health through various ways of contact (Mohammadpour et al., 2022).

Zarrin Dasht city in Fars province, Iran is located in a region with hot and dry climate. The crisis of safe drinking water is a serious issue for human health especially in areas with hot and dry climate. However, no comprehensive study has been done on the quality of drinking water resources in this area. Hence, the present study aims at investigating the quality of drinking water and assessing the health risks of drinking water containing nitrate and fluoride, as well as tea containing fluoride in the study area.

## 2. Materials and methods

## 2.1. Study area description

The study area is Zarrin Dasht, Fars province, which is located at 28° 20' 0'' N,  $54^{\circ} 20' 0''$  E in DMS. The surface area of this county is 462,600 ha, which is 3.7% of the area of Fars province. Zarrin Dasht plain is very poor in terms of water resources. The unauthorized abstraction of groundwater resources in this area severely affects the quality and quantity of water resources. The average annual rainfall in Zarrin Dasht is 224.4 mm, and the average air temperature is 22.7 °C. In this county, August with an average temperature of 47.7  $^\circ C$  and December with an average temperature of 3.8 °C are the warmest and coldest month of the year, respectively. In the recent years, the amount of rainfall has been much lower than long-term average, leading to a severe drought in this region. Geologically, the study area is dominated by quaternary low level fan and terrace sediments. The main lithological units include Pliocene and Miocene conglomerate, sandstone and siltstone, Cretaceous limestone and shale, late Cretaceous gypsum and marl. There exist some limited outcrops of acidic to intermediate extrusive and intrusive igneous including diabase, rhyolite, and trachyte (Khademi, 1998). There are two main Precambrian salt-dome outcrops related to Hormoz series in the north and east of the area. Groundwater in Zarrin Dasht plain is extracted and discharged by 1304 extraction wells, 4 ganats, and 4 springs. The main groundwater recharging zones are located in northern highland dominated by Cretaceous limestone, and Pliocene conglomerate. Marl and shale form the basement rocks in the area. The discharge zone mostly is composed of Quaternary evaporite deposits and salt panes.

## 2.2. Sampling and analysis

Based on the fieldwork conducted in Zarrin Dasht in 2021, 23 groundwater samples and 23 tea samples were collected from 23 points in the region using systematic random sampling to analyze the physical and chemical parameters. The Total Dissolved Solids (TDS), pH, and Electrical Conductivity (EC) of the samples were measured at the sampling sites. In addition, turbidity and alkalinity were determined by nephelometric method and titration, respectively. The sampling locations were recorded using Garmin eTrex GPS, and the groundwater sampling locations are depicted in Figure S1.

Two samples were collected from each point for the analysis of cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and anions (F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). After collecting the samples in polyethylene bottles and labeling them, they were transferred to the Water and Wastewater Laboratory at the Shiraz University of Medical Sciences and were kept in the refrigerator at 4 °C to maintain stability. The concentrations of nitrate and other anions and cations were measured via ion chromatography (850 Professional IC Anion – MCS). The accuracy of the sampling process and the experiments is determined according to the standard method (EPA, 2006) (Amin et al., 2008; Ion et al., 2014).

#### 2.3. Water quality index

The WQI is used to assess the quality of water based on the allowable concentrations of pollutants (Uddin et al., 2021). In this study, the WQI is calculated using the following formula:

$$WQI = \sum_{i=1}^{n} W_i \times Q_i \tag{1}$$

where  $W_i$  is the relative weight of each parameter, and  $Q_i$  is the quality rating of each parameter.

Relative weight ( $W_i$ ) and quality rating scale ( $Q_i$ ) of each parameter are computed using equations (2) and (3).

$$W_i = \frac{W_i}{\sum_i^n W_i} \tag{2}$$

$$Q_i = \frac{C_i \times 100}{S_i} \tag{3}$$

where  $W_i$  is the relative weight of each parameter;  $w_i$  is the weight of each parameter; n is the total number of parameters;  $Q_i$  is the quality rating;  $C_i$  is the concentration of each parameter (mg/L); and *Si* represents the standard value of each parameter.

