Study on Environmental Factors of Fluorine in Chagan Lake Catchment, Northeast China

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Abstract: The Chagan Lake Catchment is located in the midwest of Songnen Plain, which is a typical high fluoride groundwater area. High fluoride water has an important impact on the economic development and ecosystem stability of Chagan Lake. In this study, the spatial distribution characteristics and influencing factors of fluorine in Chagan Lake Catchment are discussed by using hydrochemistry and mathematical statistical analysis. The groundwater in the study area was characterized as Na+-rich and Ca2+-poor, with a high pH value and high HCO3− content. The average concentration of F− was 3.02 mg/L, which was the highest in Qian’an County. The dissolution of fluorine-containing minerals and the desorption of F− in soil provided the source of F− in groundwater, while calcite and dolomite precipitation, cation exchange, and evaporation concentration provided favorable conditions for F− dissolving, migration, and enrichment in water. In addition, the concentration of F− in surface water was 4.56 mg/L, and the highest concentration was found in Hongzi Pool and Hua’ao Pool. The elevated concentrations of F− in both surface water and groundwater in the study were affected by human factors, such as rice planting and water conservancy project construction.

Keywords: fluoride (F−); spatial distribution; influence factors; Chagan lake catchment

1. Introduction

Fluorine is one of the essential trace elements for life, its intake level seriously affects human health and the growth of plants and animals. Studies have found that when the concentrations of F− in drinking water is low, it can prevent dental caries and strengthen bones. But when the concentration of F− in drinking water is higher than 1.5 mg/L, it will cause fluorosis [1–3]. When the concentration of F− in water is too high, it can affect the metabolic activities of aquatic plants, damage the growth of plants, and lead to a large number of deaths of aquatic plants [4]. At the same time, F− can also affect the growth of animals in water, affecting their nervous system and bones, leading to their abnormal growth, and even affecting their offspring [5–8]. When the concentration of F− in water exceeds the standard, F− accumulation in aquatic animals such as fish would endanger human health indirectly through the effect on the food chain.

Fluorine is widely distributed in the earth and has strongly metallogenic capacity, with the main form of cryolite (Na₃AlF₆), fluorite (CaF₂), fluorapatite (Ca₅(PO₄)₃F), topaz (Al₂SiO₄(F,OH)₂), and amphibole (NaCa₂(Mg,Fe)O₁₀(OH,F)₂) [9]. The dissolving of fluorine-containing minerals is an important source of F− in water. In addition, anthropogenic inputs including agricultural irrigation, phosphate fertilizer application, brick kiln use, electroplating, metallurgical activities, and coal burning also promote the enrichment of F− in water [9,10]. Fluoride in water mainly exists in the form of F−, which accounts for more than 95% of the total fluoride [11]. In addition, F− can form a series of soluble complexes with iron (Fe²⁺), aluminum (Al³⁺), magnesium (Mg²⁺), sodium (Na⁺), calcium.
(Ca\(^{2+}\)), and hydrogen (H\(^{+}\)) [12]. F\(^{-}\) concentration in water changes due to various factors, such as the F\(^{-}\)-bearing minerals, ion exchange, residence time, dilution, temperature, pH, salinity, and evapotranspiration. The concentration of F\(^{-}\) has obvious regional characteristics [13]. The countries with the higher fluoride concentration in waters are included in the so-called Global Fluoride Belt [14]. Endemic fluorosis induced by high concentrations of fluoride in water and soils is a major health problem in several countries, particularly in volcanic areas, where the fluoride concentration in rocks is very elevated [15,16]. In some tropical areas of Ghana, high fluoride risk is caused by high per capita water consumption. In arid areas of northwest China, the enrichment and depletion of F\(^{-}\) in natural water are related to rich material sources, a relatively closed hydrological environment, and arid climate conditions [17].

The Chagan Lake Catchment area is located in Jilin Province, China. As a crucial part of the natural water resources protection area in northeast China, Chagan Lake plays an important role in regulating and storing river runoff, providing water sources, flood control and disaster resistance, fishery breeding, and maintaining ecological environment safety [18]. However, because the study area is located in the midwest of Songnen Plain, surrounded by volcanic rocks, secondary volcanic rocks, and fluorite veins, it constitutes a typical fluorine-rich geochemical environment zone [16,19]. At the same time, human activities such as the expansion of the irrigation area around Chagan Lake, the construction of the river–lake connection project in western of Jilin, and the exploitation of groundwater have changed the original hydrological and water quality environment and promoted the enrichment process of fluorine in Chagan Lake. Therefore, it is necessary to explore the formation mechanism and influencing factors of high F\(^{-}\) water in the Chagan Lake Catchment. This study takes the Chagan Lake Catchment as its research object, analyzes the distribution characteristics of fluorine in soil, surface water, and phreatic water, and explores the influencing factors of F\(^{-}\) combined with the test results of hydrochemical properties so as to provide a theoretical basis and technical support for the environmental protection of this regional water.

