Enrichment Characteristics of Nitrate and Fluoride in Groundwater and Surface Water in the Yellow River South Bank Irrigation District of Hanggin Banner

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Abstract

Composite nitrate and fluoride pollution poses a serious threat to ecological environmental security and human health in arid and semi-arid irrigation areas; however, systematic research on this type of pollution in the irrigation area on the south bank of the Yellow River in Hanggin Banner remains limited. Accordingly, this study collected 89 water samples from the study area in November 2024, including 39 groundwater samples, 39 canal water samples, and 11 Yellow River water samples. Self-organizing map neural networks (SOM), principal component analysis (PCA), and the Monte Carlo model (MCM) were comprehensively applied to systematically investigate the enrichment characteristics, driving mechanisms, and human health risks of nitrate and fluoride in water bodies. The results showed that the water bodies in the study area were generally weakly alkaline, with pH values ranging from 7.35 to 9.41 and total dissolved solids (TDS) concentrations of 418 to 30000 mg · L -1. Nitrate and fluoride concentrations in some water samples exceeded the Class III water quality limits. SOM analysis classified the 89 water samples into three groups (C1-C3): C1 represented Ca · Na-HCO 3 type water with moderate nitrate and fluoride contents, C2 represented Na-SO 4 · Cl type water with high nitrate and fluoride enrichment, and C3 represented high-salinity Na-SO 4 · Cl type water. Hydrogen and oxygen isotope tracing confirmed that surface water and groundwater in the study area were mainly recharged by atmospheric precipitation and were significantly affected by evaporation. PCA extracted three principal components, including water-rock interaction (57.30%), the alkaline aquatic environment (14.62%), and anthropogenic input (10.84%). Among them, anthropogenic input was the dominant factor controlling nitrate enrichment, while water-rock interaction and the alkaline aquatic environment jointly drove fluoride release. The health risk assessment indicated that groundwater posed the highest health risk in the study area, and the non-carcinogenic risk for children was significantly higher than that for adults. Overall, priority should be given to strengthening the prevention and control of nitrate and fluoride pollution in groundwater in the study area, with particular emphasis on ensuring the safety of drinking water for children.

Full Text

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Enrichment Characteristics of Nitrate and Fluoride in Groundwater and Surface Water in the Yellow River South Bank Irrigation District of Hanggin Banner

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Abstract: Co-contamination by nitrate and fluoride poses a serious threat to ecological and environmental security and human health in arid and semi-arid irrigation districts; however, systematic research on this type of pollution in the Yellow River South Bank Irrigation District of Hanggin Banner remains relatively limited. Accordingly, in November 2024, this study collected 89 water samples from the study area, including 39 groundwater samples, 39 canal-water samples, and 11 Yellow River water samples. By comprehensively applying a self-organizing map neural network (SOM), principal component analysis (PCA), and a Monte Carlo model (MCM), the enrichment characteristics, driving mechanisms, and human health risks of nitrate and fluoride in water bodies were systematically investigated. The results show that the water bodies in the study area are generally weakly alkaline, with pH values ranging from 7.35 to 9.41 and total dissolved solids (TDS) contents of 418–30000 $mg \cdot L{-1}$; nitrate and fluoride concentrations in some water samples exceed the Class III water-quality limits. SOM analysis divided the 89 water samples into three categories (C1–C3): C1 represents $Ca \cdot Na - HCO_3$-type waters with moderate nitrate and fluoride contents; C2 represents $Na - SO_4 \cdot Cl$-type waters highly enriched in nitrate and fluoride; and C3 represents high-salinity $Na - SO_4 \cdot Cl$-type waters. Hydrogen and oxygen isotope tracing confirms that surface water and groundwater in the study area are mainly recharged by atmospheric precipitation and are significantly affected by evaporation. PCA extracted three principal components, including water–rock interaction (57.30%), the alkaline environment of the water body (14.62%), and anthropogenic input (10.84%); among them, anthropogenic input is the dominant factor driving nitrate enrichment, while water–rock interaction and the alkaline aquatic environment jointly drive fluoride release. The health-risk assessment results indicate that groundwater in the study area has the highest health risk, and that the non-carcinogenic risk for children is significantly higher than that for adults. In summary, priority should be given in the study area to strengthening the prevention and control of nitrate and fluoride pollution in groundwater, with particular emphasis on ensuring the safety of children' s drinking water.