#### 2.4. Estimation of the optimal fluoride concentration

The WHO has set the optimum fluoride concentration for temperate regions. As temperature is an important factor in determining the optimal concentration of fluoride in drinking water, the WHO's limit is not suitable for the areas with higher temperatures. Thus, we use the average Annual Mean Maximum Temperature (AMMT) for a period of five years or more to estimate the optimal fluoride concentration in drinking water (Naderi et al., 2020). By considering the climatic conditions of the study region and the average AMMT in the study period, the optimal concentration of fluoride in drinking water varies from 0.5 to 1.5 mg/L. The optimal concentration of fluoride in drinking water is determined using Equation (4):

$$Optimum fluoride \ concentration\left(\frac{mg}{l}\right) = \frac{0.022}{(0.0104 + 0.000724 \times AMMT \ ^{\circ}C)}$$
(4)

#### 2.5. Risk assessment and multivariate statistical analysis

In the present study, Hazard Quotient (HQ) and Chronic Daily Consumption (CDI) are used to evaluate the non-carcinogenic effects of these two compounds in drinking water and tea based on the US EPA method (Joodavi et al., 2021). In order to estimate the health risk of drinking water consumption for each pollutant, the average daily dose is first calculated by Equation (5) (Dehbandi et al., 2018):

$$CDI = \frac{Ci \times IR}{BW}$$
(5)

where  $C_i$  is concentration of chemicals in water (mg/L); *IR* is the average daily water intake (L/d); and *BW* is the body weight (kg).

To estimate the non-carcinogenic health effects of nitrate (in drinking water) and fluoride (in drinking water and tea), the HQ of each element is calculated using Equation (6), as the ratio of the average daily consumption of the element to the oral reference dose (Li et al., 2019; Guo et al., 2022):

$$HQ = \frac{CDI}{RfD}$$
(6)

where *HQ* is the hazard quotient (mg/kg/day); and *RfD* is the reference dose (mg/kg/day). The reference dose is 0.06 for fluoride and 1.6 for nitrate (Karunanidhi et al., 2019; Liu et al., 2022).

To estimate the total non-carcinogenic health effects due to exposure to nitrate and fluoride, the Hazard Index (HI) is calculated using Equation (7):

$$HI_{Fluoride} = HQ_{water} + HQ_{tea} \tag{7}$$

$$HI_{Nitrate} = HQ_{water} \tag{8}$$

In the present study, we use Monte Carlo simulation via the Crystal Ball software (Version 11.1.2.3) to analyze the sensitivity and determine the uncertainties related to the risks. The parameters used to calculate HQ values are presented in Table S1.

One of the important issues in water resources quality management is to find the relationship between various physical and chemical

parameters affecting the quality of water resources, which can be used for more accurate exploration of pollutant sources and provision of solutions to reduce their negative effects. In this respect, multivariate statistical methods can be used for correlated parameters, and Pearson's correlation table is used. PCA is a data conversion method and a dimensional technique that is used to create an underlying structure in a multivariate set by removing unwanted information and retaining useful information. In PCA, based on the Kaiser criterion, the components whose value of a specific vector is greater than or equal to 1 are used. As a result, all the factors with a variance greater than standard variables are accepted, and then the factors are graded based on their values. The first factor or component with the highest specific vector is the most important source of changes in the data, and the last factor causes minimum chemical changes. Varimax rotation is used to maximize changes in the key factors. Maximizing variance represents a range of components that are strongly inclined toward positive, negative, or near-zero numbers. Additionally, hierarchical cluster analysis (HCA) is used to group drinking water samples into clusters based on their squared Euclidean distance(Okiongbo and Douglas, 2015; Subba Rao and Chaudhary, 2019). In this study, SPSS (v23), and Crystal Ball software are used for data analysis, and to present descriptive statistics and correlation coefficients.

## 3. Results and discussion

## 3.1. Physicochemical parameters

The mean, minimum, maximum, and standard values of the physicochemical parameters obtained from analyzing the samples are presented in Table 1. Among the measured cations and anions, sodium with an average of concentration 368.12 mg/L and sulfate with an average of concentration 557.59 mg/L have the highest values, which are higher than the standard values.

