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Hydrogeochemical Characteristics and Human Health Risk Assessment of Fluoride Enrichment in Water in Faulted Basins of Qinghai-Tibet Plateau—A Case Study of Sanhe Plain in Guide Basin

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Abstract: Fluoride (F) is an essential element of drinking water for human health, especially for bone development and enamel creation. However, if the fluoride content in drinking water is higher than 1.5 mg/L or lower than 0.5 mg/L, it will cause endemic diseases, such as dental fluorosis. There are two main hydrogeological characteristics: the properties of the water-bearing rocks and groundwater conditions controlled the groundwater in guide basin. The geothermal water can be divided into fracture convection and sedimentary basin geothermal water according to its geological environment and heat transfer mode. Inductively coupled plasma spectrometry is a significant tool for groundwater quality analysis. The geochemical factors of fluoride enrichment in confined geothermal water mainly include pH, ion exchange, and mineral saturation. Both groundwater samples are slightly alkaline, while the phreatic water and surface water record pH values of 8.5, 7.78, and 7.8, respectively. The salinity of groundwater water is not high, but for confined geothermal water, phreatic water, and surface water measures 706.0, 430.1 and 285.9 mg/L respectively. The higher the pH of groundwater, the more beneficial it is to the enrichment of fluoride. In contrast, the main cations in phreatic water and surface water are calcium ions and magnesium ions. The anions in groundwater and surface water mainly include SO_4^{2-} and HCO_3^-, followed by Cl^-, indicating that the groundwater and surface water here is mainly leaching. Fluoride was shown to be positively correlated with sodium and bicarbonate. Moreover, the results indicate that F^- enrichment is usually associated with high HCO_3^- and Na^+ concentrations in water, while a high Ca^{2+} concentration tends to lower the F^- concentration in water. This means that the ion exchange between calcium ions and sodium ions may lead to fluoride enrichment in natural water. As mentioned above, high-sodium and low-calcium water are favorable for fluoride enrichment. Moreover, saturation indices of fluorite, gypsum, dolomite, and calcite, as well as the saturation index of fluorite, represent a vital method to understand the fluoride enrichment. According to this study, fluoride as a pollutant poses great risks to human health overall, whether lower than or higher than the drinking water limit. Children face higher health risks than adults caused by confined geothermal water drinking intake. This study suggests that groundwater treatment should be conducted to reduce fluoride concentration in drinking water. It is suggested that when confined geothermal water is used as drinking water, it should be mixed with phreatic water and surface water in a certain proportion to make the fluoride in groundwater reach the range of safe drinking water.

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Citation: Liu, R.; Liu, F.; Xu, Y.; Zhu, H.; Jiao, J.; El-Wardany, R.M. Hydrogeochemical Characteristics and Human Health Risk Assessment of Fluoride Enrichment in Water in Faulted Basins of Qinghai-Tibet Plateau—A Case Study of Sanhe Plain in Guide Basin. *Water* **2023**, *15*, 1968. https://doi.org/10.3390/w15101968

Academic Editor: Maurizio Barbieri

Received: 2 March 2023
Revised: 3 May 2023
Accepted: 17 May 2023
Published: 22 May 2023

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Keywords: Qinghai-Tibet plateau; Sanhe Plain in guide basin; confined geothermal water; fluoride; hydrogeochemistry; human health risks

1. Introduction

Fluoride (F) is an essential element of drinking water for human health, especially for bone development and enamel creation. A small amount of fluoride in drinking water is highly beneficial to dental health, capable of preventing dental caries [1,2]. Nevertheless, a high fluoride concentration in drinking water is one of the most critical problems in the world. It is known that a fluoride content in drinking water is higher than 1.5 mg/L or lower than 0.5 mg/L will cause endemic diseases, e.g., dental fluorosis. Approximately 200 million people suffer from chronic fluorosis in 28 developed and developing countries, including India, Brazil, the African continent, Pakistan, and China [3]. The high fluoride content in groundwater is closely related to the geothermal distribution area in terms of geochemical and hydrogeochemical characteristics, especially the geothermal water highly affected by the water–rock interaction through the migration process. On the other hand, the effects of the natural conditions and human activities on the physical and chemical features of groundwater rise day after day. On the other hand, the most significant and main priority is to understand the influence of water–rock interaction on element concentration to face and resolve these challenges [4]. Many authors have focused on the fluoride concentration and the factors which control and affect the behavior of fluoride ions in the groundwater. Liu [2] and others pointed out that the essential factors which control the enrichment of the fluoride ions include the alkaline environment, temperature, cycle depth, Lithology, and dissolution of fluoride-bearing minerals (fluorite or fluorspar apatite, cryolite, etc.), in addition to the cation exchange, as the main geochemical process which controls the hydrochemical characteristics of high-fluoride geothermal water [2,5–8]. Generally, the environmental studies and their issues, especially green energy, have global attention regarding to its potential development and utilization value. China has been considered the sconed richest country globally in terms of geothermal resources and reserves. The development and utilization of geothermal energy are increasing at an annual rate of 10%. accompanied by many environmental problems, such as air pollution, groundwater level decline, land subsidence, etc., posing a hidden danger to the safety of the local drinking water.

The Qinghai-Tibet Plateau, known as the "Asia Water Tower", is the main birthplace of major rivers in China and Asia. In addition, the groundwater of the Qinghai-Tibet Plateau represent an important part of China's water resources, with a high abundance of underground geothermal resources. Since 1978, there have been more than 20 artesian wells with a depth of 200~600 M in this area. Up to now, more than 10 hot water wells have been used as a drinking water source for humans and animals for a long time. An estimated 59,000 people are at risk from water-borne fluorosis and arsenic poisoning [9]. Shi [9] and Zhang [10] believed that fluoride in hot water exists in a confined artesian hot water in the Guide Group, and is controlled by structure, depth, and temperature [9,10]. The chemical types of geothermal water in the Guide basin are SO_4.Cl-Na. Instead, the local crustal partial melting or magma chamber at 15~35 km beneath the Gonghe basin is characterized by a relatively high geothermal background induced by the continental collision between the Indian and Eurasian plates [11]. δD and $\delta^{18}O$ indicated that the meteoric water is the most likely source of the geothermal water in the Zhacang field, with depleted δD and $\delta^{18}O$ in deeper water indicative of recharge via snow melt and/or from cooler climates [12]. In contrast, precipitation is the main recharge source for unconfined and confined groundwater in the study area, where the chemical composition of unconfined groundwater mainly derives from the weathering of silicate and the dissolution of carbonate in the aquifer, while that of confined groundwater is mainly controlled by the dissolution of evaporite, which increases along the flow path. The chemical composition of unconfined groundwater is variable seasonally, while the chemical composition of confined groundwater is temporally constant [13]. Dai [14] studied the convective geothermal water from five faults in the Guide Basin as the research object and comprehensively utilized the hydrochemical characteristics and the evolution of geothermal water in Guide Area, Qinghai, etc., suggesting that the water–rock interaction degree in Guide Basin is high, and the geothermal water comes from atmospheric precipitation [14]. Sun et al. [15] concluded that the enrichment degree of fluoride ions in the water of the hydrochemical type Na in Tibet geothermal water is higher than that of the water of the type of Ca. The enrichment mechanism of high fluoride geothermal water mainly includes the upwelling mixing of the deep geothermal fluid and the leaching of fluoride silicate minerals and fluorite during the downward seepage of make-up water [15]. Zhang et al. [16] suggested that the typical harmful elements in geothermal water in Tibet have an impact on river water quality [16]. The control function, hydrogeochemistry, and human health risks of basin-type high-fluoride groundwater have not been discussed in detail by the scientists in the context of the Qinghai-Tibet Plateau. This paper will discuss the hydrogeochemical effects of the spatial distribution of fluoride ion content on geothermal water and human health in the Guide Basin as an example, in order to study the occurrence and the mechanism of faulted basins in Qinghai-Tibet Plateau and the various risks caused by drinking water to provide a basic reference data for the development and utilization of geothermal energy in fluoride-rich areas.

