Concentration mechanism of fluorine, arsenic, and uranium in groundwater of the Hailar Basin, China

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Abstract

Located in a semiarid region of the Hulun Buir League in China’s Inner Mongolia Autonomous Region, the Hailar Basin is a region with less precipitation, where groundwater is the most important water supply source. It is important to study groundwater characteristics and hydrogeochemical processes for the better management of groundwater resources. Fluorine (F), arsenic (As), and uranium (U) cocontamination currently exists in the groundwater of the Hailar Basin, China. To understand the concentration mechanism of F, As, and U in groundwater in the study area, groundwater samples were collected for detection and analysis. The results showed that the main hydrochemical types in the study area were Cl–Na, HCO₃–Na, and HCO₃–Ca. The median values of F, As, and U were 3.32 mg/L, 0.029 mg/L, and 0.066 mg/L, respectively, which all exceeded the World Health Organization (WHO) guidelines. Through a Gibbs diagram and endmember diagram, it can be seen that the groundwater in the study area is mainly affected by the hydrogeochemical effects of evaporative crystallization, rock weathering mechanisms, and the dissolution of silicate rock and evaporative salt rock minerals. Mineral dissolution, cation exchange, and weakly alkaline environments are important factors affecting F concentrations. Low NO₃⁻ and SO₄²⁻ concentrations cause a reducing environment, and the competitive adsorption of HCO₃⁻ promotes As pollution. The concentrations of Ca²⁺, Mg²⁺, SO₄²⁻, and NO₃⁻ have a great influence on the concentration of U.

Keywords Hydrogeochemistry · Groundwater contamination · Potentially toxic elements (PTEs) · Semiarid regions

Introduction

In recent years, understanding the occurrence, mobility, transport, and fate of potentially toxic elements (PTEs) in natural water has been of great concern due to their widespread distribution and potential toxicity (Pourret et al. 2021; Pourret and Hursthouse 2019); specifically, fluorine (F), arsenic (As), and uranium (U) in groundwater are being widely studied in many countries (Alarcón-Herrera et al. 2013; Das et al. 2018; Farooqi et al. 2007; Finneran et al. 2002; Smedley et al. 2003). The cocontamination of F, As, and U in groundwater has become an increasingly serious global problem. This phenomenon is especially critical in semiarid regions, where groundwater is used as a major water source for domestic and agricultural use.

Drinking groundwater with a high-arsenic concentration (> 0.01 mg/L) for a long time can induce cancer and chronic kidney disease risks to humans (Jayasumana et al. 2015; WHO 2011), while drinking groundwater with a high fluorine concentration (> 1.5 mg/L) (Handa 1975; WHO 2011; Ripa 1993) can induce dental fluorosis and bone diseases. Groundwater with excessive uranium concentrations (> 0.03 mg/L) easily causes nephritis and other diseases (WHO 2011; Wu et al. 2014). In particular, the chemical toxicity of U absorbed through ingestion is more serious than its radiation risk (EFSA 2009). Uranium entering the human body can cause damage to tissues and organs such as the kidneys, bones, lungs, liver, brain, and reproductive system (Ma et al. 2020).

The concentrations of F and As in groundwater are mainly affected by natural factors such as geological and
topographic conditions. The major sources of As are arsenopyrite (FeAsS), orpiment (As₂S₃), and realgar (As₄S₄) (Kim et al. 2003). F is mainly released from minerals such as fluorspar (CaF₂), sellaite (MgF₂), and fluorapatite (Ca₅(PO₄)₃F) (Sarma and Rao 1997). Numerous studies have been conducted on groundwater pollution with the coexistence of F and As, especially in arid and semiarid areas such as China’s Datong Basin (Pi et al. 2015), Pakistan’s Lahore and Kasur regions (Farooqi et al. 2007), the Comarca Lagunera region in Mexico (Armienta and Segovia 2008), and the Diphu region in India (Kumar et al. 2016). However, few studies have focused on the hydrochemistry of groundwater cocontaminated by F, As, and U (Table 1). The Hailar Basin, located in the western Hulun Buir League in China’s Inner Mongolia Autonomous Region, is an arid to semiarid region that is prone to high F and As concentrations (Wen et al. 2013). Previous studies have shown that the Hailar Basin is rich in sandstone-type uranium deposits (Huang et al. 2021), and the groundwater in the Hailar Basin is at potential risk of contamination by F, As, and U. Therefore, government management departments have funded certain environmental research projects to solve and investigate related environmental problems in this area.

