

Article

Distribution, Formation and Human Health Risk of Fluorine in Groundwater in Songnen Plain, NE China

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Abstract: Songnen Plain is one of the three great plains in northeast China with abundant groundwater resources. The continuous population growth and the rapid development of agriculture and economy in China has caused a series of environmental problems in the plain, such as endemic diseases caused by the accumulation of harmful substances in drinking water. This paper conducts a systematic investigation of fluorine in the groundwater of Songnen Plain. The results showed that fluorine was widespread in the groundwater of the plain in the concentration range of BDL–8.54 mg·L⁻¹, at a mean value of 0.63 mg·L⁻¹ and detectable at a rate of 85.91%. The highest concentrations of fluorine were found in central and southwest areas of the plain. The concentration exceeded the guideline values for fluorine in drinking water and may have varying degrees of adverse effects on adults, and especially children, in the study area. The fluorine in groundwater mainly came from the dissolution of fluorite and other fluorine-containing minerals, and the concentrations and distribution of fluorine were affected by cation exchange, groundwater flow field and hydrochemical indexes (pH, TDS and HCO₃⁻). The study provides scientific basis for the investigation, evaluation and prevention of endemic diseases caused by fluorine.

Keywords: Songnen Plain; groundwater; fluorine; distribution; formation; human health risk



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1. Introduction

Water is an important natural resource to guarantee normal human life and socio-economic development. As one of the main components of water resources, groundwater is exerting a more and more significant influence on society, and groundwater is also a prerequisite for the development of other resources, especially in arid and semi-arid areas [1]. However, the accumulation of harmful elements caused by geological causes or human activities not only harms the water environment, but also seriously affects the safety of drinking water [2,3]. Fluorine is an essential element of the human body and moderate intake (0.5–1.5 mg·L⁻¹) is beneficial to human health, according to the WHO guidelines [4–6]. However, excessive fluoride, after long-term consumption may lead to fluorosis, and it is also a serious problem for the world's geological environments [2,7]. Studies have shown that over 260 million people are at risk of fluorosis all over the world, reported in locations such as America, Argentina, China, Mexico, and India [8–13]. Therefore, the research on high fluorine groundwater have gradually become a research focus.

Drinking water is the primary route by which fluoride enters the human body [14]. The National Health Commission of the PRC [15] and the WHO [16] guidelines have set values for fluorine in drinking water at 1.0 and 1.5 mg·L⁻¹, respectively. Fluorine is widespread in natural minerals, such as fluorite, cryolite, fluorapatite, etc. [8,9,17]. Studies have shown that the main reason for the formation of high-fluorine groundwater in many regions of the world is dissolution of fluorine-bearing minerals [18–20]. However, the

distribution, formation and risk of high-fluorine groundwater in Songnen Plain, China have not been systematically studied.

Songnen Plain is one of the largest and most fertile plains in China, and an important agricultural production base [21,22]. The plain has a large groundwater aquifer system with multiple aquifers and abundant groundwater resources [23]. With the continuous growth of population and the rapid development of agriculture and economy, the contradiction between supply and demand of water resources is becoming more and more prominent in the area [24], and has caused a series of environmental problems, such as metal pollution [25], nitrate pollution [26,27], and endemic diseases caused by excessive content of fluorine, iodine and arsenic [28,29].

In this paper, the high content of fluorine in the groundwater of Songnen Plain is investigated systematically. Through a series of processes such as field sampling, index determination, sample preservation, pretreatment, detection and data analysis, the concentration, distribution, formation and human health risk of fluorine in groundwater in Songnen Plain are revealed. This provides scientific basis for the investigation, evaluation, and prevention of endemic diseases caused by fluorine.

2. Materials and Methods

2.1. Study Area

Songnen Plain is in the northeastern part of China and located at longitude $121^{\circ}21'–128^{\circ}18'$ and latitude $43^{\circ}36'–49^{\circ}26'$. Songnen Plain is an important grain commodity production base and animal husbandry base of China. It covers an area of 103,200 km², and is placed in the Songhua River basin. The plain evolved from the Mesozoic-Cenozoic faulted basin and has accumulated over 8 km of Cretaceous terrestrial clastic deposits. Gravel, sand and loam are the main components of strata in the study area, and cohesive soil interlayers are locally distributed [1,26]. Analysis of the strata minerals revealed that fluorine-bearing minerals are rich in the central and southwest strata of the plain, mainly including fluorite, apatite, cryolite, topaz, biotite, hornblende, tourmaline [26]. The regional groundwater resources are abundant and the largest groundwater system of the entire aquifer includes Neogene fissure-pore water, Cretaceous pore-fracture water, Quaternary pore water and Paleogene fissure-pore water. Irrigation and precipitation constitute the main sources of local groundwater recharge [30]. The shallow groundwater (depth is less than 50 m) are greatly affected by anthropogenic activities, complicated and changeable chemical composition. With the rapid development of agriculture and industry in northeastern China, groundwater exploitation in this region is expanding and, coupled with decreasing precipitation, the water table is declining and the groundwater environment in the study area changed greatly.