The guide basin is located in the southeast of Hainan Tibetan Autonomous Prefecture, Qinghai province, approximately 97 km from Xining, and the basin is surrounded by mountains (the Lagrange in the north, and Chamah in the south). The terrain is high in the north and south, low in the middle, with an average elevation of about 3100 m. The water system is developed in the basin, where steep slopes, low mountains, and hills are common. The Yellow River enters from the Longyangxia Gorge in the western part of the basin. Tributaries flow into the northern and southern sides of the river, forming multi-level river and hilly landforms, where the two main largest tributaries flow into the Yellow River on the east and west sides of Guide County's seat. The confluence of these three tributaries form a wide valley plain called the "Sanhe plain" (Figure 1). On the other hand, the region is considered semi-arid continental climited, with an average annual temperature of 8.5 °C, with large diurnal variations. The annual average rainfall is 275.8 mm, and the precipitation mainly concentrates from June to September. Moreover, the mean annual potential evaporation is 1417.1 mm.

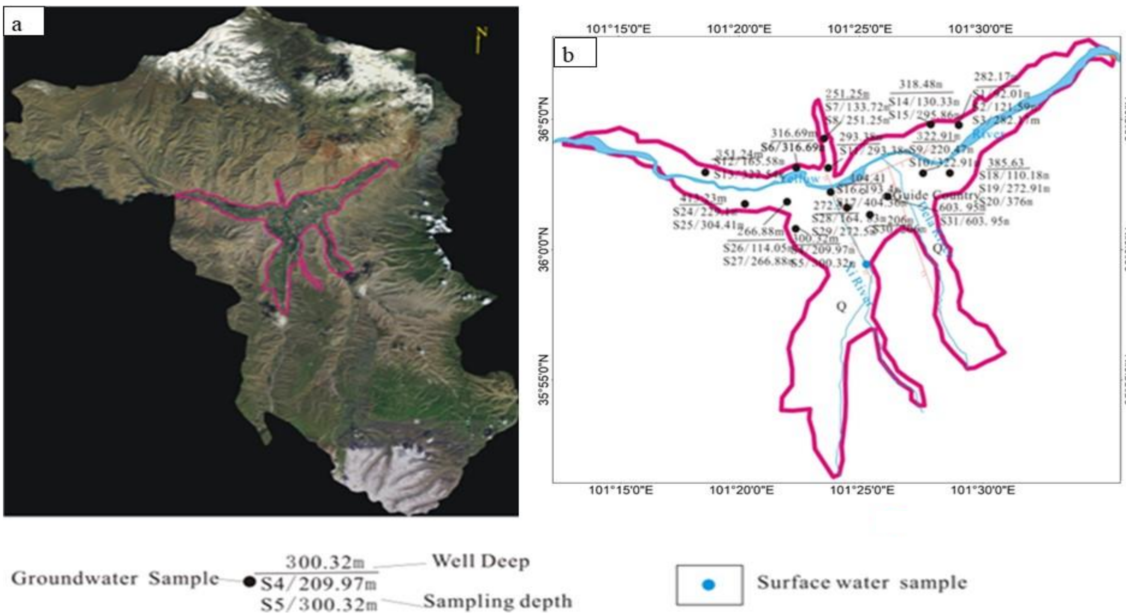

Figure 1. (**a**,**b**) Groundwater and surface water sampling distribution map, (**a**)—Remote sensing image map of the Guide Country.

2. Geological Setting

Proterozoic and Palaeozoic strata are exposed around the basin, Paleocene-Oligocene Xining Group, and Miocene-Pliocene Guide Group, which are in turn from bottom to top. Notably, the Neogene Guide Group and Quaternary have the widest distribution area and greatest thickness. The Neogene Guide Group not only includes a confined artesian water, but also confined artesian hot water (Figure 2) [17].

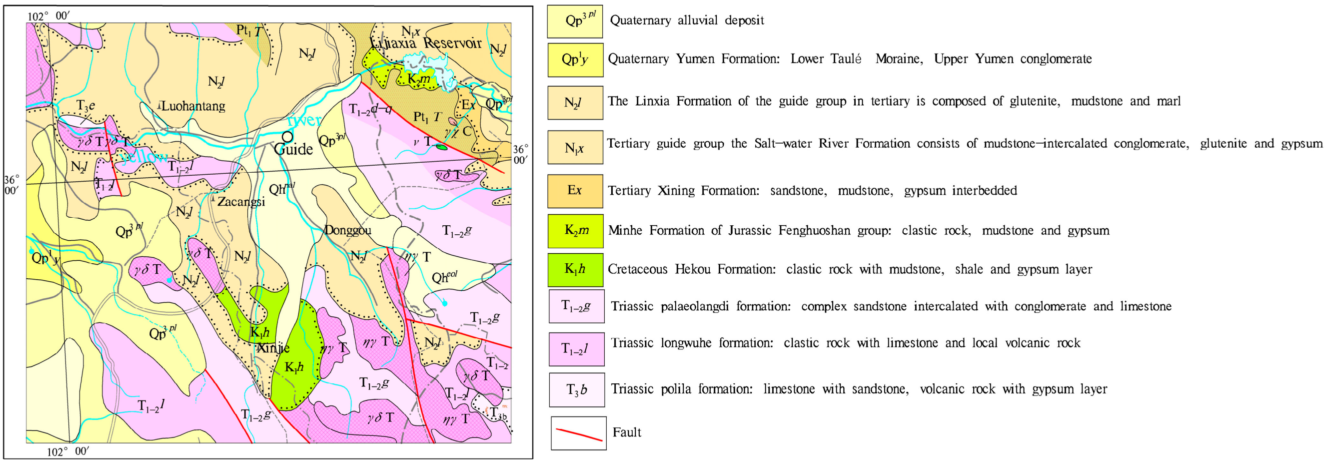

Figure 2. Geological map of Guide County.

Xining Group is composed of brownish-red mudstone, sandy mudstone, gray-green, gray-white gypsum rock, and sandy argillaceous gypsum rock interbedded with sandstone and siltstone convex mirror, which is a lacustrine gypsum-containing red clastic rock deposit in a dry climate.