In the present study, shallow groundwaters were collected within the Hailar Basin. The concentrations of major ions were analyzed to understand the solute geochemistry and the hydrochemical process of shallow groundwater within the Basin, and the formation mechanism of F, As, and U in groundwater in the Hailar Basin is preliminarily understood based on the analysis of groundwater pollution. The results can provide scientific and useful implications for groundwater environmental management in the Hailar Basin and other similar basins.

| Sampling location | Range of U (μg/L) | Range of As (μg/L) | Range of F (mg/L) | Prevailing environmental conditions | References |
|-------------------|------------------|-------------------|------------------|------------------------------------|------------|
| The semiarid region of SW Punjab, India | 9.6–282.9 | 0.33–30.99 | 0.20–2.41 | Unconsolidated quaternary alluvial plain | Paikaray and Chander (2022) |
| The case of the Gerania Mountains, NE Peloponnese, Greece | BDL ~ 2.22 | 0.9–15 | – | The karstic aquifer; The fractured ultramafic aquifer; The granular alluvial unconfined coastal aquifer | Papazotos et al. (2020) |
| The central Gangetic Plain, Uttar Pradesh, India | BDL ~ 21.60 | BDL ~ 68.00 | 0.16–1.28 | The deposition of Quaternary River born alluvium | Yadav et al. (2020) |
| The Brahmaputra River floodplain | – | 0.80–22.1 | 0.01–1.31 | Alluvial flood plains, high precipitation and groundwater recharge rates | Nilotpal et al. (2018) |
| The Dawukou area | – | 0.25–22 | 0.06–2.8 | Evaporation strong; Rare precipitation | Chen et al. (2017) |
| The Jorhat district of Assam | – | 0.19–73.0 | – | Flood Plains; Tropical Monsoon Climate | Das et al. (2015) |
| The Datong Basin | – | 5.6–2680 | 0.40–3.32 | Arid regions; Alluvial lacustrineplains; Quaternaryaquifers | Pi et al. (2015) |
| The Chacho and Diplo districts of Tharparkar | – | 2.0–1390 | 0.966–60.5 | Sediment-filled basin; Low precipitation | Brahman et al. (2013) |
| The western Jilin province | – | 0.11–12.04 | 0.16–14 | Semiarid; Confined aquifers; Phreatic aquifers | Bian et al. (2012) |
| The Datong basin | BDL ~ 470 | BDL ~ 10.4 | – | Arid regions; Alluvial lacustrineplains; Quaternaryaquifers | Li et al. (2012) |
| The Lahore and Kasur districts | – | BDL ~ 1900 | 0.16–21.1 | Quaternary sediments; semiarid and subtropical continental climate | Farooqi et al. (2007) |
| The Huhhot Basin | 0.01–53 | 0.91–1290 | 0.25–6.60 | Arid regions; poorly permeable sediments | Smedley et al. (2003) |

“–” is untested data, BDL is below the detection limit.
Study area

The Hailar Basin is located in the transition zone between the Great Xing’an Mountains and the Mongolian Plateau from longitudes E115°20′–E120°10′ and latitudes N46°00′–N49°50′. The study area has a temperate continental climate, with cold and dry winters, hot and rainy summers, four distinct seasons, and large annual temperature differences (the average temperatures in summer and winter are 21.3 °C and –22.5 °C, respectively), with an average annual temperature of 0.2 °C and annual precipitation of approximately 280 mm. The Hailar Basin is a Mesozoic–Cenozoic fault-depression basin developed on the Hercynian fold basement, located on the suture line between the Sino-Korean plate and the Siberian plate (Guo et al. 2014a, b; Wu et al. 2006). The Hailar Basin has experienced multiple periods of tectonic movement and different degrees of damage and transformation, forming a relatively complex tectonic pattern. Therefore, the thickness of aquifers in different areas of the Beier Lake depression varies greatly and is not uniformly distributed, mainly in the Cretaceous Yimin Formation strata, and the lithology is all sandstone, mainly composed of sandstones with different particle sizes, such as silt, fine sand, medium sand, coarse sand and glutenite. The aquitard (weakly permeable layer) is mainly mudstone and clay with stable thickness and is a regional aquitard. The diving in the study area is recharged by atmospheric precipitation in the southeast and southwest directions and runs from south to north, moving to the vicinity of the Wuerxun River, where the burial depth of the groundwater table gradually decreases until it is close to the surface, forming a strong evaporation area. The clastic rock-like fracture pore pressurized water moves from southeast to northwest to Hulun Lake and the Hailar River, and the groundwater system is continuous and complete. Hulun Lake, the Cuogang Uplift, the Beier Lake Depression, the Hilly Uplift, and the Bayan Mountain Uplift lie from west to the east in the study area. The sampling points are mainly distributed around the surrounding area centered on the Beier Lake Depression (Fig. 1).