2.2. Sampling

In this paper, a comprehensive groundwater pollution survey was carried out in Songnen Plain from 2012 to 2014. Sampling time was concentrated in May to October each year, due to the cold winters in northeast China. Groundwater sample collection in the study area relied on local mechanized wells. A total of 2683 groundwater samples were collected; their locations are shown in Figure 1. Prior to groundwater collection, the original well water was pumped more than three times to flush the well's pump [3]. The sampling bottles (500 mL) were made of polyethylene plastic and were soaked in a 10%-sodium hydroxide solution for 3 h [11], then cleaned with deionized water and distilled water in turn, and finally dried at 60 °C for 5 h and stored in ziplock bags. Additionally, 2 mL of concentrated nitric acid (1:1) was added to the sampling bottle for measuring heavy metals [26]. Then, 2 mL of concentrated sulphuric acid (1:1) was added to the sample bottles for the measurement of Fe and Mn [1]. The sample bottles were washed three times with the corresponding water before each sampling. Each water sample collected was refrigerated at -4°C , and handled within 48 h. Unstable parameters, such as water temperature (T), pH, electrical conductivity (EC) and also water-table depth were measured in situ.

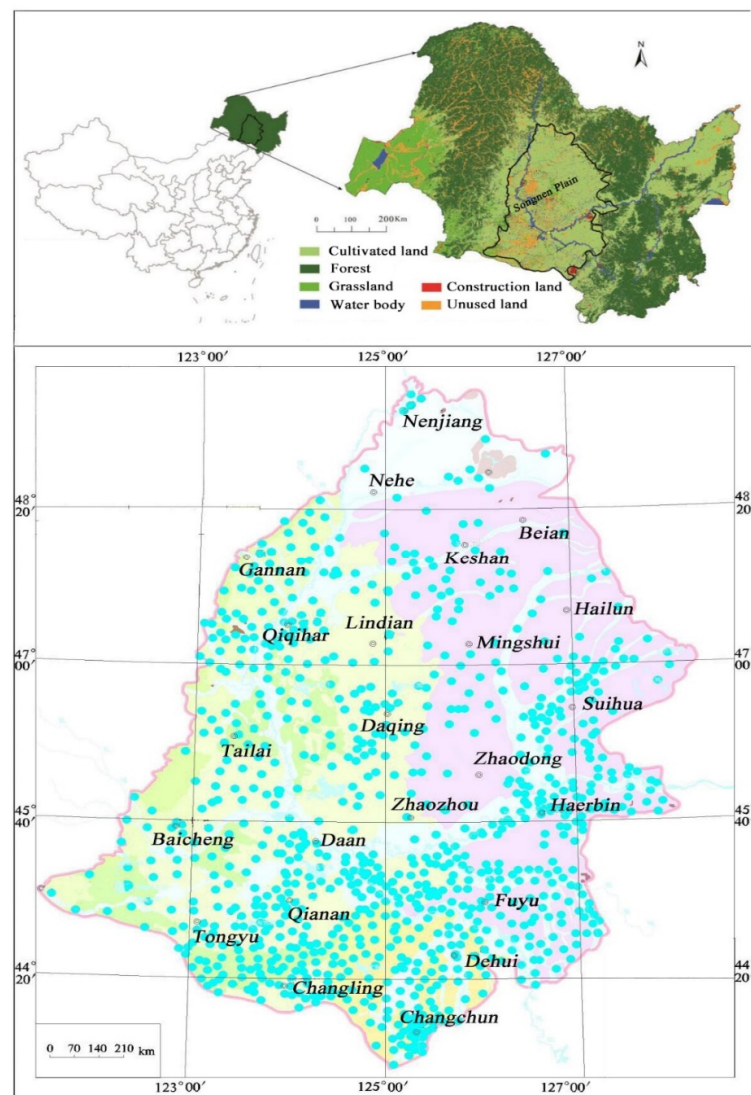


Figure 1. Location of sampling points in the study area.

2.3. Analysis Methods

2.3.1. Data Analysis Method

In this paper, a variety of data analyses are reported; a hydrochemical analysis, simulation methods, spatial analysis and mapping software are used herein to process the large volume of groundwater-sample testing data collected. The comprehensive parameters that can reflect groundwater characteristics and kriging method in statistics are selected as spatial interpolation method. Based on variogram theory and structural analysis, the comprehensive parameter zoning maps of groundwater at each layer are drawn with the help of ArcGIS and Surfer professional mapping software. The SPSS software was used to carry out descriptive statistical analysis on the main components of the sampled groundwater. SUPCRTBL and PHREEQC were used to calculate the saturation index (SI) of various rocks in combination with the latest database.