Guide Group is a set of a stratigraphic sequence composed of khaki, brownish yellow mudstone, sandy mudstone, grayish white fine-medium conglomerate, gravelly sandstone, sandstone, and marlstone, and this sedimentary environment is composed of salt lakeside-brackish water or freshwater lakeside facies. This set of strata is widely distributed in the Guide Basin. Except for the local areas along the fault zone in the basin edge belt, it inclines slightly from the basin edge to the center of the basin. On the other hand, the upper part of the Guide area is covered by the Lower Pleistocene of Quaternary sediments.

The Neogene Guide Group was formed in the environment of saltwater lakeside-brackish water or freshwater lakeside in an arid and hot climate and is mainly composed of fine-grained lacustrine strata, which are rich in organic matter. Rock cutting statistics show that the sources of fluoride and arsenic in the strata are mainly Archean to Lower Proterozoic metamorphic rocks and volcanic rocks in the Riyueshan and Lajishan areas in the northern part of the basin [10]. The modern semi-enclosed topography and hydrogeochemical environment of underground hot water are the main promoting factors to form drinking water endemic fluorosis and arsenic poisoning areas.

The Guide Basin is dominated by fault structures, followed by fold structures. There are mainly NWW-oriented structures in the north, NW-oriented structures and NNW-oriented structures in the south-central part, and SN-oriented structures in the central and eastern margins, with the development of EW-oriented and NE-oriented structures.

3. Hydrogeological Characteristics

Hydrogeological characteristic can be divided into two main categories, the first part related to the type and properties of the water-bearing rocks and the second part related to the main groundwater conditions.

3.1. The Water-Bearing Rock Includes Four Essential Groups

(1) Loose Rock Pore Group:

This group is mainly distributed in the plain area of Sanhe Valley in the basin and emerges as pores of Quaternary loose alluvial proluvial. The loose sediment is thick, and the water quantity is controlled by the irregular recharge source. The variation in diving water level is affected by rainfall, river recharge, and burial depth.

(2) Clastic Rock Fissure Pore Group:

This group is mainly distributed in the red bed, hilly area, and presents in the fissures and pores of Paleogene clastic rocks. The lithology of this aquifer is mainly sand and conglomerate, with pressure bearing poor to good water quality.

(3) Granite Fissure Group:

This group is mainly distributed in the Zhongshan area in the west of the survey area and occurs in bedrock fissures or fault zones in Mesozoic clastic rocks and Indosinian intrusive rocks, with poor to good water quality.

(4) Frozen Layer of Water:

The frozen layer of water is mainly distributed in mountainous areas above 3800 m above sea level at the edge of the basin, and there are two modes of occurrence. The first mode occurs in moraine and ice-water deposits of the middle and late Pleistocene and Holocene, while the second occurs in Triassic sand slate and granite.

3.2. Groundwater Conditions (Recharge, Diameter, and Discharge)

The formation and circulation of groundwater in the study area are influenced by stratum lithology, geological structure, hydrometeorology, and other factors. According to the different types of groundwater, there are four main types of water in the study area:

(1) Porewater (Groundwater):

The groundwater is mainly recharged by rivers and a lateral supply of bedrock fissure water in mountainous areas. The runoff condition is controlled by topography, with horizontal runoff as a main factor, while the underground runoff is sluggish. Instead, the main ways of discharge are evaporation and discharge to the Yellow River.

(2) Pore fissure water:

The hilly area is a distribution area of clastic rock fissure pore water, with strong terrain cutting and well-developed valleys. Pore fissure water is laterally replenished by atmospheric precipitation and bedrock mountain areas, with discharge usually to the surface forming some springs in the valleys after a short run-off. The clastic fissure-confined artesian water occurs usually in a fault contact with bedrock mountain areas as a complex structure and extends to the Neogene water storage structure after being guided by a fault zone.

(3) Fissure water:

The mountainous area exhibits high elevation, strong weathering of rocks, and steep terrain with abundant precipitation, which is conducive to infiltration and replenishment of atmospheric precipitation and the formation of bedrock fissure water. During the process of groundwater migration and runoff along its fissures, there is some discharge into the valleys in the form of springs, whereas the residual is supplied to the fissure pore water of clastic rocks in the hilly area in a hidden way through stratum contact parts or pore water of Quaternary loose rocks.

(4) Frozen layer water

Frozen soil (rock) is widely developed in Zhongshan and Gaoshan areas about 3800 m above sea level and contains a frozen layer of water. Frequently, the groundwater in this area present seasonal phase changes of liquid and is solid in shallow depths of 1~20 m [14].

4. Occurrence of Geothermal Water

In general, the study area can be divided into fracture convection geothermal water and sedimentary basin geothermal water according to its geological environment and heat transfer mode. Meanwhile, the code for the geological exploration of geothermal resources (GB-T-11615-2010) stipulates that the temperature of cold water is <25 °C and that of hot water is ≥25 °C.

4.1. Fracture Convection Geothermal Water

Convective geothermal water is often distributed in the well-developed fault zone around the basin in the form of hot springs. The Waligong Mountain fault zone in the west is the most active geothermal area in the whole basin, with many hot springs, such as Qunaihai, Zhacang Temple, and Xinjie Hot Springs, with the highest temperature reaching the local boiling point of 93 °C. Furthermore, hot springs, such as Lancai, are also developed in the Duohemao fault zone on the east side.

4.2. Sedimentary Basin Geothermal Water

The geothermal water in the sedimentary basin is exposed as a geothermal well, which are distributed in the Sanhe Plain basin, with a width of approximately 6 km from north to south and a length of approximately 20 km from east to west. There are two NS-trending compressive fractures and one EW-trending tensile fracture in the plain. These fractures are good heat conduction channels. On the other hand, there are no hot springs exposed. The thermal reservoir in Sanhe Plain can be divided into three thermal reservoirs:

(1) The Neogene thermal reservoir cap is approximately 160~240 m thick, while the thermal reservoir section is approximately 180 m thick. The water content mostly is good, and the orifice temperature is approximately 18.5~28 °C, reaching 34.6 °C. In contrast, the geothermal gradient is generally approximately 6.67~9.70 °C/100 m, which is the low-temperature thermal reservoir.

(2) The buried roof depth of the Paleogene thermal reservoir cap is between 1200 and 1500 m, and the thickness of the thermal reservoir section is approximately 600~800 m, with good water-rich properties and high temperature.

(3) The buried top plate depth of Cretaceous and Jurassic thermal reservoirs is 2700~3400 m, and the thickness of thermal reservoirs is 1000~1600 m. The poor property of water and the low temperature of the thermal fluid can be attributed to the lack of water and heat [17]. More than 20 exploratory and mining combined hydrogeological boreholes with a depth of 200~600 m have been established out in the Guide area. The revealed confined artesian water of fissures and pores of clastic rocks in the basin mainly occurs in the Guide Group of Neogene, and the water-bearing rock group is composed of multiple aquifers, with complex distribution and water abundance. The confined artesian water mainly occurs in the siltstone of the Zhongyan Formation [9].