### 2. Materials and Methods

#### 2.1. Study Area

The Chagan Lake Catchment (123°25′–125°00′ E, 44°40′–45°35′ N) spans Qianguo County, Da’an County, Qian’an County, and the Ningjiang District of Jilin Province and is located at the confluence of the Huolin River and Nen River [20]. The geographical location is shown in Figure 1. The study area belongs to a temperate continental monsoon climate, with obvious climate change during the four seasons. From 2000 to 2019, the rainfall ranged from 247 to 647 mm, and the annual average rainfall was 434 mm (Figure 2), mainly concentrated in July to August, accounting for more than 50% of the annual rainfall. The average annual temperature is 6.05 °C and the average annual evaporation is 964 mm [21]. The zonal soil types in Chagan Lake area mainly include anthropic soil, pedocal, saline–alkali soil, and luvisols.
Figure 1. Distribution map of sampling sites. (a) Location of western Jilin Province in China; (b) soil types and the location of study area in western Jilin; (c) sampling sites in Chagan Lake Catchment.
The study area is located in the Midwest of Songnen Plain. The terrain of Dongchuan-tou and Xichuantou on the right bank of Chagan Lake is high, 140–160 m, while the rest is low [21]. The landform is dominated by alluvial lacustrine plain and valley alluvial plain. Since the Cenozoic Era, the study area has continuously subsided in a large area, which is generally covered by Quaternary loose sediments with a thickness of about 60–100 m. The loose layers are distributed from the Lower Pleistocene to the Holocene, while the Lower and Middle Pleistocene are widely developed and thick. Groundwater is widely distributed in these strata. Aquifer types include Quaternary pore unconfined aquifers, confined aquifers, Neogene pore-fracture confined aquifers, and Cretaceous pore-fracture confined aquifers [19]. Phreatic water mainly occurs in Quaternary loose sediments, and is primarily recharged by precipitation infiltration, followed by lateral runoff of groundwater, and part of surface water. The runoff direction is from southwest to northeast, with a slow speed [22]. The drainage methods are evaporation, replenishment of confined water, and artificial mining.

Lake and lake beach are widely distributed in the study area, among which Chagan Lake is the largest. Chagan Lake is a vital ecological barrier in the central and western regions of Jilin Province. The main lake area is composed of “one lake and two pools”. The “one lake” is Chagan Lake, which is a typical soda saline–alkali plain shallow lake. The “two pools” are Xindian Pool and Xinmiao Pool, respectively. Water supply of Chagan Lake can be divided in two ways: natural river supply and artificial channel supply. The natural river supply from Huolin River, natural precipitation, and runoff of surrounding pools is an important source of water of Chagan Lake [23], while the artificial channel supply is the primary water supply in this region [24]. The artificial channel supply includes drainage in the Qianguo Irrigation Area, Da’an Irrigation Area, and Shenzhong Waterlogging Area. The average water withdrawal in the Qianguo Irrigation Area is $2.85 \times 10^8$ m$^3$, of which $1.13 \times 10^8$ m$^3$ enter Chagan Lake through the main canal of the diverted Songhua River built in 1984 and $172 \times 10^8$ m$^3$ enter Chagan Lake by groundwater. The Da’an Irrigation Area was put into use in 2015, and its water withdrawal increased year by year with the
increase of paddy field development. At present, both of them account for 70% of the total supply of Chagan Lake [25]. In addition, a river–lake connection project was constructed in Jilin province in 2017 so that the surplus water during flood periods from the second Songhua River, Nen River, Tao’er River, and Huolin River, as well as the return water from irrigation areas, are diverted to the empty or half-empty lake by using the large-scale water conservancy projects that have been built. These water conservancy projects provide a way for the diffusion and accumulation of $F^-$ [26]. The primary way of water discharge from Chagan Lake is through flowing into the Nen River through Kuli Pool, followed by the evaporation of surface water and discharge of groundwater [23].

2.2. Sample Collection and Analysis

The water sample data sources in this paper mainly included four aspects: (1) The data on surface water numbered 7–8 and groundwater numbered 1–32 were all from a geological survey project undertaken by the research group—Ecological and environmental geochemical assessment of high fluorine and high arsenic areas in Western Jilin Province (2006–2009, Project No. 1212010511208). (2) The data on surface water numbered 1–5 and groundwater numbered 33–38 were quoted from the overall plan for the construction of commodity grain capacity with an increase of 10 billion catties in Jilin Province [27], which was compiled by Jilin Provincial Academy of Environmental Sciences in 2008. (3) The data on surface water numbered 6 was quoted from the 2008 data from the environmental impact report of the Chagan Lake wetland protection and restoration project [28]. (4) In 2019, we sampled and investigated the groundwater and surface water in the Da’an Irrigation Area and Qianguo Irrigation Area and found that the concentration of $F^-$ in groundwater generally increased. However, due to the larger number of samples in 2008, the research was carried out with the data from 2008.