2.3.2. Instrumental Analysis

The instrumental analysis method used for the determinations of the water samples is referenced from a previous study [1,26]: the pH and redox potential were determined by dual-channel multi-parameter water quality analyzer (HQ40D, Field Case, cat. No:58258-00, HACH, Loveland, CO, USA); K, Ca, Na, Mg, Mn and Fe concentrations were measured by ICP-AES (IRIS Intrepid II XSP, Thermo Scientific, Waltham, MA, USA); the concentrations

of Cl^- and NO_3^- in the water samples were measured by ion chromatograph (Dionex2500, Dionex, Sunnyvale, CA, USA).

2.3.3. Saturation Index

The saturation index (SI) is, itself, derived from the formula of a theoretical derivation and used to describe the equilibrium state of the water with respect to mineral phases therein and to determine the dissolution or precipitation of minerals in rock–water interactions [31,32]. The index was calculated by Equation (1):

$$SI = \log \left(\frac{IAP}{K_s} \right) \quad (1)$$

where IAP is the ion activity product of the solution and K_s is the solubility product of the mineral. Different SI values indicate different states of ion in solution: $SI > 0$ indicates oversaturation (precipitation), $SI = 0$ indicates equilibrium and $SI < 0$ indicates undersaturation (dissolution).

2.3.4. Human Health Risk Assessment

A human health risk assessment consists in determining potential adverse effects of a target pollutant. The health risk assessment model (RBCA) was created to assess non-carcinogenic risks. We have mainly referred to oral exposures to pollutants in this study because the mouth is considered the primary route thereof. The calculations of non-carcinogenic risk (hazard quotient, HQ) of directly consuming water resources were extrapolated from the oral reference dose (RfD), hazard index (HI) represents the total non-carcinogenic risk to humans when the ADI (average daily intake) was unavailable, as shown in Equation (2). $HI > 1$ indicates that the exposed individual was adversely affected.

$$HQ = \frac{EDI}{RfD} = \frac{CS \times IR \times EF \times ED}{BW \times AT \times RfD} \quad \text{and} \quad HI = \sum_{i=1}^n HQ_i \quad (2)$$

where CS ($\text{mg} \cdot \text{L}^{-1}$) is the concentration of OPPs in the water; IR is the average daily water intake (1.5 and $0.7 \text{ L} \cdot \text{d}^{-1}$ for adults, children, respectively); EF stands for exposure frequency ($365 \text{ d} \cdot \text{y}^{-1}$). The ED s (exposure durations) for children and adults were 12 and 30 years, respectively; BW s (body weights) for children and adults were 10 and 60 kg, respectively [16]. AT represents average lifetime, and was 4380 and 1095 days for adults and children, respectively. RfD stands for the reference dose of the carcinogen consumed orally. The value of the RfD for fluoride was $0.04 \text{ mg} \cdot \text{kg}^{-1} \cdot \text{day}^{-1}$ [33,34].

2.4. Quality Assurance/Quality Control (QA/QC)

In order to make sure the accuracy of the measurement results, blank samples and standard samples were taken from each batch during sampling. After analysis, the standard deviations ranged from 0.09% to 0.23% and the target pollutant was not detected in the blank samples, which conformed to the stated data processing standards [35,36]. In determining groundwater quality parameters, the recovery indicator was added before the water sample was processed; samples' recovery rates ranged from 84.4 to 95.7%, and the average was 89.4%; moreover, we compiled the standard curve for target objects and the results of the analysis show that the correlation coefficient of the linear equation was over 0.99; all conformed to quality assurance standards for the processing of groundwater [37,38].

3. Results and Discussion

3.1. Hydrochemical Parameters and Types

The concentrations of hydrochemical parameters are shown in Table 1. The main cations in groundwater in the study area were Ca and Na, the concentration of Ca ranged from 1.56 to $567.65 \text{ mg} \cdot \text{L}^{-1}$, with an average of $95.04 \text{ mg} \cdot \text{L}^{-1}$ and the concentration of Na ranged from 4.51 to $1107.36 \text{ mg} \cdot \text{L}^{-1}$, with an average of $74.45 \text{ mg} \cdot \text{L}^{-1}$. According to the

groundwater index detection values, the Piper diagram of groundwater hydrochemistry types in the study area was drawn in Figure 2. Generally speaking, the main groundwater chemical type in the study area was HCO₃–Ca type [1], accounting for 24.83% of the total water samples. Other main groundwater types include HCO₃–Ca·Mg type, HCO₃–Na·Ca type, HCO₃–Na·Mg·Ca type and HCO₃·Cl–Ca type, accounting for 19.43%, 16.78%, 13.92%, 12.11% and 9.56% of the total water samples, respectively.

Table 1. Concentrations of hydrochemical parameters and saturation indexes of minerals.