5. Methodology

The groundwater samples were obtained from the anysis data in some previous works [9] combined with the test results of "Investigation on Mineral Resources Development and Geological Environment Impact of Qinghai-Tibet Plateau" from 2012 to 2015 by Xi'an Geological Survey Center of China Geological Survey. The groundwater samples were taken in layers and preserved at 4 °C, and then to the lab for analysis within 4 days. An inductively coupled plasma spectrometer was used for groundwater quality analysis, and the contains of Na^+, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, and HCO_3^- were measured by double indicator-neutralization titration. The content of F^- in groundwater was analyzed by ion chromatography. All analysis was performed by the Qinghai Hydrogeological Engineering Geological Environment Geological Survey Institute. Hydrochemical components were compared with Chinese national groundwater quality guidelines [18,19] to assess their suitability for drinking water. Therefore, only drinking water intake was considered in this study. Fluoride is a non-carcinogenic risk factor. Therefore, the non-carcinogenicity evaluation risk model recommended by the US EPA [20] was used to evaluate the fluorine content in groundwater in the study area for health risks.

Based on the assessment results, F^- was selected to perform the non-carcinogenic health risk assessment using the model recommended by the U.S. Environmental Protection Agency (USEPA) [21], with parameter values suitable for the study area. In terms of exposure pathways of fluoride, drinking water intake was considered. The assessment model of intake-induced risks to health is as follows:

$$HQ = CD_i / RFD \quad (1)$$

where HQ denotes the hazard quotient of noncarcinogenic health risks, and $HQ > 1$ means high potential health risks that are unacceptable for adults and children.

The daily average exposure doses per unit weight (CD_i) through drinking water are expressed using CD_{id} and CD_{if}, respectively. They can be calculated as follows:

$$CD_{if} = (C_i \times Y_{fi}) / BW \quad (2)$$

$$CD_f = \Sigma CD_{if} \quad (3)$$

$$CD_{id} = (C_i \times IR \times EF \times ED) / (BW \times AT) \quad (4)$$

The calculation parameters are shown in Table 1.

Table 1. Parameters in the health risk assessment model.

Parameter	Meaning	Children	Adults	Reference Standards
C_i	Contaminant concentration in water			
IR	Daily intake of drinking water	1.0 L/d	0.6 L/d	
EF	Exposure frequency	365 days	365 days	
ED	Exposure duration	12 years	25 years	
BW	Body weight	15.9 kg	56.8 kg	USEPA 2017
AT	Average time for noncarcinogenic effect	4380 days	9125 days	
CD_i	Quotient			
RFD	non-carcinogenic reference dose of F^- through oral intake	0.03 mg/(kg·d)	0.06 mg/(kg·d)	
HQ	Non-carcinogenic risk			

6. Results and Discussion

6.1. Hydrochemistry and Water Quality Assessment

According to the statistical data of water samples listed in Table 2, both groundwater and surface water samples are slightly alkaline, with average pH values of confined geothermal water, while the phreatic water and surface water measure 8.5, 7.78, and 7.8, respectively. The salinity of groundwater and surface water is not high, but for confined geothermal water, phreatic water, and surface water, 706.0, 430.1, and 285.9 mg/L, respectively. Therefore, groundwater and surface water in Guide Basin are freshwater resources. The cations of underground hot water are mainly sodium and potassium ions followed by calcium and magnesium ions. The cations in phreatic water and surface water are mainly calcium ions and magnesium ions. The anions in groundwater and surface water mainly include SO_4^{2-} and HCO_3^- followed by Cl^-, indicating that the groundwater and surface water here is mainly leaching. The fluoride concentration in hot water under pressure is 0.43–5.7 mg/L, which is relatively high, while the fluoride content in diving water and surface water cannot be detected. The fluoride content in most of the confined hot water in the study area at 160–240 m exceeds the standard, except in the upper reaches of Xihe River and Donghe River. From an epidemiological point of view, excessive fluoride in drinking water will increase the risk of dental fluorosis and skeletal fluorosis (Figure 3b). Consequently, the drinking water must be treated to reduce fluoride concentration.

Table 2. Statistical analysis of physicochemical indices of samples against drinking water guidelines.

Index		TDS (mg/L)	pH	T	$Na^{+} + K^{+}$ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (mg/L)	F^{-} (mg/L)
Confined Geothermal water	Min.	379.8	7.35	18.5	113.1	4.4	0.3	15.5	44.8	82	0.4
	Max.	1393.2	8.9	41.4	368.1	48.8	5.3	406.1	901	411.5	5.7
	Mean	706.0	8.5	29.7	211.1	9.60	1.79	143.7	132.73	199.79	2.7
Phreatic water		430.1	7.78	9.5	2.8	21.5	74.6	13.1	26.4	49.4	0
Surface water		285.9	7.8	14.0	7.4	7.4	51.4	9.2	7.2	24.6	0
Chinese guidelines		1000	6.5–8.5		200	/	/	250	250	/	1
WHO guidelines		1000	6.5–8.5		200	/	/	250	250	/	1.5