Groundwater (n = 38) and surface water (n = 8) sampling sites are shown in Figure 1. The pH was measured onsite with a portable meter (PHB]-206, REX). The water samples were collected in 500 mL polyethylene bottles, which were washed with distilled water before sampling and rinsed three times with water at the sampling location to avoid contamination. During sampling, all water samples were filtered through 0.45 µm membranes on site. For cation analysis, reagent-quality HNO₃ was added to one of the polyethylene bottles until the pH of the sample was less than 2. The sample bottles were completely filled, sealed with caps, and then labeled appropriately. All samples were immediately transferred to a refrigerator regulated at 4 °C prior to testing.

The contents of Ca²⁺, Mg²⁺, HCO₃⁻, SO₄²⁻, Cl⁻, CO₃²⁻, and total hardness (TH) were measured by titration method. K⁺ and Na⁺ were measured by flame photometry (AA6200, Shimadzu). The concentrations of NO₃⁻ and NO₂⁻ were determined using ultraviolet spectrophotometry (UV-1700, Shimadzu) and colorimetry with detection limits of 0.01 and 0.002 mg/L, respectively. The total dissolved solids (TDS) was determined by ion addition. The content of $F^-$ was determined by ion-selective electrode method (PF-1, REX) with the detection limit of 0.01 mg/L [29]. The analytical precision for the cation and anion measurements is indicated by the ionic balance error, which was within the standard limit of ±5%. The total fluorine content in soil was determined by ion selective electrode method (PF–1, REX), which was all supplied by Jilin Geological Research Institute.

2.3. Data Analysis Method

ArcGIS 10.2 software was used for remote sensing interpretation to draw the thematic maps, as well as analyzing the spatial distribution characteristics of $F^-$ in surface water, groundwater, and soil in the study area. Pearson correlation analysis in SPSS 24 software was used to study the influence of groundwater chemical parameters on $F^-$. Piper trigram was drawn using AquaChem 3.70 (Waterloo Hydrogeologic, ON, Canada) software to study the chemical types of groundwater. The PHREEQC module in AquaChem 3.70 was used to calculate the saturation index (SI) of related minerals and to check the relationship between water samples and solid phases of interest. Three kinds of values were distinguished:
oversaturation (SI > 0; precipitation), undersaturation (SI < 0; dissolution), or saturation (SI = 0; equilibria) [30].

3. Results
3.1. Land Use Change

Landsat 8 (Operational Land Imager) remote sensing image data from 1989, 2000, 2010, and 2018 were downloaded from the Geospatial Data Cloud (http://www.gscloud.cn/ (accessed on 16 July 2019)). The remote sensing images were pretreated by geometric correction and mosaic and mask extraction. With the preprocessed satellite remote sensing images as the main data source and ArcGIS software as the platform, the human–computer interaction interpretation was carried out according to the remote sensing image target and the surrounding image characteristics. The information factors such as grassland, saline–alkali land, and paddy field were extracted to obtain the land use/cover spatial distribution maps in the study area, as shown in Figure 3. The total area of the study area was 7492.69 km². In 2018, the main land types were upland field, grassland, and paddy field, with the area of 2829.77, 1802.96, and 1222.28 km², respectively. Upland field was mainly distributed in Qian’an County and Da’an County. Grassland was mainly distributed in the west of Da’an County and around the lake marsh. The paddy fields were mainly distributed in the Qianguo Irrigation Area, Da’an Irrigation Area, and the coast of Haiborige River.

![Figure 3. Spatial distribution of land use/cover for (a) 1989, (b) 2000, (c) 2010, and (d) 2018.](image-url)
Based on the land area data obtained from the interpretation, the land use type transfer matrix from 1989 to 2018 was established (Table 1). From 1989 to 2018, the increase of population, economic growth, continuous advancement of land development and consolidation projects, and the local government’s attention to saline–alkali land management and ecological environment restoration in the study area led to the increase of grassland, paddy field, woodland, and urban land area by 454.17, 745.61, 38.91, and 108.55 km$^2$, respectively. The area of upland field and saline–alkali land decreased by 129.63 and 793.80 km$^2$, respectively. However, due to climate and environmental degradation and human activities, the area of waters, beaches, and wetlands decreased by 200.80 and 138.92 km$^2$, respectively.