Parameters	Concentration		
	Minimum	Maximum	Mean
K ⁺ (mg·L ⁻¹)	0.85	234.18	8.55
Na ⁺ (mg·L ⁻¹)	4.51	1107.36	74.45
Ca ²⁺ (mg·L ⁻¹)	1.56	567.65	95.04
Mg ²⁺ (mg·L ⁻¹)	2.43	589.88	36.77
HCO ₃ ⁻ (mg·L ⁻¹)	11.61	1838.05	354.69
SO ₄ ²⁻ (mg·L ⁻¹)	0.19	1198.79	86.93
Cl ⁻ (mg·L ⁻¹)	BDL	1831.56	113.45
NO ₃ ⁻ (mg·L ⁻¹)	BDL	1751.89	100.23
TH (g·L ⁻¹)	0.15	2.44	0.98
TDS (g·L ⁻¹)	0.58	6.17	1.46
pH	5.76	9.99	7.37
F ⁻ (mg·L ⁻¹)	BDL	8.54	0.63
SI (Flourite)	-5.57	-0.48	-1.88
SI (Calcite)	-1.87	-0.10	-0.98
SI (Gypsum)	-6.01	3.11	-0.79
SI (Halite)	-7.16	-0.05	-3.08
SI (Dolomite)	-2.80	-0.35	-1.01

Unit: BDL = below detection limit. TH: total hardness; TDS: total dissolved solids.

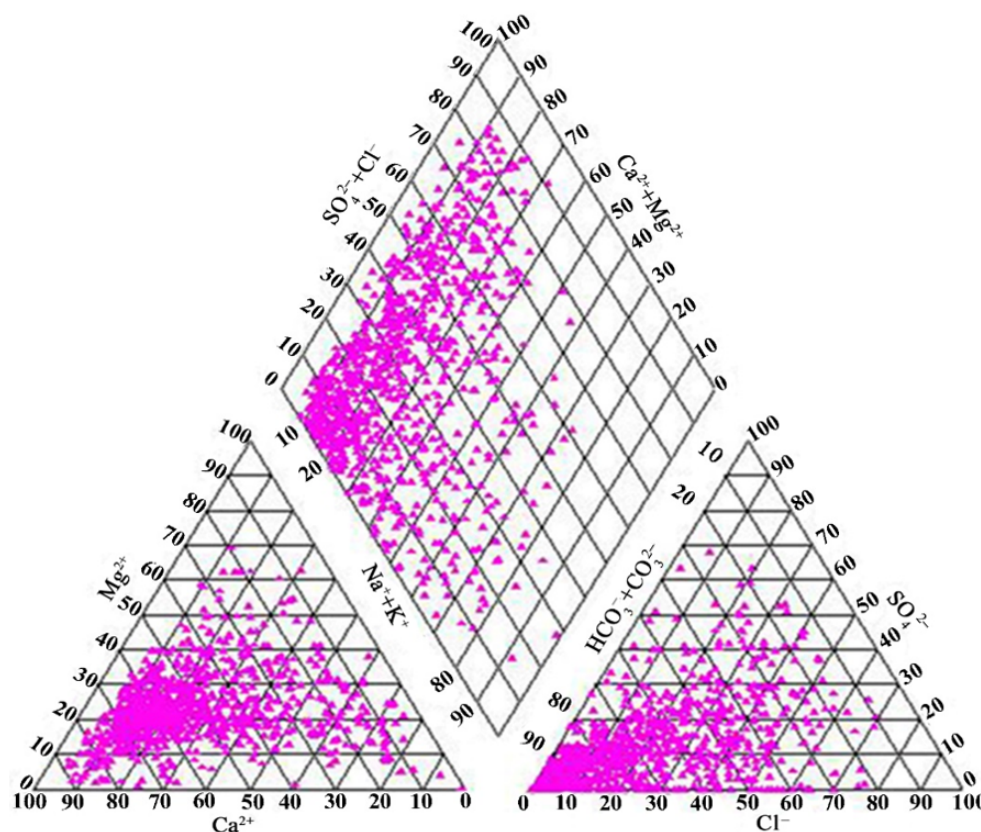


Figure 2. Piper diagram of groundwater samples.

3.2. Distributions of Fluorine

The concentration range of fluorine in groundwater was BDL–8.54 mg·L⁻¹, with a mean value of 0.63 mg·L⁻¹, and its detection rate was 85.91%. The content distributions of fluorine are showed in Figure 3; in the study area's groundwater the highest concentrations of fluorine (over 2 mg·L⁻¹) were found in the central and southwest areas of the Songnen Plain, such as Tongyu, Qianan, Baicheng, Lindian, Daqing, Zhaozhou, Zhaodong—and, the observed concentrations exceeded the maximum fluorine content (1.5 mg·L⁻¹) that is beneficial to human health [6] and within the guideline values set by the National Health Commission of the PRC (1.0 mg·L⁻¹) [15] and the WHO (1.5 mg·L⁻¹) [16].