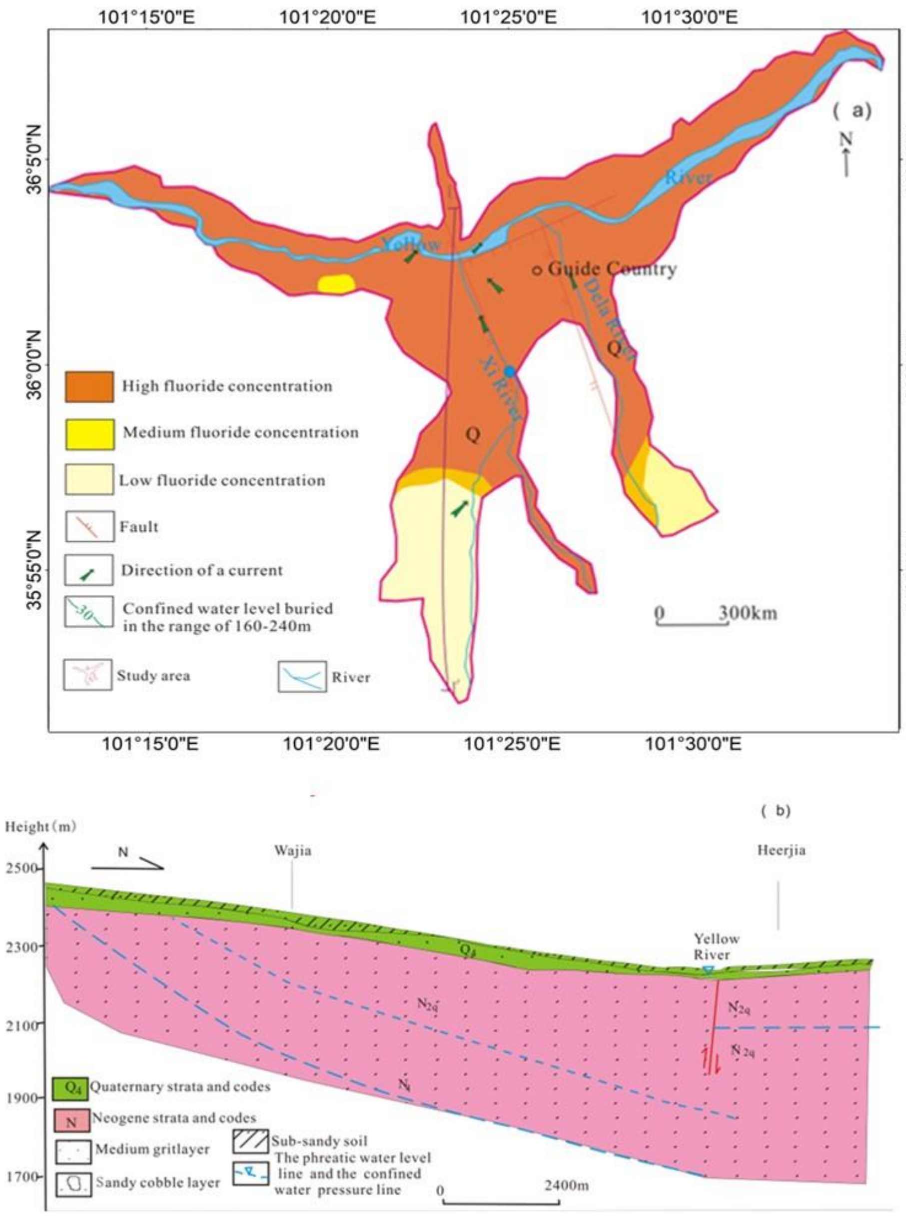

Figure 3. Spatial distribution of fluoride in groundwater. (**a**) Spatial distribution of fluoride in groundwater in Sanhe plain of Guide Country (The depth is 160–240 m under confined Geothermal water) (**b**) Hydrogeological section.

6.2. Hydrogeochemical and Their Influencing Factors

6.2.1. Dominant Zones of Hydrogeochemical Process

The Gibbs diagram was used to further analyze the fluoride sources of water samples. (Figure 4). All water samples fell within the dominant zone of rocks, indicating that the chemical properties of the groundwater and surface water in the study area are controlled by weathering or the rock and water–rock interactions. In contrast, the groundwater samples which fall in the partially balanced or mixed water area indicate that the geothermal water may be mixed with cold water near the surface (Figure 5).

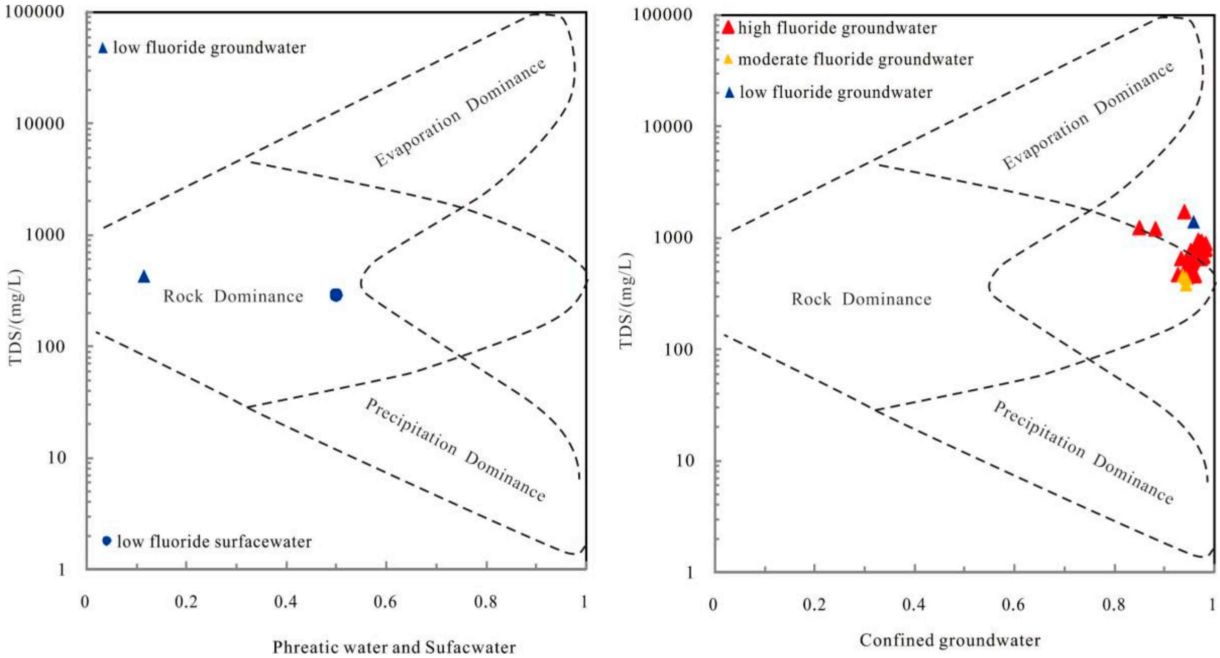

Figure 4. Gibbs diagram showing the control mechanisms of natural water chemistry.

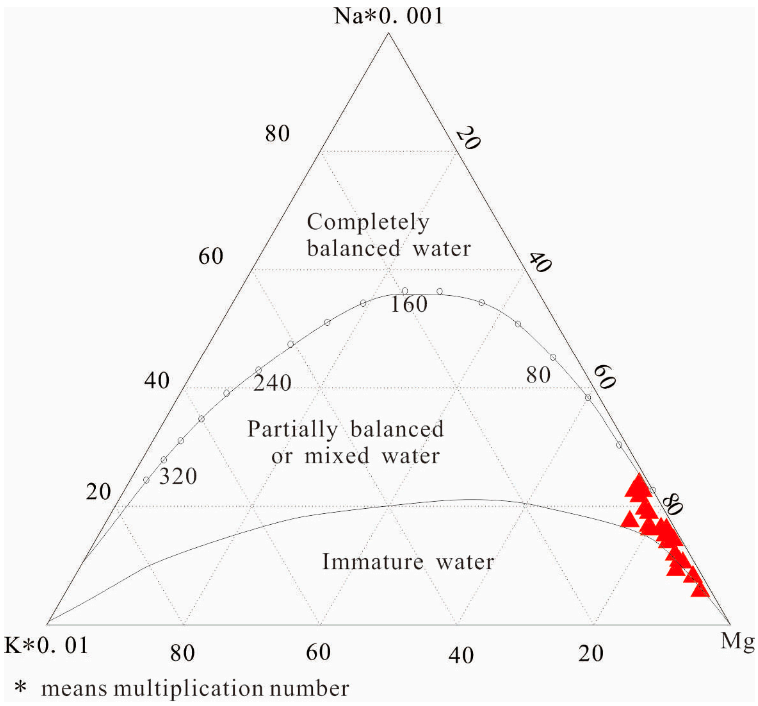

Figure 5. Geokit diagram showing the mixing mechanism of pressurized geothermal water and other types of water.