### Table 1. Land use type transfer matrix from 1989 to 2018 (km$^2$).

| Year | GL  | PF  | UF  | WL  | W   | BL  | RL  | SL  | Wt  | Total Area | Increase | Change |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------------|----------|--------|
| 1989 | GL  | 8.96| 231.88| 9.26| 114.61| 7.32| 17.65| 643.91| 115.15| 1148.73 | 454.17    |         |
| 2018 | GL  | 8.96| 231.88| 9.26| 114.61| 7.32| 17.65| 643.91| 115.15| 1148.73 | 454.17    |         |
| GL   | PF  | 231.88| 155.22| 11.36| 70.88| 53.40| 24.45| 78.91| 97.39| 803.20 | 745.61    |         |
| GL   | UF  | 9.26| 114.61| 15.36| 48.17| 68.26| 12.99| 604.79|             | 119.17 | 273.66 |
| GL   | WL  | 7.32| 17.65| 34.9 | 34.9 | 12.99| 12.99| 604.79|             | 119.17 | 273.66 |
| GL   | W   | 114.61| 70.88| 21.2 | 48.17| 68.26| 12.99| 604.79|             | 119.17 | 273.66 |
| GL   | BL  | 7.32| 17.65| 34.9 | 34.9 | 12.99| 12.99| 604.79|             | 119.17 | 273.66 |
| GL   | RL  | 643.91| 115.15| 115.15| 115.15| 115.15| 115.15| 115.15|             | 115.15 | 273.66 |
| GL   | SL  | 115.15| 115.15| 115.15| 115.15| 115.15| 115.15| 115.15|             | 115.15 | 273.66 |
| GL   | Wt  | 115.15| 115.15| 115.15| 115.15| 115.15| 115.15| 115.15|             | 115.15 | 273.66 |
| GL   | Total area reduction | 694.57| 57.59| 734.42| 96.35| 319.98| 97.00| 911.46| 273.66 |         |          |

GL, PF, UF, WL, W, BL, RL, SL, Wt are the abbreviations of Grass Land, Paddy Field, Upland Field, Wood Land, Water, Bare Land, Saline–alkali Land, and Wetland, respectively.

### 3.2. Hydrochemistry

The statistics of the samples are listed in Table 2. The pH value of surface water in the study area ranged from 8.23 to 9.36, with an average of 8.63, inferring that is alkaline water. The groundwater was also alkaline for the pH value ranged from 7.23 to 9.21, with an average of 8.73. The variation of TH was 100.10–973.95 mg/L, with an average of 427.61 mg/L. The average of TDS was 884.79 mg/L, with the minimum value of 324.80 mg/L, and the maximum value of 2700.80 mg/L. The order of cation concentration in groundwater was Na$^+$ > Mg$^{2+}$ > Ca$^{2+}$ > K$^+$, for their average values were 6.12, 4.70, 3.31, and 0.02 meq/L, respectively. The rank of anion concentration was HCO$_3^-$ > Cl$^-$ > SO$_4^{2-}$ > CO$_3^{2-}$, and the average values were 5.61, 3.74, 1.01, and 0.65 meq/L, respectively. The concentrations of NO$_3^-$ and NO$_2^-$ ranged from 0.00 to 600.00 mg/L and 0.00 to 1.10 mg/L, respectively. The coefficient of variation (Cv) of NO$_3^-$ and NO$_2^-$ were 108.87% and 237.81%, respectively, which suggested strong variation. This result showed big differences in NO$_3^-$ and NO$_2^-$ concentration among sampling points.

### 3.3. Fluoride in Water

Figure 4a shows that the F$^-$ concentration of surface water ranged from 0.02 to 13.69 mg/L, with an average of 4.56 mg/L. Seventy-five percent of surface water samples exceeded 1.0 mg/L, the standards of surface water III in Chinese environmental quality [31]. The highest F$^-$ concentrations were obtained in Hongzi Pool (13.69 mg/L) and in Hua’ao Pool (8.08 mg/L), while the lowest concentration was in Xinmiao Pool (0.017 mg/L). It was shown that the F$^-$ concentration largely connected with rivers or artificially fed was lower than that of the large lakes without connection with rivers or artificially fed. The variation range of F$^-$ concentration in groundwater was 0.32–14.00 mg/L, with an average of 3.02 mg/L. Moreover, 63.16% of the groundwater samples were higher than 1.5 mg/L (WHO drinking guideline standard) [1], and 73.68% of the groundwater samples were
higher than 1.0 mg/L (Chinese maximum contaminant level) [32]. Topographically, the F\(^{-}\) concentration of groundwater samples in Qian’an County was higher than that in Da’an County (Figure 4a). In the study area, the terrain of Qian’an County was relatively low. The high fluoride groundwater from the direction of the Greater Xing’an Mountains had a slow flow rate and accumulated here, which made the F\(^{-}\) concentration increase. Thus, the F\(^{-}\) concentrations of Yanzi Village and Naizi Village were the highest, with concentrations of 13.20 and 14.00 mg/L, respectively. In addition, the concentration of F\(^{-}\) in the groundwater of Naizi Village and the nearby Hua’ao Pool was higher, which might be related to the hydraulic connection between surface water and groundwater (Figure S1).