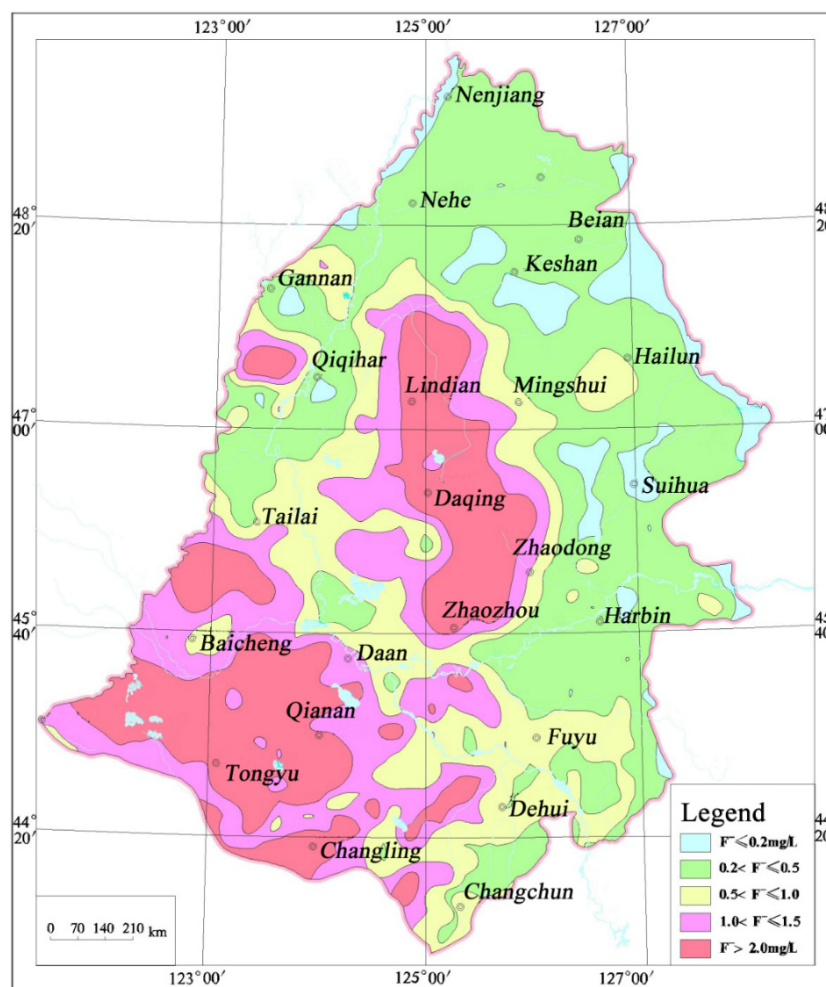


Figure 3. Distribution of fluorine in groundwater.

3.3. Formation and Influencing Factors of Fluorine in Groundwater

3.3.1. Dissolution and Precipitation of Minerals

Research has shown that the dissolution of fluorine-bearing minerals and the precipitation of calcium-bearing minerals are the main influencing factors of F⁻ enrichment in groundwater [8,20,39,40]. Analysis of the strata minerals in the study area revealed an abundance of fluorine-bearing minerals in the central and southwest strata of the plain, mainly fluorite, apatite, cryolite, topaz and hornblende [1,26]. The saturation indices of SI_{fluorite} in almost all groundwater samples in the study area were less than zero, and there was a significant positive correlation between F⁻ concentration and SI_{fluorite} (Figure 4a), suggesting that the dissolution of fluorite is the main source of F⁻ in the groundwater of these areas. According to other mineral saturation indices (SI_{Calcite} < 0, SI_{Halite} < 0, SI_{Dolomite} < 0), calcite, halite and dolomite had not reached the saturation state and were

easy to dissolve in reaction. SI_{fluorite} had a logarithmic increase, with an increasing concentration of F^- in groundwater (Figure 4a). Where fluorite tended to saturate, the concentration of F^- reached the upper limit, indicating that the concentration of F^- was restricted by the equilibrium constant of fluorite ($K_{sp} = 10^{-10.059}$, 22 °C). By comparing the concentration relationship between Ca^{2+} and F^- (Figure 4b), fluorine in the groundwater samples below the fluorite dissolution curve (dotted line in Figure 4b) mainly came from the dissolution of fluorite, and the fluorine in the groundwater samples above the dissolution curve came not only from the dissolution of fluorite, but also from other sources. The results show that the dissolution of fluorine-bearing minerals is main reason for the deposition of significant fluorine in the groundwater of Songnen Plain—similar to conditions found elsewhere in China [14,41] and the world, such as America [11], Mexico [8] and India [10].