6.2.2. Impacts of pH

In geothermal water, fluorite (CaF_2) is one of the most vital minerals because it will react to produce fluoride ion (F^-), which can react with calcium ion Ca^2 [22]. The reaction formula is as follows:

$$CaF_2 \rightarrow 2F^- + Ca^{2+} \quad (5)$$

Groundwater with high pH can dissolve aluminosilicate minerals, so the alkali metal hydrolysis will increase the alkalinity of water and promote the dissolution of fluorosilicate minerals, e.g., fluorite and fluorosilicate minerals, then release fluoride to increase the fluoride content in groundwater. Therefore, the higher the pH of groundwater, the more beneficial it is to the enrichment of fluoride [23]. According to the investigation, the pH value of pressurized geothermal water in the study area is between 7.35 and 8.9, and the pH value of surface water is 7.8, which can facilitate the dissolution of fluoride-containing minerals. On the other hand, a Pearson correlation matrix showed that fluoride is positively correlated with sodium (r = 0.583) and bicarbonate (r = 0.629) (Table 3). Consequently, it can be inferred from Pearson correlation matrix that the fluoride-rich groundwater is highly alkaline and low in hardness [24]. The range of water hardness in the study is 5–51.2 mg/L, which is below the national drinking water standard of 450 mg/L. Furthermore, in alkaline environments, hydroxyl can replace fluoride-containing minerals, such as biotite and muscovite [25], which leads to an increase of the fluoride content in the groundwater. The main rock type in Zhacangsi geothermal field is granite, which mainly contains quartz, mica, and feldspar [26]. Moreover, the Guide County Basin is a geothermal anomaly area with characteristics of both structural fault-type thermal anomaly and structural basin-type thermal anomaly. The heat source of the Piedmont Zone in the southwestern part of the basin is Indosinian Granodiorite [27]. There are a lot of biotite/muscovite/chrysotile in granite. The exchange between hydroxyl and biotite/muscovite/chrysotile asbestos is as follows:

$$KMg_3(AlSi_3O_{10})F_2 + 2OH^- \rightarrow KMg_3(AlSi_3O_{10})(OH)_2 + 2F^- \quad (6)$$

$$KAl_2\ (AlSi_3O_{10)}F_2 + 2OH^- \rightarrow KAl_2(AlSi_3O_{10})(OH)_2 + 2F^- \quad (7)$$

$$Na_3A1F_6 \rightarrow 6F^- + 3Na^+ + A1^{3+} \quad (8)$$

Table 3. Pearson correlation matrix of hydrogeochemical parameters of confined geothermal water in guide basin.

	pH	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**Cl^-**	**$SO_4{}^{2-}$**	**$HCO_3{}^-$**	**F^-**
pH	1	−0.664 **	−0.669 **	−0.737 **	−0.316	−0.737 **	−0.079	−0.163	−0.151
K^+		1	0.616 **	0.823 **	0.364 *	0.772 **	−0.005	0.110	0.194
Na^+			1	0.411 *	0.469 **	0.699 **	0.004	0.635 **	0.583 **
Ca^{2+}				1	0.106	0.772 **	0.198	−0.315	−0.127
Mg^{2+}					1	0.410 *	−0.208	0.526 **	0.125
Cl^-						1	0.169	0.037	0.126
$SO_4{}^{2-}$							1	−0.215	−0.384 *
$HCO_3{}^-$								1	0.629 **
F^-									1

Notes: ** Correlation is significant at the 0.01 level (2-tailed). *: Correlation is significant at the 0.05 level (2-tailed).

6.2.3. Hydrochemical Environment

The enrichment of fluoride in water is controlled by a specific hydrochemical environment. A Piper diagram (Figure 6) was plotted to understand the impacts of the hydrochemical facies on the fluoride enrichment in water, as well as the high-fluoride groundwater mainly distributed in areas with Na^+ contents (meq) > 80%; and $HCO_3{}^-$

contents (meq) > 60%. Hydrochemistry analysis of geothermal fluids shows that the high-temperature thermal water is mainly of $SO_4 \cdot Cl$–Na type, and the low-temperature thermal water is mainly composed of SO_4–Na, $SO_4 \cdot HCO_3$–Na. The piper diagram indicates that F^- enrichment is usually associated with high HCO_3^- and Na^+ concentrations in water (Figure 5), while a high Ca^{2+} concentration tends to lower the F^- concentration in water. Therefore, fluorite (CaF_2) can be dissolved and F^- is released into groundwater with Na-bearing salts, or alternatively F^- can react with Ca^{2+} to form fluorite (Figure 7).

Fundamentally, the concentrations of major ions are the most affected factor in the hydrochemical environment. As shown in the Pearson correlation matrix (Table 3), HCO_3^- is significantly correlated with Mg^{2+} (r = 0.526) and the saturation index is lower than 0, indicating that carbonate mineral dissolution is an essential process in the groundwater system. This is consistent with the result of Wang Zhen's research, which promotes the increase of bicarbonate chemical compositions of confined groundwater. This process is controlled mainly by the dissolution of evaporite, which commonly increases along the flow path [13]. Moreover, the ion exchange between calcium ions and sodium ions may lead to fluoride enrichment in natural water. As mentioned above, high-sodium and low-calcium water are favorable for fluoride enrichment, and thus the changes in sodium and calcium concentrations caused by ion exchange will inevitably affect fluoride behavior. In this study, the binary graph of Na^+-Cl^- vs. (Ca^{2+} + Mg^{2+})-(HCO_3^- + SO_4^{2-}) is utilized to explain the cation exchange process [2]. This shows that there is a linear relationship between Na^+-Cl^- and (Ca^{2+} + Mg^{2+})-(HCO_3^- + SO_4^{2-}), with a slope of −0.279 (r = 0.767). The slope is far less than 1, indicating that the ion exchange is not too strong, and most of the samples are located in the cation exchange control area rather than the anion exchange area, which indicates that the exchange of Na^+ and Ca^{2+}/Mg^{2+} may occur in the study area (Figure 7a). Indeed, this is good evidence that the cation exchange plays an important role in regulating the chemical evolution of natural water. Additionally, the positive correlation between F^- and Na^+/Ca^{2+} ratio with a slope of 0.002 (r = 0.563) indicates that the cation exchange between Na^+ and Ca^{2+} affects the fluoride enrichment in the study area (Figure 7b).

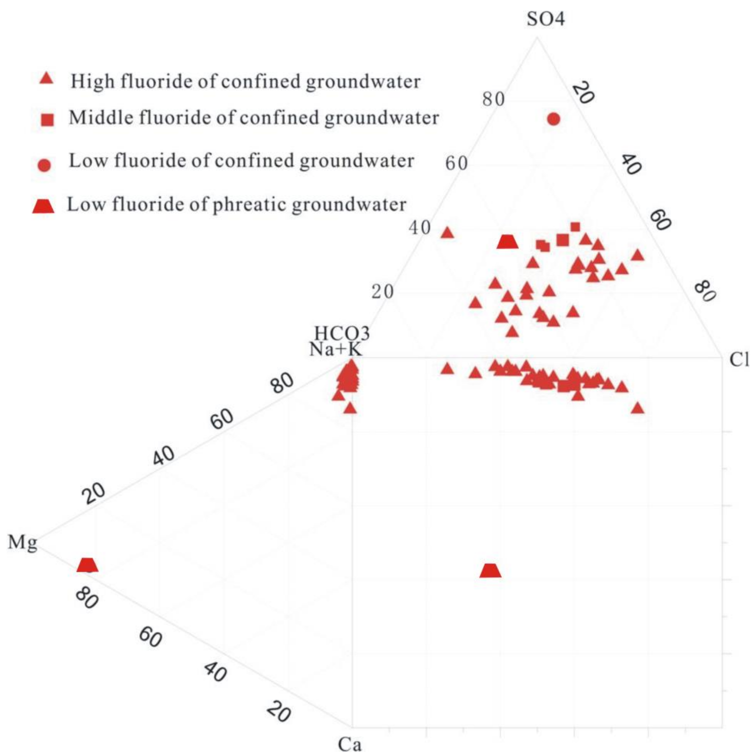

Figure 6. Piper diagram showing the hydrochemical characteristics of groundwater.

