Hydrochemical Characteristics of Groundwater and Formation Mechanism of High-Fluoride Water in the Plain Area of the Irtysh River Basin, Xinjiang (Postprint)

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Abstract

To investigate the controlling factors of groundwater hydrochemistry and the genesis of high-fluoride water in the plain area of the Irtysh River basin, Xinjiang, 70 groundwater samples were collected from the basin in 2018. The spatial distribution characteristics of hydrochemical components and fluoride were analyzed, the formation and enrichment mechanisms of high-fluoride water were elucidated, and the contributions of different factors to the hydrochemical components of groundwater in the basin were quantitatively calculated using the Absolute Principal Component Score-Multiple Linear Regression (APCS-MLR) model. The results indicate that: (1) The groundwater in the study area is generally neutral to weakly alkaline. Fresh water predominates north of the Irtysh River, while slightly saline water predominates south of the Irtysh River. The exceedance rates of F- in groundwater north and south of the Irtysh River are 27.91% and 44.44%, respectively. The hydrochemical types of groundwater both north and south of the Irtysh River are predominantly HCO3·SO4—Na·Ca type. (2) SOM results suggest that F- may originate from fluorine-bearing minerals mixed with multiple elements; the APCS-MLR model demonstrates that the formation of groundwater hydrochemical components in the study area is primarily influenced by leaching-enrichment (58.03%), groundwater pH (16.28%), and primary geological environment (10.28%). (3) Mineral dissolution-precipitation, evaporation-concentration, rock weathering, and cation exchange are the principal factors controlling the formation of high-fluoride groundwater; groundwater environment, climatic factors, topographic and geomorphological features, and human activities are the principal factors controlling the enrichment of high-fluoride groundwater.

Full Text

Hydrochemical Characteristics and Genesis Mechanism of High-Fluoride Groundwater in the Irtysh River Basin Plain, Xinjiang

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Abstract

To investigate the hydrochemical control factors and genesis mechanisms of high-fluoride groundwater in the plain area of the Irtysh River Basin, Xinjiang, 70 groundwater samples were collected in 2018. The spatial distribution characteristics of hydrochemical components and fluoride were analyzed, and the formation and enrichment mechanisms of high-fluoride water were examined. Using an absolute factor analysis-multiple linear regression (APCS-MLR) model, the contributions of different factors to the hydrochemical components of groundwater in the basin were quantitatively calculated. The results show that: (1) The groundwater in the study area is generally neutral to slightly alkaline. The north of the Irtysh River is dominated by fresh water, while the south is dominated by brackish water. The fluoride exceedance rates in groundwater north and south of the Irtysh River are 27.91% and 44.44%, respectively. The primary hydrochemical type of groundwater in both areas is $HCO_3 \cdot SO_4$-$Na \cdot Ca$ type. (2) SOM analysis results indicate that fluoride may originate from fluorine-containing minerals mixed with various elements. The APCS-MLR model reveals that the formation of groundwater chemical components in the study area is mainly influenced by leaching enrichment (58.03%), groundwater pH (16.28%), and the primary geological environment (10.28%). (3) The main factors controlling the formation of high-fluoride groundwater include mineral dissolution and precipitation, evaporation and concentration, rock weathering, and cation exchange. The groundwater environment, climatic factors, topography, and human activities are the primary factors controlling the enrichment of high-fluoride groundwater.

Keywords: groundwater; hydrochemistry; fluorine enrichment; Irtysh River Basin Plain