Materials and methods

Field sampling was carried out in accordance with the Technical Specifications for Environmental Monitoring of Groundwater (HJ 164-2020), with a total of 35 shallow well groundwater samples (Fig. 1). At least three well-bore volumes of groundwater were purged before taking samples. Water samples were collected only after pH and EC stabilized and when the fluctuations in pH and relative EC were less than 0.1% and 5%, respectively. We used 500 mL
polyethylene bottles on site to collect chemical samples of groundwater. The polyethylene bottles were washed with 10% nitric acid solution, control dried, filled with 10% nitric acid solution, sealed and stored for 24 h, and then washed three times with deionized water. After fully pumping and washing the well for sampling, the polyethylene bottles were washed with the water sample to be collected 2–3 times to ensure that the sampling bottle was filled with water, air was expelled, and the bottle was sealed. When sampling, after filtering with a 0.45 μm membrane, 500 mL polyethylene bottles were filled. Then, the cationic samples were acidified to pH < 2 with HNO₃. Water samples used for the analysis of anions were only treated with filtration during sampling. To ensure that the samples were not affected during storage, all samples were stored in a refrigerator (1–5 °C). The instrument was calibrated according to standard methods before testing. The pH, redox potential (Eh), total dissolved solids (TDS), electrical conductance (EC), and HCO₃⁻ hydrochemical parameters were tested on site. The pH and Eh were determined by a portable acidity meter (HI8424HANNA). The reference electrode of Eh was the AgCl electrode; TDS and EC were determined by a portable water quality multiparameter analyzer. HCO₃⁻ was determined with the acid–base indicator titration method. K⁺, Na⁺, Mg²⁺, Ca²⁺, U, As, and total Fe were measured using an inductively coupled plasma spectrometer (Agilent 5100 ICP–OES); F, Cl⁻, SO₄²⁻, and NO₃⁻ were tested using ion chromatography (ICS–1100). For all parameters, blank and check samples were sequentially measured, and the variance of duplicate measurements was less than 3%. The accuracy of the analyses was estimated for major ions using an electrical balance (Goldberg 2006; Hallouche et al. 2017). The normalized inorganic charge balance of most of the samples was less than 10%, indicating the accuracy of our data. A significant imbalance between negative and positive charges was observed for some samples, with a deficit of negative charge. The cause of imbalance may be attributed to the influence of organic anions (Xiao et al. 2012).

All data statistical analyses were performed using Excel 2010 (Microsoft Office), the sampling point map was drawn using ArcGIS 10.0 and Corel DRAW X4, and the experimental analysis figures were made using Origin 2018 and Aq-QA.

**Results and discussion**

**Characteristics of the groundwater environment**

Table 2 lists the physicochemical parameters of the groundwater samples. The main anions in groundwater are HCO₃⁻ and Cl⁻; the main cations are Na⁺ and Ca²⁺. The pH values are slightly alkaline, ranging from 7.12 to 8.63, the median value is 7.77, the coefficient of variation is small (0.04), and the degree of fluctuation is relatively stable. HCO₃⁻ ranges from 90.04 to 803.11 mg/L, with a median value of 409.10 mg/L. The TDS content is relatively high, the concentration ranges from 244 to 3690 mg/L, the median value is 1090.00 mg/L, and 51.43% of groundwater samples are brackish water (Huang et al. 2005). Cl⁻ ranges from 4.16 to 909.33 mg/L, the median value is 185.61 mg/L, and 28.57% of groundwater samples exceed national standards for drinking water quality (GB5749-2006) (> 250 mg/L) (Ministry of Environmental Protection of P.R. China 2006). The median concentrations of SO₄²⁻, NO₃⁻, and total Fe are 82.05, 5.80, and 0.17 mg/L, respectively. Eh ranges from –133 to 329 mV, indicating that there is a transition from a reducing environment to an oxidizing environment in the study area.