The spatial distribution of fluoride concentration in water and tea samples and nitrate concentration in water samples are shown in Fig. 1. The results indicate that Dehno station with 0.38 mg/L has the lowest concentration and Darreh Shur station with has the highest fluoride levels of 2.79 mg/L. The average concentration of fluoride is 1.45 mg/L in the 23 studied stations. Fluoride concentrations of 1.5 mg/L and higher, 1–1.5 mg/L, 0.5–1 mg/L, and 0.5 or lower mg/L are found in 43.48%, 43.48%, 8.7%, 4.3% of the water samples, respectively. The WHO's limit is 1.5 mg/L. Considering fluoride concentration in the tea samples, the concentrations of fluoride are more than 1.5 mg/L in more than 78% of the samples, and 1–1.5 mg/L in 21.7% of the samples. The minimum, maximum, and average fluoride concentrations in the 23 tea samples are 1, 9.29, and 2.71 mg/L, respectively.

Based on the meteorological data of the last ten years and using the Galagan and Vermillion equation, the optimal concentration of fluoride

laple	1	
Nater	quality	characteristic

Parameters	Minimum	Maximum	Mean	WHO's standard	
pH	8.02	9.22	8.38	8.5	
TDS (mg/L)	132	2608	1096.35	500	
EC (µmoh/cm)	331	6160	2680.96	1500	
Turbidity (NTU)	1.2	7.48	2.41	5	
F <sup>-</sup> (mg/L) (Water)	0.38	2.79	1.45	1.5	
F <sup>-</sup> (mg/L) (Tea)	1	9.29	2.71	-	
K <sup>+</sup> (mg/L)	0.43	8.46	3.38	12	
Na <sup>+</sup> (mg/L)	13.5	1044.46	368.12	200	
$Cl^{-}$ (mg/L)	17.85	1126.28	363.12	250	
$NO_3^-$ (mg/L)	2.6	32.33	11.04	50	
$Ca^{2+}$ (mg/L)	56.81	381.16	224.12	75	
$Mg^{2+}$ (mg/L)	25.63	166.9	96.66	50	
$SO_4^{2-}$ (mg/L)	50.12	1142.26	557.59	250	
Alkalinity (mg/L)	91.66	347.45	166.91	200	



Fig. 1. Spatial distribution maps of (a) fluoride (in water), (b) fluoride (in tea), and (c) nitrate.

in drinking water of Zarrin Dasht is 0.67 mg/L (AMMT is 31 °C in this county), which is less than WHO's standard for fluoride in drinking water. Comparison of fluoride concentrations in water samples from Zarrin Dasht to the optimal amounts are illustrated in Figure S2. Based

on the findings, the concentration of fluoride is higher than the optimal amount in 95.6% of the water samples consumed in Zarrin Dasht. Generally, fluoride concentration depends on geological characteristics and varies from region to region (Ijumulana et al., 2020). The study of Ghanbarian et al., shows that the concentration of fluoride ranges from 0.086 to 2.61 mg/l in drinking water in Fars province (Ghanbarian et al., 2022). In addition, they show that the concentration of fluoride in drinking water is higher than the WHO's limit in more than 17% of urban areas in Fars province, and is less than the allowable limit in 48.27% of the samples. Yousefi et al. report that the fluoride concentration in groundwater in Showt city, West Azerbaijan province, Iran is higher than the WHO's recommended value in 36.36% of the water samples, which could be the reason for dental fluorosis in this area (Yousefi et al., 2019). In the present study, the high concentration of fluoride in drinking water of Zarrin Dasht could be attributed to the geological texture of Fars province, which mostly includes dolomitic, limestone, and calcareous rocks (Mouthereau et al., 2007a,b). Based on the current study results, the distribution of nitrate concentration varies from 2.6 to 32.3 mg/L (average 11.04 mg/L) in the study area, which are within the WHO's limit. In another study on nitrate concentration in drinking water in Sabzevar, Iran, the nitrate concentration was within the allowable limit (less than 50 mg/L) in all measured samples (Mouthereau et al., 2007a,b). However, the findings of the other studies conducted in Iran show high concentrations of nitrate in Shiraz, Tehran, Ardabil, Ahvaz, Mashhad, Zahedan, and Qom (Darvishmotevalli et al., 2019; Moradnia et al., 2019).