Introduction

With regional population growth and economic development, groundwater resources are becoming increasingly vital for domestic, industrial, and agricultural water supply in arid and semi-arid regions. Groundwater hydrochemical characteristics and their controlling factors vary across different regions under multiple influences. Investigating groundwater hydrochemical characteristics can elucidate the origin and formation processes of groundwater in specific areas, which is crucial for the development, utilization, and protection of groundwater resources. Fluoride is an essential trace element for human growth; appropriate intake strengthens health, but deficiency can cause dental caries while excess leads to fluorosis. The national standard "Groundwater Quality Standard" (GB/T 14848-2017) specifies that the fluoride concentration in drinking water should be less than 1.0 $\mathrm{mg \cdot L^{-1}}$. Statistics indicate that 8% of the global population is affected by high-fluoride groundwater, with China, Ethiopia, India, and Argentina in South America being severely affected countries. Previous data analysis reveals serious fluoride exceedance in groundwater of the Irtysh River Basin, impacting local water safety. However, systematic studies on the hydrochemical characteristics, fluoride distribution, and enrichment mechanisms in this basin are still needed. Therefore, this study employs mathematical statistics, hydrogeochemical simulation, the APCS-MLR model, and self-organizing map (SOM) neural networks to investigate the hydrochemical characteristics and genesis mechanisms of high-fluoride groundwater, providing support for comprehensive ecological management and scientific water resource management in the basin.

1.1 Study Area Overview

The Irtysh River originates from the northern slope of the Altai Mountains in Fuyun County, Xinjiang, flowing through China, Kazakhstan, and Russia before emptying into the North Sea. This study focuses on the Chinese section of the river, covering an area of 5.7×10^{4} km^2 between 46°55 -49°10 N and 85°30 -90°30 E. The region features a north temperate continental cold climate with annual precipitation <120 mm and annual evaporation >1500 mm. The terrain slopes downward from north to south and west to east in a stepped pattern. The river system is comb-shaped, with all tributaries flowing into the Irtysh River from the right bank and no tributaries on the left bank. The exposed strata in the northern mountainous area include the Proterozoic, Sinian, Devonian, Cretaceous, and Silurian systems, with granite, diorite, and other igneous rocks. Quaternary deposits are poorly developed, primarily consisting of glacial and glaciofluvial sediments. In the plain area, Carboniferous, Quaternary Pleistocene and Holocene strata are exposed, with granite, carbonate rocks, sulfur-bearing minerals, feldspar minerals, and granite pegmatite. Quaternary genetic types are mainly alluvial-proluvial, alluvial, and aeolian deposits, with the vadose zone composed mainly of sand-gravel and sub-sandy soil. Influenced by neotectonic movement, the Quaternary in the plain area is relatively thin (<30 m), with aquifer lithology primarily sand and gravel, and aquitard lithology primarily mudstone and tuff. Groundwater types include unconsolidated rock pore water, Mesozoic-Cenozoic clastic rock fissure-pore water (with unconfined water overlying fissure-pore interlayer water), bedrock fissure water, and frozen layer water. Groundwater generally flows from north to south following the terrain, with runoff conditions gradually weakening from the piedmont to the plain area and hydraulic gradients decreasing. The alpine zone is the recharge area, the mid-mountain piedmont is the runoff area, and the river valley and low-lying areas are the discharge zones. Groundwater recharge is primarily atmospheric precipitation, supplemented by surface water. In mountainous areas, groundwater mainly recharges river water through springs, while river water recharges groundwater through unconsolidated rock pores or bedrock fissures along both sides of the riverbed. Groundwater discharge occurs mainly through phreatic evaporation, spring overflow, ditch drainage, and artificial extraction.