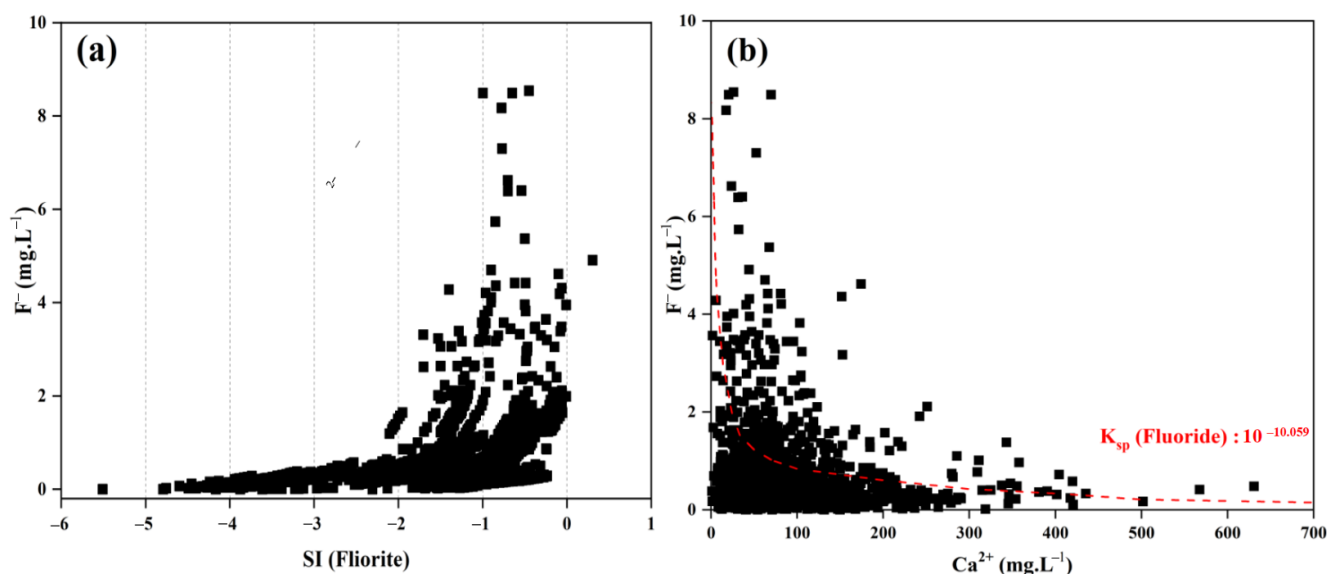


Figure 4. Relationship between F^- concentration and SI(Fluorite) (a); Ca^{2+} concentration (b).

3.3.2. Cation Exchange

The formation of groundwater hydrochemistry is often closely related to cation exchange [40], and cation exchange is the significant factor affecting the formation of fluorine in this study area. Cation exchange was confirmed with chloro-alkaline CAI 1 and CAI 2, and the indices were calculated by Equations (3) and (4).

$$CAI\ 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \quad (3)$$

$$CAI\ 2 = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-} \quad (4)$$

where, if $CAI\ 1 > 0$ and $CAI\ 2 > 0$, it is indicated that the dissolved Na^+ and K^+ in the groundwater will exchange cations with the absorbed Mg^{2+} and Ca^{2+} . However, when less than zero, it is indicated that the dissolved Mg^{2+} and Ca^{2+} will exchange with the absorbed Na^+ and K^+ . Moreover, the greater the absolute value, the stronger the cation exchange. Figure 5 shows the CAI 1 and CAI 2 of the groundwater samples. All values of CAI 2 do not exceed zero, and most values of CAI 1 were negative. This suggested that the cation exchange process of dissolved Mg^{2+} and Ca^{2+} exchanging cations with the absorbed Na^+ and K^+ was the driving process explaining local mineral concentrations, and it is also responsible for the decreased contents of Mg^{2+} and Ca^{2+} in the groundwater. This process may promote the hydrolysis of fluorite and other fluorine minerals (including apatite, cryolite, topaz, hornblende, tourmaline, etc.), thereby increasing the fluorine in

groundwater. This indicates that the cation exchange process can affect the fluorine content in groundwater, as is consistent with previous studies [12,19,40,42].