To determine and chemically characterize the groundwater of Zarrin Dasht, a Piper diagram using AqQA 1.5.0 software is shown in Fig. 4. Based on the Piper diagram, eight chemical facies can be detected. These eight facies are located in three main types of fresh water, saline water, and combined water. Based on this diagram, different types of water identified in the samples collected from different parts of Zarrin Dasht are divided into zones C, F, A, and B. A single sample of Dehno is allocated to zone B. Sulfate and chloride anions and sodium and potassium cations are the predominant ions in zone C, while zone F represents a mixed zone. As shown in Fig. 2, some specimens including the sulfate-chlorate (sodium-potassium) type are located in zone C, which might originate from the dissolution of halite, ion exchange, or both. Piper diagram also shows that saline water is dominant type in the Zarrin Dasht, which has a severe impact on the water resources in the Zarrin Dasht.

## 3.2. Water quality index

To evaluate the quality of different areas of Zarrin Dasht, the WQI is calculated. The calculated parameters of the water samples, the intended weight for each parameter, and the relative weight of each parameter are presented in Table S2. Additionally, the WQI values for the sampling points and the WQI distribution in the study area are shown in Figs. 3 and 4, respectively. Based on the results, the calculated WQI values in the study area varied from 31.02 to 274.79. Accordingly, the WQI is within the excellent range for drinking purposes in 4% of the samples (Dehnu sample only) and within the good range in about 13% of the regions, respectively. Reduction of rainfall in the recent years and uncontrolled abstraction of groundwater for municipal and agricultural water supply cause a decrease in the aquifer water level. This was followed by water salinization, leading to negative changes in groundwater quality.

# 3.3. Health risk assessment

Health risks related to fluoride in drinking water and tea as well as nitrate in drinking water are assessed for different age groups on the basis of consumption rate.

The results related to the calculation of HQ and HI for fluoride and



Fig. 2. Piper trilinear diagram showing the hydrogeochemical features of the groundwater samples of the study area.







Fig. 4. Distribution of WQI in the study area.

nitrate in drinking water and fluoride in tea for children, teenagers, and adults are summarized in Table 2. According to the US EPA guidelines, if the HQ values for an element or the HI for an age group are greater than 1, there will be a non-carcinogenic health risk for humans. Considering the drinking water samples, the HQ<sub>fluoride</sub> values vary from 0.34 to 2.53 (mean 1.31), 0.25 to 1.86 (mean 0.97), and 0.21 to 1.56 (mean 0.81) for children, teenagers, and adults, respectively. According to the HQ<sub>fluoride</sub> of the drinking water samples, there is a health risk for children in 65.2% of the samples in the study area. This measure is 43.4% among teenagers and 30.4% in adults. Moreover, computation of HQ for fluoride related to tea consumption shows that it is higher than 1 in 95.6%, 78.3%, and 69.6% of the samples for children, teenagers, adults, respectively. Overall, it can be inferred from the results that children are more vulnerable to non-carcinogenic risks compared to adults in Zarrin Dasht due to the consumption of fluoride-contaminated groundwater. Additionally, teenagers are at more risk in comparison to adults. This could be due to the lower weight of children compared to teenagers as well as the lower weight of teenagers compared to adults. Considering the high concentration of fluoride in drinking water and tea consumed in this region, it is expected to detect such complications as dental and skeletal fluorosis in the residents of Zarrin Dasht. Dental problems in this area are shown in Figure S3.

The HQ values of nitrate are 0.09–1.10 (mean 0.31) in children, 0.07–0.81 (mean 0.28) in teenagers, and 0.05–0.68 (mean 0.23) in adults. The HQ values of nitrate are less than 1 for teenagers and adults in all the samples, but for children is 8.7% of the samples above 1. The NHQ is higher than 1, which represented non-carcinogenic health risks for this age group.