Keywords: Yellow River South Bank Irrigation District of Hanggin Banner; water quality; self-organizing map neural network (SOM); principal component analysis (PCA); health risk assessment

Groundwater and surface water are the main sources of water supply in arid and semi-arid regions and are essential for daily life, industrial development, and agricultural production[1]. However, rapid urbanization and industrialization have threatened the quality of groundwater and surface water in many regions[2]. Among these threats, fluoride (F^-) and nitrate (NO_3^-) have become the major pollutants in regional groundwater and surface water[3]. Long-term excessive intake of fluoride can damage the bones, teeth, and nervous system[4]; meanwhile, infants who ingest excessive nitrate over a long period may develop methemoglobinemia (blue baby syndrome)[5]. In view of these health risks, it is crucial to identify the sources of F^- and NO_3^- in groundwater and surface water, as well as their enrichment mechanisms. Existing studies have shown that the main factors affecting the contents of these two pollutants include natural factors, such as water–rock interaction and an alkaline aquatic environment, and anthropogenic factors, such as agricultural activities[6]. Therefore, it is urgently necessary to determine the effects of natural and anthropogenic factors on the enrichment characteristics of F^- and NO_3^- in groundwater and surface water, thereby providing a scientific basis for optimizing water-resource management and safeguarding human health.

Located in northwestern China, the Yellow River South Bank Irrigation District of Hanggin Banner is one of the country' s large-scale irrigation districts. Agricultural production there requires large amounts of water, and groundwater and Yellow River water are important water sources on which it depends[7]. However, frequent agricultural activities have led to the deterioration of groundwater and surface-water quality in the irrigation district, with agricultural drainage serving as a key pathway by which pollutants migrate into water bodies. From 2017 to 2022, the proportion of irrigation drainage volume to water withdrawal increased markedly from 15.50% to 27.00%[8]. Under farmland percolation, drainage carries large quantities of pollutants into water bodies, directly threatening regional water-quality security. The formation of this pollution problem is closely related to high-intensity agricultural inputs and extensive irrigation methods. Specifically, excessive use of chemical fertilizers, pesticides, and agricultural films creates a high pollution load. Flood irrigation promotes the entry of pollutants into drainage systems through soil leaching, further aggravating the burden on the water environment[9]. Among these pollutants, the enrichment of F^- and NO_3^- is particularly prominent and has become a key factor affecting groundwater and surface-water quality in the Yellow River South Bank Irrigation District of Hanggin Banner[10]. Field investigations and data integration show that, after autumn irrigation, the irrigation district contains

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salt content and pollutant enrichment reach their annual maximum, and water quality at this time can reflect the overall level of contamination. Therefore, this study used groundwater and surface-water quality data after the end of autumn irrigation (November) to carry out the research. Existing studies have revealed the driving roles of natural and anthropogenic factors in the enrichment of F^- and NO_3^- in groundwater of the Ordos Basin at the large regional scale[11]. However, for the specific area of the Yellow River South-Bank Irrigation District in Hanggin Banner, the enrichment characteristics of F^- and NO_3^- in groundwater and surface water still lack detailed characterization. Therefore, studying the enrichment mechanisms and potential health risks of F^- and NO_3^- in this irrigation district is of key significance for remedying insufficient understanding at the regional scale, accurately guiding water-quality improvement, and effectively safeguarding human health.

In recent years, studies on groundwater and surface-water quality and their potential health risks have developed into a model that combines hydrochemical analysis with mathematical algorithms, such as multivariate statistical analysis and machine learning[12]. Among these, the combination of self-organizing map neural networks (Self-Organizing Map, SOM) and principal component analysis (Principal Component Analysis, PCA) has been proven effective for processing complex hydrochemical datasets and identifying spatial patterns in groundwater chemistry[13]. In addition, some scholars have found that combining health-risk assessment with Monte Carlo simulation (Monte Carlo Health Risk Assessment Model, MCM) can effectively improve the accuracy and reliability of assessment results[14]. Accordingly, this study combines three methods—SOM, PCA, and MCM—to analyze the enrichment mechanisms and potential health risks of F^- and NO_3^- in groundwater and surface water of the Yellow River South-Bank Irrigation District in Hanggin Banner, with the aims of: (1) clarifying the regional spatial patterns of F^- and NO_3^- enrichment in groundwater and surface water of the irrigation district; (2) analyzing the main driving factors of F^- and NO_3^- enrichment in groundwater and surface water of the study area; and (3) evaluating the potential health risks of F^- and NO_3^- in groundwater and surface water of the irrigation district.

1 Data and Methods

1.1 Overview of the Study Area

The Yellow River South-Bank Irrigation District in Hanggin Banner is located in the southwestern part of the Inner Mongolia Autonomous Region, in northern Hanggin Banner, Ordos City ($40°19' \sim 40°51'$N, $107°5' \sim 108°51'$E). It is one of the six large Yellow River diversion irrigation districts in the Inner Mongolia Autonomous Region (Fig. 1). The study area has a temperate continental climate, with relatively low mean air temperature ($7.4 \sim 7.5\,°C$). Precipitation varies greatly from year to year and is mostly concentrated from July to September, while evaporation is far greater than precipitation[15]. The terrain is higher in the southwest and lower in the northeast; the land surface is flat, and the area is distributed in a long, narrow shape along the flow direction of the Yellow River. Its geomorphology is dominated by plains formed by alluvial deposition of sediment carried by the Yellow River and by dunes formed through aeolian transport and accumulation. The aquifer lithology in the Yellow River South-Bank Irrigation District of Hanggin Banner is mainly composed of fine sand and silt. Groundwater is mainly recharged by precipitation and irrigation infiltration, and evaporation and artificial pumping are the main discharge pathways[10]. Groundwater levels are relatively high, and flow is generally parallel to the direction of the Yellow River.