### Table 2. Statistical summary of physiochemical parameters in Chagan Lake Catchment. TH, total hardness; TDS, total dissolved solids.

| Unit     | Ground Water | Surface Water |
|----------|--------------|---------------|
|          | n  | Min | Max | Mean | SD | Cv (%) | n  | Min | Max | Mean | SD | Cv (%) |
| pH       | –  | 38  | 7.23 | 9.21 | 8.73 | 0.51 | 5.80 | 7  | 8.23 | 9.36 | 8.63 | 0.41 | 4.75 |
| TH mg/L  | 38  | 100.10 | 973.95 | 427.61 | 208.67 | 48.80 |
| TDS mg/L | 38  | 324.80 | 2700.80 | 884.79 | 500.64 | 56.58 |
| F\(^{-}\) mg/L | 32  | 0.32 | 14.00 | 3.02 | 3.07 | 101.73 | 8  | 0.02 | 13.69 | 4.56 | 4.82 | 105.49 |
| Ca\(^{2+}\) meq/L | 38  | 1.25 | 9.37 | 3.31 | 1.82 | 55.11 |
| Mg\(^{2+}\) meq/L | 38  | 0.27 | 13.65 | 4.70 | 3.57 | 76.07 |
| Na\(^{+}\) meq/L | 32  | 1.43 | 29.13 | 6.12 | 5.72 | 93.53 |
| K\(^{+}\) meq/L | 32  | 0.01 | 0.05 | 0.02 | 0.01 | 58.45 |
| Cl\(^{-}\) meq/L | 38  | 0.20 | 15.18 | 3.74 | 3.44 | 92.08 |
| SO\(_4^{2-}\) meq/L | 38  | 0.00 | 15.18 | 3.74 | 3.44 | 92.08 |
| HCO\(_3^{-}\) meq/L | 38  | 1.46 | 13.02 | 5.67 | 2.98 | 52.53 |
| CO\(_3^{2-}\) meq/L | 38  | 0.00 | 2.85 | 0.65 | 0.60 | 92.01 |

### Figure 4. (a) Distribution characteristics of F\(^{-}\) concentration in water; (b) distribution characteristics of total fluoride in soil.

#### 3.4. Fluoride in Soil

The minimum and maximum values of total fluorine content in soil were 172 and 1000 mg/kg, respectively (Table S1). The average value was 409.05 mg/kg, lower than the background value of 478 mg/kg in China but higher than the world average value of 200 mg/kg [33]. As shown in Figure 4b, the fluorine contents of soil samples along Huolin River, the southwest coast of Chagan Lake, Yinsong Canal, the southwest coast of Hongzi
Pool, and Songhua River were more than 400 mg/kg. In these areas, suffering the rainfall leaching and runoff scouring, fluoride from the soil entered into the surface water and groundwater and then became a crucial source of F$^-$ in the water, which increased the risk of endemic fluorosis via the food chain.

3.5. Pearson Correlation Analysis

Table 3 shows the correlational relationships between groundwater quality parameters. The concentration of F$^-$ showed a strong positive relationship with HCO$_3^-$ ($r = 0.797$), CO$_3^{2-}$ ($r = 0.737$) and Na$^+$ ($r = 0.721$). There was a moderate positive correlation between F$^-$ and pH ($r = 0.418$), TDS ($r = 0.541$), Mg$^{2+}$ ($r = 0.482$), Cl$^-$ ($r = 0.401$), NO$_2^-$ ($r = 0.514$). TDS was positively correlated with Mg$^{2+}$ ($r = 0.807$), Na$^+$ ($r = 0.877$), Cl$^-$ ($r = 0.921$), HCO$_3^-$ ($r = 0.569$), and CO$_3^{2-}$ ($r = 0.647$). This means that F$^-$ increased with the increase of TDS. The positive correlation between F$^-$ and the cation of Na$^+$ and Cl$^-$ indicates that evaporation was one of the reasons for the formation of high fluoride groundwater. In addition, alkaline conditions were not only conducive to the dissolving of fluorinated minerals but also to the substitution of OH$^-$ for F$^-$ adsorbed on metal oxides and hydroxides. However, F$^-$ was not related to TH, Ca$^{2+}$, K$^+$, SO$_4^{2-}$, and NO$_3^-$ in the study ($p > 0.05$).