| Index     | Min   | Max   | Mean  | Median | Standard Deviation | Coefficient of Variation |
|-----------|-------|-------|-------|--------|-------------------|--------------------------|
| pH        | 7.12  | 8.63  | 7.77  | 7.77   | 0.34              | 0.04                     |
| TDS (mg/L)| 244   | 3690  | 1195.44 | 1090.00 | 819.06            | 0.69                     |
| EC (μS/cm)| 330   | 5240  | 1675.21| 1526.50| 1172.50           | 0.70                     |
| Eh (mV)   | –133  | 329   | 188.52| 221.00 | 100.86            | 0.54                     |
| K⁺ (mg/L) | 0.67  | 49.17 | 5.28  | 3.95   | 7.98              | 1.51                     |
| Na⁺ (mg/L)| 12.87 | 625.79| 240.83| 233.17 | 175.62            | 0.73                     |
| Ca²⁺ (mg/L)| 5.79  | 123.11| 49.85 | 43.23  | 26.62             | 0.53                     |
| Mg²⁺ (mg/L)| 5.23  | 164.03| 42.35 | 38.06  | 28.78             | 0.68                     |
| Cl⁻ (mg/L)| 1.16  | 909.33| 224.41| 185.61 | 230.55            | 1.03                     |
| SO₄²⁻ (mg/L)| 4.17 | 417.82| 97.44 | 82.05  | 94.47             | 0.97                     |
| NO₃⁻ (mg/L)| 0.00  | 32.81 | 7.59  | 5.80   | 6.96              | 0.92                     |
| HCO₃⁻ (mg/L)| 90.04 | 803.11| 405.36| 409.10 | 160.13            | 0.40                     |
| Total Fe (mg/L)| 0.124 | 4.609 | 0.46  | 0.17   | 0.87              | 1.88                     |
Based on the Piper diagram (Fig. 2) (Piper 1944), five main hydrochemical types are identified in groundwater: Cl–Na (40.00%), HCO₃–Na (34.29%), HCO₃–Ca (14.29%), HCO₃–Mg (8.57%), and Cl–Ca (2.86%). Obviously, Cl–Na and HCO₃–Na are the main hydrochemical types in the Hailar Basin. The HCO₃–Na (Mg) hydrochemical type is predominant in the Bayan Mountain Uplift. Because of the large terrain drop and steeper hydraulic gradients in this area, dissolution and filtration easily occur, which dissolve the carbonate in the water.

In the Beier Lake Depression, the Cl–Na hydrochemical type is predominant because the area is flat, the water flow speed is slow and shallow, the buried depth of the groundwater level has an obvious concentration effect, and evaporation becomes the main discharge path of groundwater. Due to evaporation and concentration bicarbonate by constant rock saturated exhalation of sulfuric acid, Cl⁻ and Na⁺ are the mainly components in the Beier Lake Depression. The junction of the Cuogang Uplift, Bayan Mountain Uplift, Beier Lake Depression and Hill Uplift belongs to the runoff area, where the groundwater depth is general, the terrain changes greatly, the soil particle size changes from coarse to fine, and the contained hydrochemical types are complex.

**Hydrogeochemical processes**

Reactions between groundwater and aquifer minerals play a significant role in water quality, which is also useful for understanding the genesis of groundwater (Xiao et al. 2012). The chemical characteristics of water and the relative abundance of chemical species may be used to determine the source from which the majority of the ions originate and the mechanism controlling groundwater chemistry (Haritash et al. 2017). Using the Gibbs diagram method, Paikaray and Chander (2022) demonstrated the significance of rock dominance and evaporation dominance on the contamination of PTEs in groundwater in a semiarid region of SW Punjab, India. Gibbs diagrams were drawn (Fig. 3) (Gibbs 1970), and the controlling effect and source of groundwater chemical composition in the Hailar Basin can be preliminarily discussed. Obviously, in the study area, groundwater is mainly controlled by both evaporation dominance and rock dominance. Because the topography of the study area is relatively flat, the hydraulic gradient is small, the groundwater velocity is relatively slow, and the groundwater level is shallow. Meanwhile, the study area is a semiarid region and subject to obvious evaporation and concentration, further concentrating the ionic components in the water and increasing the
concentration of TDS and pH value, resulting in the replacement of OH⁻ with F, As and U, indirectly promoting the release of F, As and U in the minerals (Dong et al. 2015).