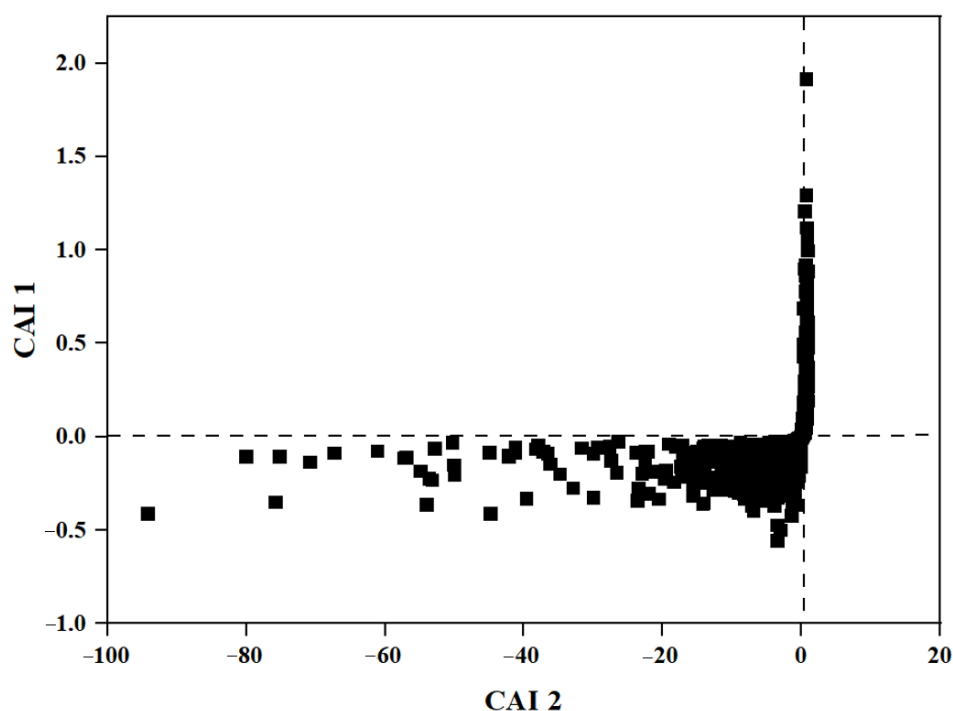


Figure 5. Relationship between CAI 1 and CAI 2.

3.3.3. Hydrochemical and Hydrological Influence Factors

Hydrochemical parameters are also one of the important factors affecting the content and distribution of fluorine [43,44]. It has been found that fluorine accumulates more easily in an alkaline environment [18], therefore, the areas with the highest pH values ($\text{pH} > 8.5$) in the study area (shown in Supplementary materials, Figure S1) also had the highest F^- contents. Correlation analysis between fluorine and other hydrochemical parameters in groundwater showed (Figure 6) that the concentrations of F^- in groundwater were positively correlated with the concentrations of TDS (total dissolved solids) and HCO_3^- . The results indicated that the concentrations and distribution characteristics of F^- in groundwater were closely related to the pH of the groundwater environment and the concentrations of TDS and HCO_3^- , again, as is consistent with previous studies [44]. Correlation analysis of fluorine and other high concentration pollutants (I^- , Mn^{2+} , Fe) in the groundwater showed (Figure S2) that fluorine was only weakly correlated with iodine (having similar properties), indicating that the pollutants in the groundwater had little influence on each other.

Hydrological conditions can partly affect the concentration and distribution of fluorine in groundwater [1,41]. The shallow groundwater system of Songnen Plain belongs to a larger groundwater catchment basin, and groundwater gather in its central low plain [16,29]. Therefore, the groundwater in the surrounding areas, especially the high-fluorine groundwater in the southwest area, will gradually migrate to the central region through the groundwater flow field, further increasing the fluorine concentrations in the already-high-fluorine groundwater in the central plain area.

3.4. Human Health Risk Assessment of Fluorine

Health risk assessments are mainly concerned with oral exposures; to that end, the risk assessment of non-carcinogens performed was based on the concentrations of fluorine in groundwater, and the results are shown in Figure 7. The sampling points ($\text{HQ}_{\text{Children}} > 1$) accounted for 92.26% of the total samples, signaling that the groundwater fluorine concentration is

high enough to have significant adverse effects on children in the study area. The sampling points ($HQ_{Adults} > 1$) accounted for 32.18% of the total samples, indicating that the fluorine content was also high enough to adversely affect adults, though much less so than children. In addition, the districts where the fluorine in the groundwater showed the greatest potential influence on children and adults were roughly the same, and were concentrated in the southwest and central Songnen Plain, such as Tongyu Lindian and Daqing.