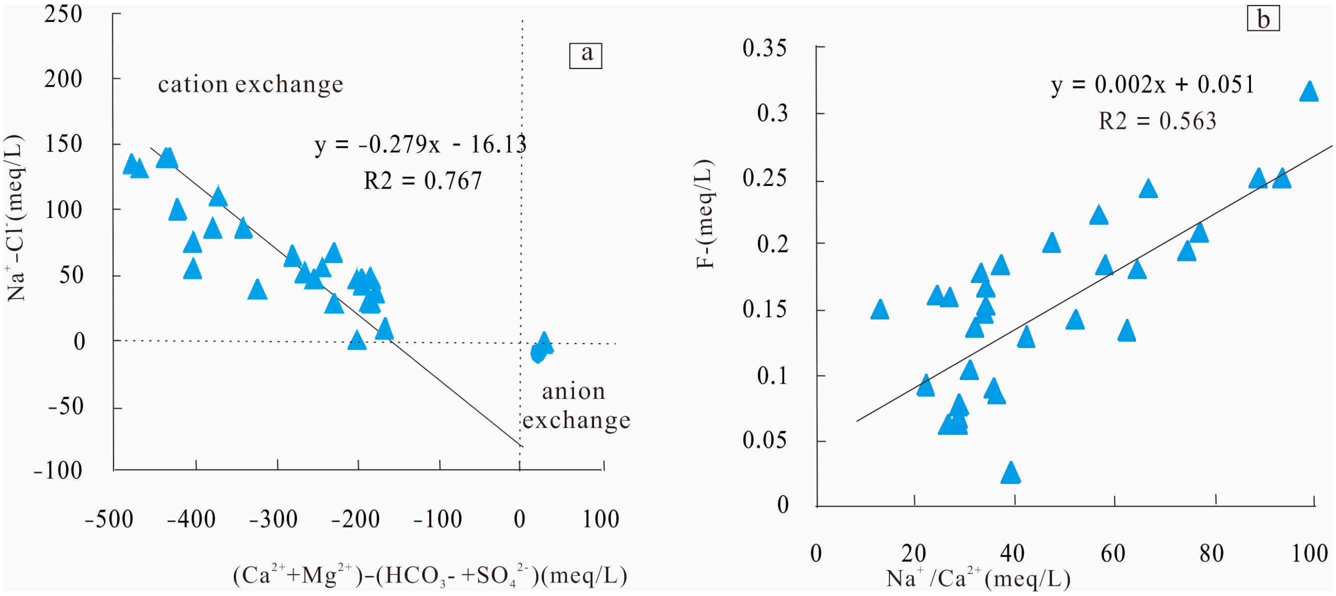

Figure 7. Bivariate plots showing ion exchange and its impacts on fluoride enrichment. (**a**) The relationship between major chemical components in groundwater. (**b**) The relationship between Na/Ca and fluoride ion.

6.2.4. Saturation Index of Minerals

The sedimentary lithology of the confined aquifer in the Guide basin is mainly composed of dark gray mudstone, earthy red clay, and dark gray fine sand. Furthermore, the main minerals in the composition are quartz, aragonite, mica, and albite. In addition, the Xining Group (Exn) is composed of reddish-brown mudstone, sandy mudstone, lime-green gypsum, lime-white gypsum, sandy argillaceous gypsum, and siltstone convex body. The rock composition of each stratum is mainly a set of flysch clastic rocks, siliceous rocks, some carbonate rocks, and a few volcanic rocks, which constitute the main provenance of Cenozoic basins in the southern and northern margin of the basin. The dissolution or precipitation of minerals depends on the saturation indices of minerals, which are used to denote the saturation state of water relative to minerals and indicate the dissolution or precipitation behavior of minerals. On the other hand, the impacts of mineral saturation on fluoride enrichment can be understood by calculating the saturation indices of fluoride bearing minerals, such as dolomite, calcite, gypsum, and fluorite. The dissolution behavior of these minerals was notably interdependent since they all contain calcium ions. The low solubility of gypsum will lead to the high solubility of fluorite [28]. Furthermore, the saturation index of calcite varied from −3.53 to 0.74, and that of dolomite ranged from 6.03 to 0.3, indicating that dolomite and calcite are unsaturated or close to saturation. The saturation index of gypsum was −3.62~−1.6, indicating that gypsum is also unsaturated. This implies that calcite, dolomite, and gypsum can continue to dissolve and release Ca^{2+} into groundwater, which will affect the fluoride enrichment in natural water (Figure 8). The saturation index of fluorite ranged from −3.37 to 0.01, indicating that fluorite is unsaturated. Meanwhile, fluorite dissolution contributes to an increase in fluoride content. This can be confirmed by the logarithmic positive correlation between fluoride and fluorite saturation index (R^2 = 0.851).