1.2 Groundwater Sample Collection and Testing

In August 2018, a total of 70 groundwater samples were collected from the study area (all unconfined water), with well depths generally <50 m (shallow groundwater), 50-100 m (middle-depth groundwater), and >100 m (deep groundwater). The shallow, middle-depth, and deep groundwater samples north of the Irtysh River numbered 43, 6, and 1, respectively, while those south of the river numbered 12, 5, and 3, respectively. Samples north of the Irtysh River were located in intermountain plain areas, while the remaining samples were in inland basin plains. Sampling point locations were determined using Real-Time Kinematics (RTK) (HCE320). Groundwater sample collection, transport, and testing strictly followed the "Technical Specification for Groundwater Environmental Monitoring" (HJ/T 164-2004). Before sampling, wells were pumped to remove three times the water volume, then sample bottles were rinsed three times with the water to be collected. Suspended solids were removed, and water samples were filtered through 0.22 m microporous membranes. Water for major cation and trace element analysis was stored in 250 mL polyethylene bottles, acidified with 1:1 HNO_3, sealed, refrigerated, and sent for testing as soon as possible. A multi-parameter analyzer (HANNA HI9828) was used to measure water temperature, pH, electrical conductivity (EC), oxidation-reduction potential (Eh), and other indicators on-site. Blank and parallel samples were collected simultaneously to ensure data reliability. All collected samples were analyzed by the Second Hydrogeological Engineering Brigade Laboratory of the Xinjiang Bureau of Geology and Mineral Resources according to the "Standard Examination Methods for Drinking Water" (GB/T 5750-2006). Test items included K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $HCO_3{}^-$, $CO_3{}^{2-}$, $NO_3{}^-$, F^-, total dissolved solids (TDS), and total hardness (TH). All sample relative errors were within $±$5%, indicating reliable data.

1.3.1 Self-Organizing Map Model

The self-organizing map (SOM) is an unsupervised artificial intelligence method proposed by Kohonen in 1982 for visualizing and clustering large, complex datasets with uniform characteristics. In SOM, multi-dimensional data are projected onto a low-dimensional space (typically two-dimensional) while preserving the original data relationships, such as topological structure. Compared with other multivariate statistical methods like principal component analysis (PCA) and factor analysis, SOM offers stronger visualization capabilities and simpler operation. K-means clustering can analyze data attributes in greater detail, grouping groundwater hydrochemical components into samples with similar hydrogeochemical characteristics.

1.3.2 Absolute Principal Component Scores-Multiple Linear Regression Model (APCS-MLR)

Traditional statistical methods cannot quantitatively analyze the influence degree of each index on groundwater hydrochemical components. To address this limitation, this study employs absolute principal component scores (APCS) as independent variables to quantify each index as an influence factor, using measured concentrations as dependent variables for multiple linear regression to construct an improved APCS-MLR model. Compared with traditional statistical methods, this approach can calculate the contribution rate of each index to groundwater hydrochemical components.

2.1 Groundwater Chemical Characteristics

Descriptive statistical analysis was performed on 13 indicators of 70 groundwater samples (Table 1). Considering the presence of some extremely high values, median values were used to reflect the overall hydrochemical parameters of the study area. The pH ranges of groundwater north and south of the Irtysh River are 7.09–8.22 and 6.50–8.37, respectively, with median values of 7.71 and 7.68, indicating neutral to slightly alkaline conditions. TDS ranges are 180.00–5668.00 $mg \cdot L^{-1}$ (median 692.00 $mg \cdot L^{-1}$) north of the river and 136.00–35776.00 $mg \cdot L^{-1}$ (median 1158.00 $mg \cdot L^{-1}$) south of the river. Fresh water (TDS < 1000 $mg \cdot L^{-1}$) accounts for 74.42% north and 20.93% south of the river; brackish water ($1000\ mg \cdot L^{-1} \leq TDS < 3000\ mg \cdot L^{-1}$) accounts for 11.11% north and 37.04% south; saline water ($3000\ mg \cdot L^{-1} \leq TDS < 10000\ mg \cdot L^{-1}$) accounts for 3.70% north and 27.91% south; brine ($TDS \geq 10000\ mg \cdot L^{-1}$) accounts for 0.00% north and 4.65% south. Fluoride concentrations range from 0.22–2.23 $mg \cdot L^{-1}$ (median 0.80 $mg \cdot L^{-1}$) north of the river and 0.20–3.84 $mg \cdot L^{-1}$ (median 0.97 $mg \cdot L^{-1}$) south of the river, with exceedance rates of 27.91% and 44.44%, respectively. The dominant cation concentration order is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in both areas. The anion concentration order is $HCO_3^- > SO_4^{2-} > Cl^-$ north of the river and $SO_4^{2-} > HCO_3^- > Cl^-$ south of the river. The primary hydrochemical type is $HCO_3 \cdot SO_4$-$Na \cdot Ca$, accounting for 46.51% of samples north and 29.63% south of the river. The Piper diagram [Figure 2: see original paper] shows that most sampling points plot in the $Na^+ + K^+$ region for cations, indicating origins from carbonate, silicate, and evaporite weathering dissolution. For anions, most points plot in sulfate and carbonate type regions, suggesting origins from sodium-bearing rock weathering dissolution. Samples south of the Irtysh River are more enriched in SO_4^{2-} than those north, likely due to stronger evaporation effects influenced by topography.