The results indicate that HI<sub>fluoride</sub> is higher than the allowable limit recommended by the US EPA (HI  $\leq$  1) for children, teenagers, and adults. This indicates the non-carcinogenic risks of fluoride (100%) and nitrate (8.7% for children) in drinking water and consumed tea. In a similar study conducted in southern India, HI-based non-carcinogenic health risk for nitrate and fluoride is higher for children than for men and women (Karunanidhi et al., 2019). In another study in Punjab, India, the HI is higher than the guideline for adults in 40.8% of the samples, and for children in 69.7% of the samples, indicating that children are more exposed to non-carcinogenic health risks compared to

## Table 2

HQ and THQ of fluoride and nitrate in drinking water and tea samples in the study region.

Parameter	Childre	en		% of samples above 1 Teenagers		% of samples above 1	Adults			% of samples above 1		
	Min	Mean	Max		Min	Mean	Max		Min	Mean	Max	
HQ <sub>fluoride water</sub>	0.34	1.31	2.53	65.2	0.25	0.97	1.86	43.4	0.21	0.81	1.56	30.4
HQ <sub>fluoride</sub> tea	0.91	2.46	8.43	95.6	0.67	1.81	6.20	78.3	0.56	1.52	5.20	69.6
HQ <sub>Nitrate water</sub>	0.09	0.38	1.10	8.7	0.07	0.28	0.81	0	0.05	0.23	0.68	0
HI <sub>fluoride</sub>	1.74	3.77	9.49	100	1.28	2.77	6.98	100	1.08	2.33	5.85	100
HI <sub>nitrate</sub>	0.09	0.38	1.10	8.7	0.07	0.28	0.81	0	0.05	0.23	0.68	0

adults. Similar results are reported in the studies performed by Adimalla et al. in India, Basli et al. in Eastern Iran, and Dehghani et al. in Southeast Iran (Adimalla et al., 2019; Bazeli et al., 2022; Dehghani et al.,

2018).



Fig. 5. Histogram of the HI of exposure to fluoride in a) children, b) teenagers, and c) adults.

## 3.4. Uncertainty of the health risk assessment model

The histograms for simulating the results of the fluoride and nitrate risk indices are shown in Figs. 5 and 6, respectively. The results of probabilistic estimation show that the HI levels of nitrate and fluoride are higher than 1 in all the age groups, except for adults, which indicates the non-carcinogenic risk of both. The simulation results also show an increase in HI levels among children, teenagers, and adults. Accordingly, the HI values with 95% confidence intervals in children, teenagers, and

adults are, respectively, 4.42, 4.01, and 2.99 for fluoride and 1.31, 1.06, and 0.75, respectively, for nitrate. The highest 95% percentiles of the calculated HI values for nitrate and fluoride are related to children, indicating a higher risk of non-carcinogenicity in this group. Higher risk levels in children than in teenagers and adults can be attributed to their lower body weight. Similar results are obtained in other studies (Zhang et al., 2017; Moeini and Azhdarpoor, 2021).

For the three age groups of children, teenagers, and adults, the sensitivity analysis of the HI parameters of fluoride and nitrate are



Fig. 6. Histogram of the HI of exposure to nitrate in a) children, b) teenagers, and c) adults.

shown in Figs. 5 and 6, respectively. As shown in Fig. 5, ingestion has the highest effect on the non-carcinogenic risk in fluoride risk assessment in all the age groups. Moreover, nitrate concentration in children and the rate of ingestion in teenagers and adults are the main parameters affecting the non-carcinogenic risk associated with nitrate consumption. The results of the sensitivity analysis also demonstrate that body weight is inversely associated with sensitivity, which confirms the higher noncarcinogenic risk of nitrate and fluoride consumption among children, as mentioned above.

## 3.5. Multivariate statistical analysis

The correlation matrix of the water quality variables is presented in Table 3. According to the Piper diagram, saline water is the predominant type in Zarrin Dasht. Moreover, the results presented in Table 3 reveal a relatively high correlation between EC and total soluble solids with chloride, sulfate, sodium, magnesium, and potassium elements. This indicates that these elements caused a decrease in the quality of Zarrin Dasht groundwater and increased the salinity of groundwater in the area. Besides, the high correlation between sodium and chloride ( $R^2 =$ 0.99) as well as the good correlation between sodium and sulfate, calcium, and magnesium imply the presence of a common source for all these ions. Very high concentrations of sodium and chloride in some samples could result from the dissolution of halite in groundwater, which releases sodium and chloride ions.