To further study, the rock dominance in the Hailar Basin, the relationships among the ratios of Mg²⁺/Na⁺, Ca²⁺/Na⁺ and HCO₃⁻/Na⁺ are used to explain the interactions between groundwater and various rock bodies (Fig. 4) (Gaillardet et al. 1999). The groundwater samples are mainly distributed between silicate rocks, and evaporative salt rocks control the endmember, indicating that the chemical composition of the groundwater in the study area is mainly controlled by silicate rocks and evaporative salt rocks. The weathering of silicate rocks has a greater impact on water chemical composition than evaporative salt rocks. Silicate rocks are mainly composed of feldspar, in which Na⁺ is abundant. Most samples had higher TDS values and higher Na⁺ and Cl⁻ concentrations and hence low Ca²⁺/Na⁺ and Mg²⁺/Na⁺ ratios. Meanwhile, Na⁺ and Cl⁻ were significantly correlated at the 0.01 level (p = 0.895), which suggests that salt rock input is the main source for their Na⁺ and Cl⁻ (Xiao et al. 2012).

Fluorine

The content of F in the groundwater of the Hailar Basin was relatively high, ranging from 0.14 to 13.89 mg/L, with a median value of 3.32 mg/L, which exceeded the Chinese
guidelines and WHO guidelines (Table 3) (Ministry of Environmental Protection of P.R. China 2006; WHO 2017). The Pourbaix diagram of F species (Fig. 5a) demonstrates that F is mainly located in the HCO₃⁻ and CaCO₃/CaMg(CO₃)₂ regions. For 7 < pH < 8, the groundwater samples are mainly distributed in the HCO₃⁻ area; as the pH increases, they transition to the CaCO₃/CaMg(CO₃)₂ area. Studies have proposed that a pH increase could promote F release from host surfaces due to the competitive adsorption effect of OH⁻ (Pi et al. 2015; Saxena and Ahmed 2003). Meanwhile, high HCO₃⁻ and low Ca²⁺/Mg²⁺ were conducive to F concentration (Adimalla and Li 2019). As shown in Fig. 5b, there was a certain positive correlation between F and HCO₃⁻ because with the increase in HCO₃⁻ concentration, Ca²⁺/Mg²⁺ in water reacted with HCO₃⁻ to generate Ca₂CO₃/CaMg(CO₃)₂ (Formulas 1 and 2). There is a negative correlation between F and Ca²⁺ (Fig. 5c), and the decrease in Ca²⁺ concentration is beneficial to promote the reaction of Formula 3 and increase the concentration of F in water. As shown in Fig. 5d, there was a significant positive correlation between F and Na⁺. To further verify the reason, we calculated the chloro-alkaline indices (CAI 1 and CAI 2) (Fig. 5e) (Schorr 1965). The chloro-alkaline indices of most sampling points were under 0, indicating that Na⁺ and K⁺ in the surrounding rock exchange with Ca²⁺ and Mg²⁺ in the groundwater (Eq. 4). This reduced the concentration of Ca²⁺ in the groundwater and promoted the dissolution of CaF₂ to release F⁻ (Eq. 3), which increased the concentration of F in the groundwater. As revealed in Fig. 2, the content of F in HCO₃⁻-Na water exceeds that of the Chinese guidelines and WHO Guidelines, which further verifies that HCO₃⁻, Na⁺ and F ions are positively correlated, which is consistent with the research results of Chae et al. (2007) and Li et al. (2014). Combining the results of the analysis in Fig. 4, the groundwater in the study area experiences large silicate mineral weathering. Formula (5) shows that dissolved silicate minerals can produce HCO₃⁻, which will promote Formulas (1) and (2) in the right direction and induce calcite and dolomite formation. The Ca²⁺ concentration in water becomes low. Finally, the reaction of Formula (3) is promoted to the right, resulting in the dissolution of fluoride and an increase in the fluoride concentration in water. Meanwhile, F can be adsorbed on the surface of hydrous ferric oxide (HFO) to form hydrous ferric oxide-fluorine (HFO-F), but in a weakly alkaline environment, HCO₃⁻ will compete with F for adsorption and then release F.