2.2 Self-Organizing Map (SOM) Results Analysis

The SOM model was trained using standardized data from 13 hydrochemical indicators. After training, the topological error was 0.00 and the quantization error was 0.38, indicating excellent model performance. The model generated neuron matrix plane maps for each parameter [Figure 3: see original paper], where color gradients identify correlations among indicators—red represents high values, blue represents low values, and similar colors indicate positive correlations. The color gradients for Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, ${SO_4}^{2-}$, ${HCO_3}^-$, EC, and TDS are similar, with maximum values dispersed in the upper right and gradually decreasing toward the lower left, indicating strong correlations and suggesting these indicators are influenced by water-rock interactions (e.g., mineral dissolution). The color gradients for F^- and pH increase from the lower left to the upper right, indicating similar sources, possibly from fluorine-containing minerals mixed with various elements. Using the SOM results as input for K-means clustering, groundwater samples were classified into three categories [Figure 3: see original paper]. Category I samples have low values for all 13 hydrochemical indicators, dominated by fresh water, with ${HCO_3}^-$ as the main anion and Ca^{2+} as the main cation, primarily influenced by leaching effects. Category II samples have moderate values, dominated by brackish water, with chemical components mainly affected by evaporation and gypsum ($CaSO_4$) and dolomite [$CaMg(CO_3)_2$] dissolution. Category III samples have high values for all indicators, dominated by saline water, with ${SO_4}^{2-}$ as the main anion and Na^+ as the main cation, primarily influenced by evaporation concentration and mineral dissolution. The maximum F^- value in Category III is 3.8 $mg \cdot L^{-1}$, while in Category I it is only 0.38 $mg \cdot L^{-1}$. Category II samples have higher values than Category I but lower than Category III, possibly because some Category II samples are located near a copper-molybdenum mine in Fuyun County and are significantly affected by human activities.

2.3 APCS-MLR Source Apportionment

Principal component analysis was performed on 13 hydrochemical indicators (F^-, pH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, ${SO_4}^{2-}$, ${HCO_3}^-$, ${CO_3}^{2-}$, ${NO_3}^-$, EC, Eh). The Kaiser-Meyer-Olkin (KMO) test yielded a value of 0.73, and Bartlett' s sphericity test was significant at $P < 0.001$, indicating good data suitability for factor analysis. Three common factors were extracted with a cumulative variance contribution rate of 84.59%. Factor 1 is the dominant control factor for groundwater, with a contribution rate of 58.03%. Factor 2 contributes 16.28%, and Factor 3 contributes 10.28%. Based on the eigenvalues and component matrix , Factor 1 is primarily loaded with Na^+, Ca^{2+}, Mg^{2+}, Cl^-, ${SO_4}^{2-}$, ${HCO_3}^-$, and EC, with contribution rates of 63.72%, 44.16%, 61.10%, 44.66%, 37.79%, 50.90%, and 20.46%, respectively. These indicators show significant positive correlations, suggesting Factor 1 represents leaching enrichment. Factor 2 is primarily loaded with F^- and HCO_3^-, with contribution rates of 61.04% and 63.64%, respectively. HCO_3^- mainly originates from carbonate dissolution and regulates groundwater pH, indicating that Factor 2 represents groundwater pH influence. Factor 3 is primarily loaded with F^-, EC, and Eh, with contribution rates of 53.09%, 44.16%, and 37.79%, respectively. F^- mainly originates from fluorine-bearing minerals, and Eh indicates redox conditions, suggesting Factor 3 represents the primary geological environment. The APCS-MLR model quantifies the contribution rates of each factor to the hydrochemical indicators [Figure 4: see original paper].