The assessment of the relationship between fluoride in the water samples and other qualitative parameters demonstrates that this element has the highest correlation with alkalinity (bicarbonate + carbonate = 0.45) and potassium (0.59). The high correlation between fluoride and bicarbonate indicates that the alkaline environment is the predominant control mechanism for fluoride leaching from the source material in groundwater (Subba Rao, 2009). As expected from the fertilizer application pattern, there is a positive relationship between nitrate and sulfate. This positive relation might be due to the use of nitrogen fertilizers, which often contain nitrate and ammonium sulfate (Esmaeili et al., 2014).

The PCA/FA results are shown in Table S3. Four varifactors (VF, rotated PCs) are extracted to be with Eigen values > 1 (Table 4). Four components, whose specific values are higher than 1 and have the highest variability (82.05%), are the main components affecting the chemical quality of Zarrin Dasht water. The principal component changes are maximized by varimax rotation, and the results are summarized in Table S3. Absolute loads higher than 0.75, between 0.5 and 0.75, and below 0.5, respectively, are classified as strong, moderate, and weak parameters affecting the water quality. The first component indicates the highest changes, which is due to the positive and strong loading of the parameters, including EC, TDS, sulfate, chlorine, calcium, sodium, and magnesium. Given the fact that saline water is the Table 4

The rotated	varimax	principal	component	matrix.

. .

	Component							
	1	2	3	4				
F	.092	.783	.169	107				
SO4	.926	023	.058	.042				
Ca	.888	096	.176	048				
Mg	.880	152	.367	.037				
К	.644	.252	.514	.097				
EC	.871	.253	229	.126				
Alkalinity	.155	.192	.916	022				
NO3	016	.085	030	.921				
Cl	.833	.362	.266	.099				
Na	.846	.360	.177	.074				
Turbidity	253	.518	075	599				
TDS	.907	.275	.134	.110				
pH	.376	.595	.133	.213				

Extraction method: Principal component analysis.

Rotation method: Varimax with Kaiser normalization.

a. Rotation converged in 5 iterations.

predominant type in Zarrin Dasht water, the high concentrations of elements such as sodium and chlorine along with the high EC and TDS of the water are parameters that can be considered as the main components of water salinity.

Sulfur is also released into the environment by the weathering of minerals containing this element. Sulfate, which is one of the main forms of sulfur in groundwater in arid areas, mostly originates from the leaching of evaporative minerals like gypsum and anhydrite from upper layers into water sources. Therefore, the placement of sulfate in the first component and the lack of correlation between sulfate and nitrate indicate that this parameter is lithogenic in the study area. In arid regions, high correlations among TDS, EC, sodium, and chlorine might indicate relationships between water, soil, and rocks, and suggest the dissolution of minerals such as halite and gypsum. In the second component, fluoride, pH and turbidity parameters have a greater impact compared to other parameters. This is due to the positive and moderate factor loadings, which could be related to the high correlation between the effect of pH on fluoride dissolution and ion exchange. In the third component, bicarbonate and potassium show high and moderate factor loadings. Nitrate, which is the most effective parameter in the fourth component with the positive and strong loading rate of 0.921, demonstrates the impact of anthropogenic processes such as the use of chemical fertilizers and wastewater discharge. Other parameters have little effects on this component.