\[
\text{Ca}^2+ + 2\text{HCO}_3^- \rightarrow \text{Ca}_2\text{CO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Ca}^2+ + \text{Mg}^2+ + 4\text{HCO}_3^- \rightarrow \text{CaMg(CO}_3)_2 \downarrow + 2\text{CO}_2 \uparrow + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{CaF}_2 \rightarrow \text{Ca}^2+ + 2\text{F}^- \quad (3)
\]

\[
\text{Ca}^2+ + 2\text{NaX} \rightarrow 2\text{Na}^+ + \text{CaX}_2 \quad (4)
\]

\[
\text{Silicate mineral} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Kaolinite} + \text{HCO}_3^- + \text{Cation} + \text{H}_2\text{SiO}_4 \quad (5)
\]

### Arsenic

Obviously, the High-As groundwater in the Hailar Basin was more serious. As shown in Table 3, in the groundwater of the study area, the concentration of As ranged from 0.005 to 0.123 mg/L, with a median value of 0.029 mg/L, and the 94.29% samples exceeded drinking water guideline (the limit is 0.01 mg/L) (Ministry of Environmental Protection of P.R. China 2006; WHO 2017). As can occur in the environment in several oxidation states, but the most prevalent forms are As(III) and As(V). As(V) is generally more soluble than the more toxic As(III) but also has a higher sorption affinity (Swift Bird et al. 2020). The Pourbaix diagram of As species indicates that HAsO₄²⁻ mainly existed in groundwater (Fig. 6). Mobility in groundwater is often controlled by sorption/desorption reactions with iron (Fe) and manganese (Mn) oxides, which are common components of sandstone (Bowell 1994). The near-neutral pH and relatively reducing conditions promote the retention of As(V) onto Fe minerals.

| Parameters | Min | Max | Mean | Median | Standard deviation | Coefficient of variation | Chinese guidelines | WHO guidelines | Percentage of samples exceeding the standards (%) |
|------------|-----|-----|------|--------|-------------------|------------------------|-------------------|---------------|-----------------------------------------------|
| F (mg/L)   | 0.14| 13.89| 3.94 | 3.32   | 2.88              | 0.73                   | 1.0               | 1.5           | 88.57<sup>ab</sup>                           |
| As (mg/L)  | 0.005| 0.123| 0.036| 0.029  | 0.025             | 0.689                  | 0.01              | 0.01          | 94.29<sup>ab</sup>                           |
| U (mg/L)   | 0.017| 0.257| 0.075| 0.066  | 0.048             | 0.637                  | –                 | 0.03          | 94.29<sup>b</sup>                            |

<sup>a</sup>Chinese guidelines (Ministry of Environmental Protection of P.R. China 2006)

<sup>b</sup>WHO guidelines (WHO 2017)
(in the form of FeO≡HAsO₄). As(III) and As(V) can occur together in groundwater due to redox disequilibrium (Bowell et al. 2014). As the Eh value decreases, As(V) on Fe mineral surfaces can be reduced into the more mobile As(III) and further strengthen As mobilization from sediment (Pi et al. 2015). Studies have shown that As(V) was released from HFO under reducing conditions without any prereduction of As(V) to As(III), especially over pH 8.5. As largely desorbed from HFO surfaces to substantially elevate the aqueous As concentration (Smedley and Kinniburgh 2002). The phenomenon of some high-As appeared in low NO₃⁻ and SO₄²⁻ groundwater samples (Fig. 6b, c). Low NO₃⁻ and SO₄²⁻ values usually represent a strong reducing environment, and a strong reducing environment may benefit As
activation and enrichment (He et al. 2021). There are also studies that show that groundwater with high concentrations of NO$_3^-$ exhibits low concentrations of As, suggesting that As remains adsorbed in Fe/Mn-oxyhydroxides in sediments/soils in a NO$_3^-$ stable environment (Guo et al. 2014a, b; Papazotos et al. 2020). If the NO$_3^-$ concentration is high, the groundwater is in an oxidizing environment, which is not conducive to the reduction and dissolution of Fe/Mn-oxyhydroxide (Weng et al. 2017). As shown in Fig. 6d, there was a significant positive correlation between As and HCO$_3^-$, which might be due to the competitive adsorption relationship between As and HCO$_3^-$, which enhances As
mobility (Swift Bird et al. 2020). However, the As concentration decreased with increasing HCO$_3^-$ concentration at some sampling points, indicating that HCO$_3^-$ was not the key factor causing high-arsenic groundwater. There was no significant correlation between As and total Fe (Fig. 6e), which might be due to the partially dissolved total Fe derived from weathering of minerals such as biotite (McArthur et al. 2001; Pal et al. 2002). Meanwhile, the release of As (III) might mediate the reduction of As (V) in a microbial manner using sulfide as the electron donor (Couture et al. 2010; Pi et al. 2015).