2.4 Spatial Distribution Characteristics of Groundwater F^- Concentration

To investigate the genesis and enrichment mechanisms of high-fluoride groundwater, the study area was divided based on F^- concentration: Type A (<1.0 $mg \cdot L^{-1}$), Type B ($1.0\ mg \cdot L^{-1} \leq F^- < 2.0\ mg \cdot L^{-1}$), and Type C ($F^- \geq 2.0$ $mg \cdot L^{-1}$), with Type C representing high-fluoride groundwater.

2.4.1 Horizontal Distribution Characteristics The distribution map of groundwater well depth zones and F^- concentration [Figure 5: see original paper] shows that high-fluoride groundwater is distributed to varying degrees across all counties and cities in the study area. Type A groundwater is mainly distributed in Habahe County and Burqin County in the western part of the study area and Fuyun County in the eastern part. Type B groundwater is distributed in Beitun City, Fuhai County, and parts of Altay City in the central part of the study area. Due to topographic effects, from the piedmont to the plain area, the terrain slope gradually becomes gentler, groundwater runoff conditions deteriorate, and F^- concentration shows an increasing trend. Beitun City, located deep inland far from the ocean, is blocked by the Altai Mountains from water vapor from the Arctic Ocean, resulting in scarce precipitation and strong evaporation. It belongs to a temperate desert climate with shallow groundwater depth (generally 1-3 m). The area of cultivated land and construction land in Beitun City has increased annually, intensifying human activities. The application of fluoride-containing pesticides and discharge of fluoride-containing waste may be one of the reasons for fluoride exceedance in this area.

2.4.2 Vertical Distribution Characteristics The vertical distribution map [Figure 5: see original paper] shows that F^- concentration fluctuates significantly at shallow well depths. Type C groundwater is distributed in shallow (<50 m), middle-depth (50-100 m), and deep (>100 m) zones. Type B groundwater is distributed in both shallow and middle-depth zones, while Type A groundwater is only distributed in shallow zones (<50 m). At shallow depths, evaporation concentration enriches F^- in shallow groundwater. At 50-100 m depth, the dissolution of fluorine-bearing minerals in groundwater provides abundant F^-. At >100 m depth, the long water-rock interaction time and high mineralization promote F^- enrichment.

2.5.1 Evaporation Concentration and Rock Weathering

The Gibbs diagram is a semi-logarithmic plot that intuitively reflects the characteristic factors of water ions, dividing controlling factors into atmospheric precipitation-controlled, rock weathering-controlled, and evaporation-crystallization-controlled types [Figure 6: see original paper]. Groundwater in the study area is mainly distributed in the evaporation-crystallization and rock weathering zones, indicating that rock weathering and evaporation-crystallization jointly contribute to F^- enrichment. Atmospheric precipitation has minimal influence on groundwater hydrochemical components. Some sampling points plot outside the model, suggesting other influences such as human activities. The relationship between Ca^{2+}/Na^+ and $HCO_3{}^-/Na^+$ can further identify rock weathering sources, dividing weathering sources into carbonate, silicate, and evaporite types [Figure 7: see original paper]. Type C groundwater is widely distributed across carbonate, silicate, and evaporite end-members. Type B and Type A groundwater plot near evaporite and silicate rocks, indicating that silicate and evaporite rocks promote F^- enrichment, while carbonate rocks have minimal effect. The relationship between F^- and F^-/Cl^- can further explain evaporation effects and geological impacts on fluoride enrichment [Figure 7: see original paper]. Most sampling points (65.71%) plot within the natural precipitation-evaporation line, while a few Type C groundwater points plot outside, indicating that evaporation and geological factors are causes of fluoride enrichment.