| F$^-$ | pH | TH | TDS | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | K$^+$ | Cl$^-$ | SO$_4^{2-}$ | HCO$_3^-$ | CO$_3^{2-}$ | NO$_2^-$ | NO$_3^-$ |
|------|----|----|-----|---------|---------|-------|------|------|--------|--------|--------|--------|--------|
| F$^-$ | 1.00** | | | | | | | | | | | | |
| pH   | 0.418** | | | | | | | | | | | | |
| TH   | 0.206 | 1.00** | | | | | | | | | | | |
| TDS  | 0.541** | 0.02 | 0.748** | 1.00** | | | | | | | | | |
| Ca$^{2+}$ | -0.207 | 0.144 | 0.689** | 0.284 | 1.00** | | | | | | | | |
| Mg$^{2+}$ | 0.482** | 0.477** | 0.868** | 0.807** | -0.454** | 1.00** | | | | | | | |
| Na$^+$ | -0.721** | 0.253 | 0.352* | 0.877** | -0.125 | 0.524** | 1.00** | | | | | | |
| K$^+$ | -0.034 | 0.077 | 0.113 | 0.005 | 0.036 | 0.124 | -0.101 | 1.00** | | | | | |
| Cl$^-$ | 0.401* | 0.217 | 0.814** | 0.921** | 0.471** | 0.796** | 0.738** | -0.036 | 1.00** | | | | |
| SO$_4^{2-}$ | -0.003 | -0.519** | 0.104 | 0.693** | -0.175 | -0.068 | 0.666** | 0.053 | 0.283 | 1.00** | | | |
| HCO$_3^-$ | 0.797** | 0.539** | 0.337* | 0.569** | -0.04 | 0.636** | 0.717** | -0.057 | 0.442** | -0.223 | 1.00** | | |
| CO$_3^{2-}$ | 0.737** | 0.626** | 0.285 | 0.647** | -0.151 | 0.599** | 0.819** | -0.068 | 0.515** | 0.033 | 0.783** | 1.00** | |
| NO$_2^-$ | 0.316 | 0.304 | 0.787** | 0.647** | -0.047 | 0.745** | 0.967** | -0.134 | 0.791** | 0.106 | 0.331* | 0.438** | 1.00** |
| NO$_3^-$ | 0.514** | 0.152 | 0.038 | 0.164 | 0.02 | 0.105 | 0.257 | 0.182 | 0.035 | -0.135 | 0.384* | 0.114 | 0.138 | 1.00** |

Correlation coefficients: 0.60–1.00 = significant correlation; 0.50–0.59 = moderate correlation; 0.40–0.49 = weak correlation; 0.00–0.39 = little or no association. * Correlation was significant at the 0.05 level (2-tailed); ** Correlation was significant at the 0.01 level (2-tailed).

4. Discussion

4.1. Effect of Sedimentary Environment on Fluorine in Soil and Groundwater

F$^-$ in the study area may come from the dissolving of fluorine-containing minerals and the release of fluoride in soil. The Chagan Lake Catchment is located in the hinterland of Songnen Plain, which is low-lying and flat terrain, with a slope of 1/8000–1/5000. The landscape is dominated by many ancient rivers, closed and semi-closed depressions left behind by many river diversions, surrounded by the Great Xing’an Mountains, Small Xing’an Mountains, Changbai Mountains, and the Songliao Watershed. These mountain rocks contain fluorine-containing minerals such as potassium cryolite, hieratite, granite, fluorite, apatite, tourmaline, and muscovite. The average fluoride content in the bedrock of the Great Xing’an Mountains is 977.70 mg/kg, which is higher than that in the crust (660 mg/kg) [34,35]. The Huolin River, originated from the Great Xing’an Mountains and injected into the area, is the primary carrier for transporting fluorine-bearing rocks and releasing fluorine. The study area is located in the lower reaches of the Huolin River. This part of the river reaches forms scattered flow, without the main channel, and even the reaches are dry due to the low water supply but high evaporation. Thus, the fluorine carried is gathered here, partly entering the inland lakes but largely enriching in soil.

The average content of fluoride in the soil was 409.05 mg/kg (Figure 4b). The total fluoride content was higher than 400 mg/kg along the lake and in the lower step of the river. In some places, it was even 2 times higher than the background value of soil fluoride.
in China. The water flow, originated from the natural rainfall or upstream, dissolves F\textsuperscript{–} in water from soil. Due to slow and sluggish flow, part of the F\textsuperscript{–} gradually accumulates in the lake, and part of it seeps into the groundwater systems, raising their fluorine content.