**Uranium**

As shown in Table 3, in the groundwater of the study area, the concentration of U ranged from 0.017 to 0.257 mg/L, with a median value of 0.066 mg/L, and the 94.29% samples exceeded drinking water guideline (the limit is 0.03 mg/L) (WHO 2017). According to the topographical conditions of the basin, the middle is low, and the surroundings are high, which provides dynamic conditions for water–rock interactions and promotes the migration and concentration of U in groundwater. The Pourbaix diagram of U species indicates that all hydrous ferric oxide -uranium (HFO-U), UO$_2$(CO$_3$)$_3^{4-}$, and uraninite (c) (Fig. 7a). Under oxidation conditions, it mainly exists in the form of HFO-U, UO$_2$(CO$_3$)$_3^{4-}$. For $7 < $ pH $< 8$, HFO-U is the main existing form; for $pH > 8$, UO$_2$(CO$_3$)$_3^{4-}$ is the main existing form. Under reducing conditions, it mainly exists in the form of uraninite(c). Therefore, under relatively alkaline oxidation conditions, it is more conducive to the desorption of uranium, and alkaline pH is more favorable for uranium mineral dissolution activity and increases the concentration of U in groundwater. Meanwhile, there was a significant positive correlation between U and Ca$^{2+}$ + Mg$^{2+}$ (Fig. 7b). With the increase in Ca$^{2+}$ + Mg$^{2+}$ concentration, U in the uranium mine would be released into water, while Ca$_2$CO$_3$ and CaMg(CO$_3$)$_2$ would be formed, which is consistent with the research results of (Liesch et al. 2015). The average concentration of SO$_4^{2-}$ was 97.44 mg/L, and there was a certain positive correlation between U and SO$_4^{2-}$ (Trend 1) (Fig. 7c), indicating that the oxidation conditions were

![Pourbaix diagram (Eh–pH) of uranium species in aqueous solutions at 25 °C and 1 atmospheric pressure](image1)

![U versus (Ca$^{2+}$ + Mg$^{2+}$) diagram](image2)

![U versus SO$_4^{2-}$ diagram](image3)

![U versus NO$_3^-$ diagram](image4)

Fig. 7  a Pourbaix diagram (Eh–pH) of uranium species in aqueous solutions at 25 °C and 1 atmospheric pressure, b U versus (Ca$^{2+}$ + Mg$^{2+}$) diagram, c U versus SO$_4^{2-}$ diagram and d U versus NO$_3^-$ diagram for groundwater in the Hailar Basin

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more conducive to the concentration of U. With the further increase in $SO_4^{2-}$ concentration (Trend 2), the combination of desulfurization bacteria with organic matter promoted the reduction of $SO_4^{2-}$ to $H_2S$, increased $HCO_3^-$ and increased the pH value (Formula 6), and U reacted with $H_2S$ to produce uranium mines ($UO_2$) (Formula 7). A low $SO_4^{2-}$ content appeared in groundwater. It can be used as an auxiliary marker to judge the structure of uranium mines. Studies have shown that $NO_3^-$ plays an important role in the concentration and migration of U (Fig. 7d) (Beaucaire and Toulhoat 1987; Nolan and Weber 2015). With the development of agricultural production in the Hailar Basin, the concentration of U(IV) could be increased by providing conditions for the oxidation of U(IV) into U(VI). Additionally, the likely reason for the strong uranium–nitrate correlation in groundwater could be due to increased fertilization of agricultural land using phosphate fertilization. Phosphate fertilization remains the main source of uranium contamination of agricultural land, primarily due to impurities in the phosphate rock used for fertilizer manufacture (Kratz et al. 2016; Papazotos et al. 2019; Schnug and Lottermoser 2013).