2.5.2 Dissolution-Precipitation Effects

The saturation index (SI) can determine the state of minerals in groundwater. The SI calculation expression is:

$$SI = \lg \frac{IAP}{K}$$

where K is the equilibrium constant of the mineral dissolution reaction at a given temperature, and IAP is the ion activity product of relevant ions. When SI < 0, the mineral is in a dissolution state; when SI $= 0$, it is in equilibrium; when SI > 0, it is in a saturated state. The hydrogeochemical simulation software PHREEQC (phreeqc.dat database) was used to calculate the saturation indices of calcite, dolomite, gypsum, halite, and fluorite to analyze water-rock interaction effects on groundwater chemical components. The mineral saturation index diagram [Figure 8: see original paper] shows that only one sampling point has SI(fluorite) > 0 (saturated state), while all others have SI(fluorite) $<$ 0 (dissolution state). F^- concentration shows a significant positive correlation with fluorite solubility [Figure 8: see original paper], indicating that fluorite dissolution provides abundant F^- to groundwater in the study area.

2.5.3 Cation Exchange Effects

The chlor-alkali index (CAI) is used to analyze cation exchange between water and aquifer minerals. The relationship between (Na^+ + K^+) - Cl^- and (Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-}) in meq/L is used to indicate cation exchange intensity. The chlor-alkali index is calculated as:

$$CAI1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-}$$

$$CAI2 = \frac{Cl^- - (Na^+ + K^+)}{HCO_3^- + SO_4^{2-} + CO_3^{2-} + NO_3^-}$$

When (Na^+ + K^+) - Cl^- is negative, groundwater Na^+ exchanges with Ca^{2+} in minerals; when positive, Ca^{2+} in groundwater exchanges with Na^+ in minerals. The larger the absolute value of the chlor-alkali index, the stronger the cation exchange reaction. F^- shows a significant negative correlation with (Na^+ + K^+) - Cl^- in meq/L, indicating strong cation exchange. The chlor-alkali index relationship diagram [Figure 9: see original paper] shows that most sampling points plot in the lower left of the 1:1 line, indicating that Na^+ in groundwater exchanges with Ca^{2+} in minerals. This Ca^{2+} deficit and Na^+ enrichment transforms groundwater into a calcium-poor, sodium-rich type favorable for fluoride enrichment. In summary, cation exchange promotes F^- enrichment.

2.6.1 Groundwater Environment

The pH environment is an important factor affecting F^- concentration in groundwater. In neutral to slightly alkaline conditions, OH^- can replace F^- in mineral lattices due to similar ionic radii (OH^-: 0.136 nm, F^-: 0.133 nm) and charges, releasing F^- into groundwater. Additionally, reduced Ca^{2+} activity in neutral and alkaline groundwater inhibits CaF_2 precipitation, favoring F^- enrichment. Besides OH^-, competitive adsorption with other negatively charged ions also promotes desorption of adsorbed F^- into groundwater. The relationship between pH and F^- [Figure 10: see original paper] shows that when groundwater pH ranges from 6.50 to 8.37, neutral to slightly alkaline conditions promote F^- enrichment. The relationship between HCO_3^- and F^- [Figure 10: see original paper] shows that F^- concentration increases with HCO_3^- concentration, indicating that HCO_3^- also influences F^- enrichment.

2.6.2 Climate Factors

Studies show that F^- easily enriches in groundwater in arid and semi-arid regions. The Irtysh River Basin has a typical arid climate with dry conditions, low natural precipitation, and annual evaporation far exceeding precipitation. Evaporation affects F^- concentration by causing continuous concentration and enrichment of F^- in shallow groundwater. The degree of primary mineral weathering and dissolution, biogeochemical cycling of elements, and migration rates are all affected by climatic conditions. The large temperature difference (summer maximum >45°C, winter minimum <-45°C) and intense freeze-thaw cycles promote dissolution of fluorine-bearing minerals, leading to F^- enrichment.