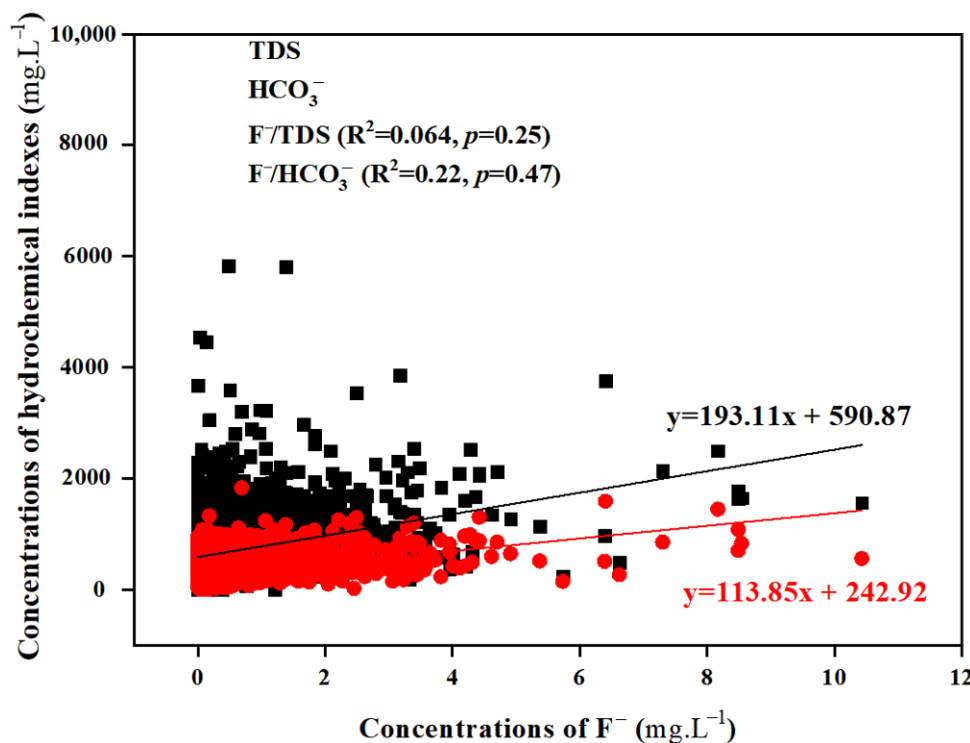


Figure 6. Correlation of F^- and Hydrochemical Indices.

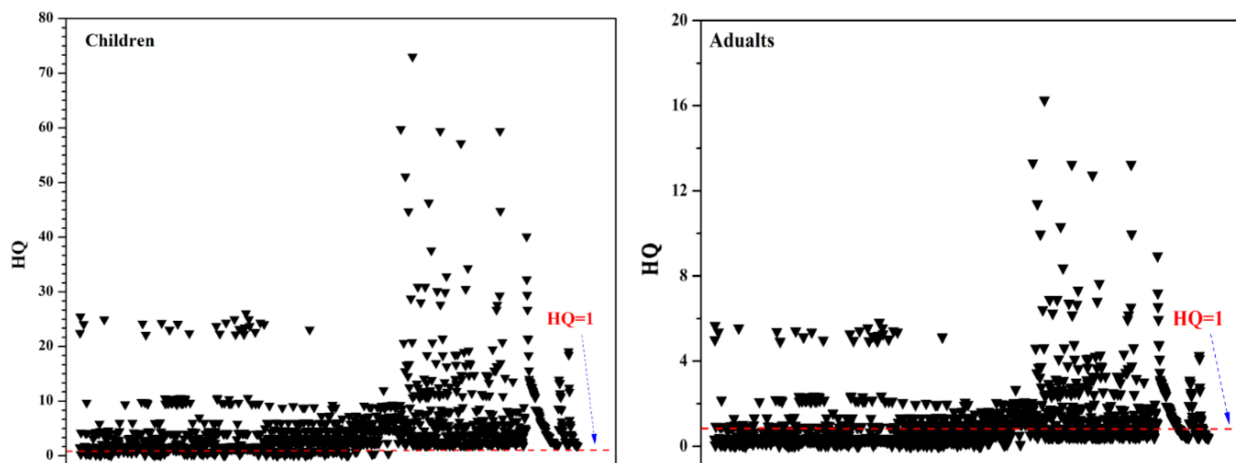


Figure 7. HQs of fluorine to children and Adults.

4. Conclusions

Fluorine is widespread in the groundwater of the Songnen Plain, at a concentration range of BDL–8.54 $mg \cdot L^{-1}$, with a mean value of 0.63 $mg \cdot L^{-1}$ and detectable at a rate of 85.91%. The highest concentrations of fluorine (over 2 $mg \cdot L^{-1}$) were found in the central and southwest areas of the plain. The concentrations there exceeded the guideline values for fluorine in drinking water set by both the National Health Commission of the PRC

(1.0 mg·L⁻¹) and the WHO (1.5 mg·L⁻¹), and represent varying degrees of adverse effect on adults, and especially children, in the study area. The fluorine in these groundwaters mainly came from the dissolution of fluorite and other fluorine-containing minerals in the study area; additionally, the concentrations and distribution of fluorine were shown to be affected by cation exchange, the groundwater flow field and hydrochemical indexes (pH, TDS and HCO₃⁻). The study provides scientific basis for the investigation, evaluation and prevention of endemic diseases caused by groundwater fluorine.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13223236/s1>, Figure S1: Distribution of pH in groundwater, Figure S2: Correlation of F⁻ and other pollutants.

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