Meanwhile, the other is the release and enhanced mobility of geogenic uranium triggered by agricultural nitrate and phosphate fertilization (Banning et al. 2013; Wu et al. 2010).

\[
SO_4^{2-} + 2C + 2H_2O \rightarrow H_2S + 2HCO_3^- 
\] 

\[
UO_2(CO_3)_2^{2-} + H_2S \rightarrow UO_2 \downarrow + S^0 + 2HCO_3^- 
\]

**Comobilization of fluoride, arsenic, and uranium**

In this study, the copollution of F, As and U occurred in the Hailar Basin. Figure 8a–c was drawn to study whether there was a synergistic effect among the three. The correlation coefficients of As and U and As and F were 0.090 and 0.237, respectively, but the relationship between U and F was more significant, with a correlation coefficient of 0.665. Because Ca$^{2+}$/Mg$^{2+}$ acts together between U-containing minerals and F-containing minerals, high $HCO_3^-$ is also

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**Fig. 8** a U versus As diagram, b F versus As diagram and c U versus F diagram for groundwater in the Hailar Basin
the reason for the significant relationship between U and F. Meanwhile, with the build-up of oxidizing conditions, Fe(II) oxidation and organic degradation caused the precipitation of Fe(III) (hydr) oxides and the production of inorganic salts and \( \text{HCO}_3^- \) (Christensen et al. 2000). Newly formed Fe(III) minerals show high affinity for As(V), resulting in As retention to the solid phase (Pi et al. 2015), and newly formed \( \text{HCO}_3^- \) promotes the desorption of U and F.

**Conclusions**

This study investigated the basic hydrogeochemical characteristics of F, As, and U in the groundwater of the Hailar Basin, China. The following conclusions can be summarized.

(1) The main hydrochemical types in the study area were Cl–Na, \( \text{HCO}_3^-–\text{Na} \), and \( \text{HCO}_3^-–\text{Ca} \). The pH median value is 7.77, the median value of \( \text{HCO}_3^- \) is 409.10 mg/L, and the groundwater is in a slightly alkaline environment, which is conducive to the enrichment of F, As, and U. Gibbis analysis shows that groundwater hydrochemistry in the Hailar Basin is affected by evaporation dominance and rock dominance, and dissolution of silicate rocks and evaporative salt rocks are the main hydrogeochemical processes in the study area, which provide basic conditions for the concentrations of F, As, and U.

(2) The median value of F was 3.32 mg/L, which exceeded the Chinese guidelines and WHO guidelines. Mineral dissolution, cation exchange, and a slightly alkaline environment were factors that affected the F concentration. The concentration of As had a median value of 0.029 mg/L, and the 94.29% samples exceeded drinking water guideline, because low \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) would cause a reduction environment, and \( \text{HCO}_3^- \) competition adsorption had a positive effect on As pollution. The median value of U was 0.066 mg/L, and the 94.29% samples exceeded drinking water guideline. The concentrations of \( \text{Ca}^{2+} + \text{Mg}^{2+} \) and \( \text{SO}_4^{2-} \) had a great influence on the concentration of U. In addition, fertilization of agricultural land is also an important source of uranium in groundwater, and the other is the release and enhanced mobility of geogenic uranium triggered by agricultural nitrate and phosphate fertilization. The correlation between U and F is good because \( \text{Ca}^{2+}/\text{Mg}^{2+}/\text{HCO}_3^- \) plays a similar role between U-containing minerals and F-containing minerals.

This study investigates the concentration mechanism of F, As, and U in groundwater in the Hailar Basin, which is of great importance for groundwater resource management in the study area, and this study could also be used as a basis for future studies.

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**Declarations**

**Competing interests** The authors have not disclosed any competing interests.

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