2.6.3 Topography and Landforms

Sampling points are mainly distributed in alluvial plains in front of mountains, with some in intermountain plain areas. Alluvial plains are formed by mountain snowmelt and river alluviation, with gentle topography and sluggish groundwater runoff. The aquifer media are primarily Quaternary alluvium, magmatic rocks, and dolomite. Intermountain plain areas are located between Altai Mountain hills at elevations >1000 m, formed by mountain snowmelt alluviation, with aquifer media primarily Quaternary alluvium and magmatic rocks. Both alluvial and intermountain plain areas share the characteristic of being located in low-lying areas of regional tectonic zones with gentle topography. Low-lying, gentle terrain leads to poor groundwater runoff conditions and prolonged water-rock interaction. Landforms and regional geological structure determine aquifer media types and material sources, affecting high-fluoride groundwater distribution. Combined with strong evaporation concentration, these factors promote gradual increases in groundwater fluoride concentration.

2.6.4 Human Activities

Gibbs diagram analysis indicates that groundwater chemical components may also be affected by human activities. The relationship between Cl^- and $NO_3{}^-$ can be used to study the dual effects of human activities and natural sources on hydrochemical components [Figure 11: see original paper]. Most sampling points show high $NO_3{}^-/Ca^{2+}$ and $SO_4{}^{2-}/Ca^{2+}$ ratios, indicating dual influence from human activities and natural sources. To further identify human activity impacts, the relationship between $NO_3{}^-/Ca^{2+}$ and $SO_4{}^{2-}/Ca^{2+}$ can be used to explore mining and agricultural activity effects while removing gypsum dissolution influences. Mining activities have higher $SO_4{}^{2-}/Ca^{2+}$ values, while agricultural activities have higher $NO_3{}^-/Ca^{2+}$ values. Most Type C groundwater samples plot above the $SO_4{}^{2-}/Ca^{2+} = 1$ line, indicating that mining activities have a more significant impact on fluoride enrichment than agricultural activities. According to the "Concise Atlas of Mineral Development in Xinjiang Uygur Autonomous Region," the study area is rich in mineral resources, including mirabilite, mica, and granite mines, all of which can affect groundwater chemical components. Mica and granite mines contain fluorine that can enter groundwater through various reactions, causing fluoride enrichment.

3 Conclusions

Through mathematical statistics, SOM analysis, APCS-MLR source apportionment, and other methods, this study investigated the hydrochemical characteristics and controlling factors of groundwater, spatial distribution patterns of high-fluoride groundwater, and the formation and enrichment mechanisms of high-fluoride groundwater in the Irtysh River Basin plain, Xinjiang. The main conclusions are:

1. Groundwater north and south of the Irtysh River is primarily neutral to slightly alkaline. The north is dominated by fresh water, while the south is dominated by brackish water. Fluoride concentration ranges from 0.22–2.23 $\mathrm{mg \cdot L^{-1}}$ north of the river and 0.20–3.84 $\mathrm{mg \cdot L^{-1}}$ south of the river, with exceedance rates of 27.91% and 44.44%, respectively. The dominant cation concentration order is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in both areas. The primary hydrochemical type is $HCO_3 \cdot SO_4$-$Na \cdot Ca$, accounting for 46.51% of samples north and 29.63% south of the river. SOM analysis indicates that fluoride may originate from fluorine-containing minerals mixed with various elements.

2. APCS-MLR model results show that the groundwater environment in the study area is mainly controlled by three factors: leaching enrichment (58.03%), groundwater pH (16.28%), and primary geological environment (10.28%). The main factors controlling the formation of high-fluoride groundwater include mineral dissolution and precipitation, evaporation and concentration, rock weathering, and cation exchange. Groundwater environment, climatic factors, topography, and human activities are the primary factors controlling high-fluoride groundwater enrichment.

3. Horizontally, Type C groundwater is mainly distributed in the western and eastern parts of the study area, while Type B groundwater is mainly distributed in the central part. Vertically, Type C groundwater occurs at various well depths, while Type B groundwater is only distributed at depths <50 m. The study provides a scientific basis for water resource management and fluoride pollution prevention in the Irtysh River Basin.

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