4.2. Effect of Evaporation on Fluorine in Soil and Groundwater

The study area is located in a temperate continental monsoon climate. The annual rainfall is 434 mm (Figure 2). The annual evaporation is 964 mm. Evaporation is 2–3-times the rainfall. Strong evaporation increases F\textsuperscript{–} concentration in groundwater. Two reasons can explain this phenomenon. First, evaporation concentrates the concentrations of all species, including F\textsuperscript{–}, in the groundwater. Second, the study area is a heavy carbonate area. Strong evaporation led to the supersaturation of calcite (CaCO\textsubscript{3}) and dolomite (CaMg(CO\textsubscript{3})\textsubscript{2}) in groundwater (Figure 5d). This reduces Ca\textsuperscript{2+} concentration, accelerates CaF\textsubscript{2} dissolution, and promotes F\textsuperscript{–} release to groundwater [26]. In addition, evaporation also increases fluoride content in soil. Evaporation, on the one hand, transports salt and F\textsuperscript{–} from soil water and groundwater to the soil surface, providing material sources for soil salinization and F\textsuperscript{–} enrichment. On the other hand, soda in the soil causes an increase of pH, replacing calcium and magnesium ions in soil colloids, increasing soil alkalinity, and further promoting the dissolving of fluoride-containing minerals. The increase of population in the study area led to a change of land use type and a decrease of the vegetation cover area, which accelerated the evaporation rate of land and promoted the enrichment of F\textsuperscript{–}.

4.3. Effect of Hydrochemistry on Fluorine in Groundwater

Water chemical composition is the product of the long-term interaction between water, environment, and human activities, which reveals the formation and evolution of water. The hydrochemical processes such as water–rock interaction, evaporation and concentration, dissolution and precipitation, and cation exchange will affect F\textsuperscript{–} in water. Therefore, it is necessary to study the source and formation mechanism of water chemical components. The high fluoride water in the study area showed unique main ionic chemical characteristics: Na-rich and Ca-poor with high pH value and high HCO\textsubscript{3}– content, with a resulting sodium-bicarbonatic dominant chemical facies [36,37]. As shown in Figure 5a, b, the groundwater sample sites in the study area were basically located in the Gibbs distribution model, mainly concentrated in the middle and upper part. It shows that the groundwater was mainly controlled by rock weathering and evaporation/concentration. The Piper diagram shows that HCO\textsubscript{3}–-Na is the main hydrochemical type in the study area (Figure 5c). HCO\textsubscript{3}– is the main anion in most groundwater samples, which promotes the formation of high F\textsuperscript{–} groundwater under alkaline conditions. On the one hand, HCO\textsubscript{3}– accelerates the dissolution of CaF\textsubscript{2} and promotes the release of F\textsuperscript{–} (Equation (1)) [38]. On the other hand, high concentrations of HCO\textsubscript{3}– compete with F\textsuperscript{–} for adsorption sites on metal oxides and hydroxides under alkaline conditions, which promotes the desorption of F\textsuperscript{–}. Different dominant cations were observed in different sampling sites. The samples with Ca\textsuperscript{2+} as the main cation were mainly located in Da’an, where the F\textsuperscript{–} concentration in the samples was low. However, the F\textsuperscript{–} concentration in the samples with Na\textsuperscript{+} as the dominant cation was high. The main reasons are as follows: first, Ca\textsuperscript{2+} will increase the positive charge on the solid surface of aqueous metal oxides compared with Na\textsuperscript{+} and enhance the adsorption of F\textsuperscript{–}. Thus, the composition of the Na-rich (compared with Ca) groundwater results in F\textsuperscript{–} mobilization [39]. Second, the cation exchange between Na\textsuperscript{+} and Ca\textsuperscript{2+} accelerates the dissolution of CaF\textsubscript{2} (Equation (2)) [40], then increases the concentration of F\textsuperscript{–} in the water [41]. The relationship between Na\textsuperscript{+}-Cl\textsuperscript{–} and Ca\textsuperscript{2+}+Mg\textsuperscript{2+}-HCO\textsubscript{3}–-SO\textsubscript{4}2– is generally used to represent cation exchange. Figure 5e shows that all samples were distributed along a straight line of −1, confirming the existence of ion exchange between Na\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+} in the aqueous environment. Figure 5f shows the source of salt in the water in the study area. The Na/Cl ratios of most samples were on the 1:1 ratio line, indicating that Na\textsuperscript{+} mainly came from the dissolution of rock salt (NaCl). A small part was above the 1:1 ratio line, indicating that the cation exchange and hydrolysis of silicate
containing Na\(^+\) might be another source of Na\(^+\), according to the literature concerning the genesis of HCO\(_3\)-Na waters \[19,36,37\]. Mineral saturation index (SI) (Figure 5d) shows that the samples of calcite (CaCO\(_3\)) and dolomite (CaMg(CO\(_3\))\(_2\)) were saturated. The results show that CO\(_3^{2-}\) combined with alkaline earth metal ions, such as Ca\(^{2+}\) and Mg\(^{2+}\) in the study area, to form insoluble carbonate precipitates, which reduced the reaction of F\(^-\) with Ca\(^{2+}\) and Mg\(^{2+}\) and thus promoted the enrichment of F\(^-\). Gypsum (CaSO\(_4\)) and fluorite (CaF\(_2\)) were unsaturated, indicating that the dissolution of gypsum and fluorite provided a material source for the enrichment of F\(^-\) in the study area.