In the present study, cluster analysis is performed on the parameters affecting water quality, and the HCA results of the Zarrin Dasht groundwater samples are presented in the dendrogram (Fig. 7). Zarrin Dasht groundwater resources are classified into three main clusters

Table	3
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The correlation coefficients of the water resources' cher	mical parameters in Zarrin Dasht.
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	F	C1	SO4	NO3	Na	Ca	Mg	K	pН	EC	TDS	Turbidity	Alkalinity
F	1.00												
Cl	0.27	1.00											
SO4	-0.06	0.57**	1.00										
NO3	-0.30	0.135	0.39	1.00									
Na	0.28	0.99**	0.59**	0.14	1.00								
Ca	-0.09	0.52*	0.88**	0.19	0.51*	1.00							
Mg	0.01	0.65**	0.87**	0.19	0.66**	0.91**	1.00						
K	0.59**	0.70**	0.55**	-0.06	0.72**	0.50*	0.70**	1.00					
pH	-0.32	-0.44*	-0.22	-0.20	-0.44*	-0.25	-0.23	-0.38	1.00				
EC	0.19	0.85**	0.60**	0.25	0.84**	0.50*	0.51*	0.47*	-0.34	1.00			
TDS	0.20	0.93**	0.61**	0.19	0.92**	0.56**	0.66**	0.60**	-0.36	0.86**	1.00		
Turbidity	0.21	-0.29	-0.29	-0.30	-0.23	-0.16	-0.28	-0.15	-0.14	-0.35	-0.32	1.00	
Alkalinity	0.45*	0.36	0.06	-0.18	0.35	0.02	0.19	0.51*	-0.21	0.08	0.28	0.01	1.00

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).



Fig. 7. Dendrogram indicating the results of HCA.

(three groups). The first cluster (C1) consists of three subgroups; EC, TDS, chlorine, and sodium are placed in one subgroup; Ca, Mg, and SO<sub>4</sub> are in the second subgroup; and K is in the third subgroup. The second subgroup reveals the effect of geogenic processes (e.g., weathering, mineral dissolution, ion exchange, and evaporation) on groundwater resources (Subba Rao and Chaudhary, 2019). Cluster 1 is considered a salinity-controlled cluster. The combination of calcium, magnesium, and sulfate parameters with chloride, sodium, EC, TDS, and potassium indices as the effective parameters in water quality indicates the common source of all these ions and the wide variety of geochemical processes in the study area. The second cluster, whose parameter values are higher than the values of the first and second clusters' parameters, includes F, turbidity, HCO<sub>3</sub>, and NO<sub>3</sub>. This indicates the effect of alkalinity on increasing the amount of fluoride and nitrate. Finally, pH that is located in the third cluster shows the impact of human activities on the pollution of water resources in the region.

## 4. Conclusion

Water samples were collected from the drinking water resources of Zarrin Dasht to evaluate the quality of drinking water and to determine the non-carcinogenic risk caused by fluoride and nitrate ions in drinking water and fluoride in the tea consumed by the residents. From our analysis we can conclude the following.

- The nitrate concentration is lower than the standard in all the samples.
- The fluoride concentration is higher than 1.5 mg/l in 56.52% of the water samples. The comparison of the fluoride values of the samples to the optimal concentration of fluoride in the region indicates that the fluoride concentration is higher than the optimal level in 95.6% of the water samples.
- Hydrogeochemical study of groundwater in Zarrin Dasht shows that saline water is the predominant type of water in this region.
- Regarding the WQI, the water quality is excellent in 4% of the samples, good in 13% of the samples, and poor and very poor in other places.
- Based on the findings of Monte Carlo simulation, children in Zarrin Dasht are more exposed to non-carcinogenic risks compared to adults due to the presence of fluoride and nitrate in drinking water, which could be attributed to the lower weight of children in comparison to teenagers and adults.

• Given the high concentration of fluoride in groundwater and tea consumed in the region, complications such as dental and skeletal fluorosis are expected to be detected in the residents of Zarrin Dasht. Therefore, appropriate measures are recommended to be taken in order to reduce the amount of fluoride in the drinking water resources of this region.

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## CRediT authorship contribution statement

Amin Mohammadpour: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing. Amin Allah Zarei: Conceptualization, Writing – review & editing. Reza Dehbandi: Conceptualization, Project administration, Writing – review & editing. Razyeh Khaksefidi: Conceptualization, Writing – review & editing. Ebrahim Shahsavani: Conceptualization, Writing – review & editing. Sajad Rahimi: Conceptualization, Writing – review & editing. Ahmed S. Elshall: Conceptualization, Writing – review & editing. Abooalfazl Azhdarpoor: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.yrtph.2022.105264.

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