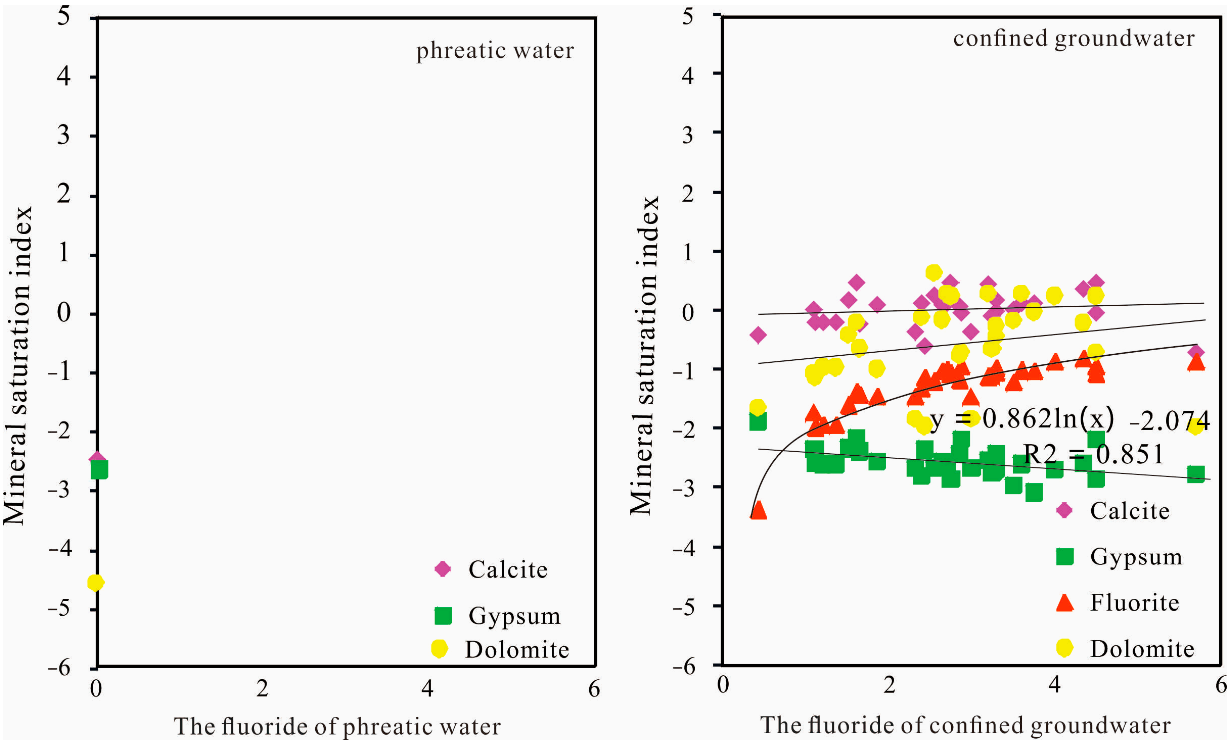

Figure 8. Relationships between F− and saturation indices F-bearing minerals (calcite, dolomite, gypsum, and fluorite).

6.3. Health Implication of Fluoride in Water

As proposed by the WHO, fluoride mainly affects human health in three ways, namely drinking water, skin contact, and food intake. The health risk of fluorine exposure through skin and air is very small [29]. This study focuses on the risks to the health of adults and children caused by excessive fluoride in drinking water. Table 4 shows that the HQ values of fluoride in confined geothermal water are between 0.54–7.17 (average: 4.12) and 0.25–3.35 (average: 1.62), respectively for children and adults. While the HQ values of fluoride in phreatic water and surface water were both 0. This indicates that the risks of fluoride through drinking confined geothermal water intake are unacceptable.

Table 4. Fluoride contents of drinking water and their non-carcinogenic health risks for adults and children.

Water	Sample Number	Statistic Parameter	Health Risks for Children	Health Risks for Adults
Confined Geothermal water	31	Average Maximum Minimum	4.12 7.17 0.54	1.62 3.35 0.25
phreatic water	1	concentration	0	0
surface water	1	concentration	0	0

Normally, if the fluoride content in water is lower than 0.5 mg/L, children will easily get dental caries after drinking for a long time. However, the formula developed by the USEPA [26] is imperfect and only aims at a design higher than the safety threshold. The authors think that the relative risk to human health can be adopted. Specifically, the fluoride concentration is expressed as the difference between the test concentration and the safety threshold concentration. Additionally, the calculated risk value is the relative risk to human health. More precisely, if the fluoride content is lower than 0.5 mg/L, there will be risks. However, there will be no risk within the safety thresholds.

Table 5 shows that the HQ values of fluoride in phreatic water and surface water for children and adults respectively were 0.63 and 0.29, respectively, while the HQ values of fluoride in confined geothermal water are between 0.00–5.28 (average: 1.67) and 0.00–2.46 (average: 0.78).

Table 5. Fluoride contents of drinking water and their modified non-carcinogenic health risks for adults and children.

Water	Sample Number	Statistic Parameter	Health Risks for Children	Health Risks for Adults
Confined Geothermal water	31	Average	1.67	0.78
		Maximum	5.28	2.46
		Minimum	0.00	0.00
phreatic water	1	concentration	0.63	0.29
surface water	1	concentration	0.63	0.29

As for the prevention and control measures in respect of fluoride in groundwater. The groundwater treatment should be conducted to reduce fluoride concentration in drinking water. It is suggested that when confined geothermal water is used as drinking water, it should be mixed with phreatic water and surface water in a certain proportion to make the fluoride in groundwater reach the range of safe drinking water.

7. Conclusions

High fluoride geothermal water has become a major public health problem in many areas of China, especially in the Qinghai-Tibet Plateau areas. In this study, the reasons for fluoride enrichment were revealed according to the hydrochemical characteristics of natural water in the confined geothermal water in faulted basins in the Qinghai-Tibet Plateau, and the potential human health risks of fluoride in drinking water were quantified. The conclusions are as follows.

(1) As indicated by the analysis of the Gibbs diagram concerning fluoride, the fluoride in groundwater is mainly related to the water–rock interaction. These geothermal waters may be mixed with near-surface cold water.
(2) The hydrogeochemical factors of fluoride enrichment in confined geothermal water mainly include specific natural factors, such as pH, ion exchange, and mineral saturation.
(3) The groundwater in the study area is slightly alkaline compared with the drinking water quality standards of China and the WHO. The confined water in the Guide basin presents high fluoride concentration (0.43–5.7 mg/L), while phreatic water and surface water present fluoride levels that are too low to drink. It is suggested that for Department of Water Resources Management that when confined geothermal water is used as drinking water, it should be mixed with phreatic water and surface water in a certain proportion to make the fluoride in groundwater reach the range of safe drinking water.
(4) Excessive fluoride in drinking confined geothermal water will cause health risks in adults and children. According to this study, fluoride is an element that causes great risks to human health over time in general. The HQ highest value of fluoride in confined geothermal water was 5.28. Meanwhile, children face higher health risks than adults caused by water drinking intake. Therefore, measures should be taken to ensure the health and safety of residents. Human health requires a groundwater fluoride concentration of less than 0.5 mg/L, which offers greater protection. This provides a reference basis for water management.

Author Contributions: R.L., Y.X. and H.Z. carried out the investigation, experiments, and sampling. R.L. wrote the manuscript. J.J. and F.L. helped R.L. Conceivably the original idea. R.M.E.-W. polished English manuscripts. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by Key R & D projects in Shaanxi Provincein 2023 (2023-ZDLSF-63), the survey projects initiated by the Land and Resources Investigation Project ([2023]06-03-04), and Basic Research Project of Scientific Research Business Fee of Central University in 2016 (Open Fund) 310829161128. Investigation on geological environment effect of Qinghai mining industry development (121201011000150022). The Qinghai-Tibet scientific research project "Geological Background Investigation of Freeze-thaw Disaster Development in Permafrost Regions of Qinghai-Tibet Plateau (2019QZKK0905)", Xi'an ecological Safety Investigation Evaluation and Risk Management Demonstration (DD20201317), and Xi'an Multi-factor Urban Geological Survey (DD20189220), Key Research and Development Program of Shaanxi (Program No. 2021ZDLSF05-01).

Data Availability Statement: The data is unavailable due to privacy can not be Published.

Acknowledgments: The authors are grateful to the experiment and testing lab of Xi'an Center, China Geological Survey for statistical data analyses. Thank you very much S.J. Assisted Sampling who coming from Qinghai Institute of Hydrogeology and Engineering geology and Environmental geology.

Conflicts of Interest: The authors declare no conflict of interest.

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