\[
\text{CaF}_2 + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + 2\text{F}^- + \text{CO}_2 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Na}_2\text{-Clay} + \text{CaF}_2 \leftrightarrow \text{Ca-Clay} + 2\text{Na}^+ + 2\text{F}^- \quad \text{where “-Clay” refers to clay minerals} \quad (2)
\]

4.4. Effects of Human Activities on Fluoride in Lake Water

Human activity is an important factor affecting the enrichment of fluorine in lakes. First of all, although the area of saline–alkali land in the study area was reduced, the salinization of land around rivers, lakes, and beaches was still serious. At the same time, the earthquake and large-scale exploitation of oil, gas, groundwater, and coal energy accelerated the land subsidence in wetland and lakeside areas \[42\]. All of these destroyed the original ecological environment and created conditions for the enrichment of F\(^-\) in soil. When the water of Huolin River, the drainage of Shenzhong Waterlogged Area, the runoff around the lake, and the natural rainfall pass through the salinized land, they intake a large amount of salt, alkali, and F\(^-\) into the lake, including Chagan Lake, which aggravates the F\(^-\) pollution in the surface water. Second, the development of agriculture promotes the enrichment of fluoride in the study area. With the advancement of land development and consolidation project in western Jilin Province, the paddy field area has increased year by year, with a total increase of 745.61 km\(^2\) from 1989 to 2018 in the study area. During paddy field development and rice cultivation, a large amount of fluorine-containing irrigation wastewater is produced and drained. As these waters run over the surface of soil, a small portion is transferred to the soil through infiltration and eventually enters the groundwater. Most of the runoff is discharged into Chagan Lake through the main channel. In Chagan Lake, evaporation is the main way of excretion, and a large amount of F\(^-\) accumulates here, which makes the F\(^-\) concentration in Chagan Lake increase year by year. The total area of paddy field in the study area was 1222.28 km\(^2\), which was mainly distributed in the Qianguo Irrigation Area and Da’an Irrigation Area. The average return water of the two areas was \(2.85 \times 10^8\) m\(^3\) and \(0.90 \times 10^8\) m\(^3\), respectively, accounting for 70\% of the total recharge water of Chagan Lake \[25\]. The construction of the river–lake connection project in western Jilin had a certain contribution to lake F\(^-\) concentration. On the one hand, irrigation with the Nen River ensures the supply of agricultural water. On the other hand, the construction of river–lake connection project also increased the hydraulic connection between the lakes. In this study, the concentration of F\(^-\) in most of the surrounding lakes of Chagan Lake was high. After the connection of rivers and lakes or flood disasters, the F\(^-\) in the surrounding lakes entered Chagan Lake through the river network, which also affects the concentration of F\(^-\) in Chagan Lake.
Figure 5. (a) TDS vs. Na⁺/(Na⁺+Ca²⁺); (b) TDS vs. Cl⁻/(Cl⁻+HCO₃⁻); (c) Piper plot; (d) saturation index (SI) vs. F⁻; (e) Ca²⁺+Mg²⁺-HCO₃⁻-SO₄²⁻ vs. Na⁺-Cl⁻; (f) Na⁺ vs. Cl⁻.
5. Conclusions

(1) The average value of $F^-$ in groundwater was 3.02 mg/L. The high $F^-$ concentrations in groundwater were mainly distributed in Qian’an County. High $F^-$ groundwater was related to obvious major ionic chemistry, Na-rich and Ca-poor, with high pH and $\text{HCO}_3^-$ content. Such hydrochemical characteristics were closely related to the dissolution of fluorine-containing minerals and evaporation and concentration in water. The dissolving of fluorine-containing minerals and the desorption of $F^-$ in soil acted as the source of $F^-$ in groundwater. Calcite and dolomite precipitate removed Ca$^{2+}$ from the solution and thus resulted in a further dissolution of fluorine-containing minerals, releasing $F^-$ into groundwater. Cation exchange transformed Ca-rich groundwater into Na-rich groundwater, which further promoted the release of $F^-$ in sediments. Competitive anions, especially $\text{HCO}_3^-$, created conditions for the enrichment of $F^-$. Meanwhile, the increased concentration of ions (including $F^-$) caused by evaporation was another factor inducing the high $F^-$ content in groundwater.

(2) The concentration of $F^-$ in surface water was 4.56 mg/L. The highest concentration was found in Hongzi Pool and Hua’ao Pool. The total area of paddy field in the study area was 1222.28 km$^2$, which was primarily distributed in the Qianguo Irrigation Area and Da’an Irrigation Area. The fluorine-containing water produced by paddy field development and rice planting was discharged into Chagan Lake, which increased the $F^-$ concentration in Chagan Lake year by year. The construction of river–lake connection projects also changed the distribution law of $F^-$ in the surface water of the study area.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/5/629/s1, Figure S1: Quaternary pore phreatic water level contour map, Table S1: Statistics of total fluorine content in soil.

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