1.2 Data Sources and Processing

In November 2024, this study conducted one round of field sampling in the Yellow River South-Bank Irrigation District in Hanggin Banner. A total of 89 water samples were collected, including 39 groundwater samples, 39 canal-water samples, and 11 Yellow River water samples (Fig. 1b). Among them, groundwater samples were collected from household wells, with water-table depths of 2 $\sim$ 10 m. pH and total dissolved solids (TDS) data were obtained through in-situ measurements. The collected samples were sent to Inner Mongolia No. 3 Geological and Mineral Exploration and Development Co., Ltd. for analysis of major ions (Na^+, K^+, Ca^{2+},

Figure 1. Schematic map of the location of the study area and distribution of sampling points

Map labels: (a) Ordos City; (b) sampling points and elevation in Hanggin Banner. Legends include rivers, Hanggin Banner, banners/counties, Ordos City, Yellow River water sampling points, groundwater sampling points, canal-water sampling points, rivers, and elevation/m.

Fig. 1 Location of the study area and distribution of sampling points

Mg^{2+}, HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-, and F^- were measured. After the analytical data were obtained, they were checked using the charge balance error (CBE). The CBE values of all samples were below 10%, satisfying the requirements for analytical precision[16]. The specific testing and analytical methods for each hydrochemical parameter are shown in Table 1. In addition to the major ion analyses, stable hydrogen and oxygen isotope data (δ^{18}O and δD) were obtained using a liquid-water isotope analyzer (LGR TIWA–45-EP) at the Key Laboratory of River and Lake Ecology of the Inner Mongolia Autonomous Region. Calibration was performed using Vienna Standard Mean Ocean Water (VSMOW), and the average analytical precisions for δ^{18}O and δD were \$±\$0.10‰ and \$±\$0.40‰, respectively.

1.3 Research Methods

1.3.1 Self-Organizing Map Neural Network (SOM)

The self-organizing map neural network (Self-Organizing Map, SOM) is an unsupervised-learning artificial neural network model first proposed by Kohonen in 1982[17]. This method mainly realizes dimensionality reduction of high-dimensional data through self-learning mapping, effectively handles complex environmental systems, and reduces computational effort, thereby enabling data visualization and clustering[18].

1.3.2 Principal Component Analysis (PCA)

Principal component analysis (PCA) is a multivariate statistical method that helps reduce the dimensionality of raw data and assist classification[19]. By condensing multiple variables into a smaller number of independent principal components, it reduces the complexity of the analysis[18]. To verify whether the data are suitable for principal component analysis, the Kaiser–Meyer–Olkin (KMO) test and Bartlett’ s test of sphericity must first be performed[20].

1.3.3 Monte Carlo Health Risk Assessment Model (MCM)

Traditional health risk assessment methods usually calculate risk by substituting specific parameters into exposure models. However, uncertainties such as human activities impose limitations on such models[21]. As a numerical simulation method based on random sampling, MCM can output risk probability distributions through a large number of random experiments, thereby improving the reliability of assessment results[22]. In this study, health risks from fluoride and nitrate in groundwater and surface water were assessed, and the assessment incorporated characteristic parameters for two different population groups: children and adults. The empirical parameters used are shown in Table 2. The calculation formulas are as follows:

$$HQ = \frac{I_{\text{oral}}}{RfD_{\text{oral}}} \tag{1}$$

$$I_{\text{Oral}} = \frac{(c_i \times IR \times EF \times ED)}{BW \times AT} \tag{2}$$

In the formulas, HQ is the hazard quotient, used to assess carcinogenic risk; $HQ < 1$ is generally considered to indicate acceptable risk, whereas $HQ > 1$ indicates that the risk requires attention. I_{oral} is the average daily exposure dose through oral ingestion $[\text{mg} \cdot (\text{kg} \cdot \text{d})^{-1}]$; $RfD_{\text{oral}}(\text{F}^-)$ is the oral reference dose for F^- $[\text{mg} \cdot (\text{kg} \cdot \text{d})^{-1}]$; $RfD_{\text{oral}}(\text{NO}_3^-)$ is the oral reference dose for NO_3^- $[\text{mg} \cdot (\text{kg} \cdot \text{d})^{-1}]$; c_i is the average pollutant concentration $(\text{mg} \cdot \text{L}^{-1})$; IR is the drinking-water frequency $(\text{L} \cdot \text{d}^{-1})$; EF is the exposure frequency $(\text{d} \cdot \text{a}^{-1})$; ED

is the exposure duration (a); BW is the average body weight (kg); and AT is the averaging time (d).

Table 2 Relevant parameters for the Monte Carlo health risk assessment model

Tab. 2 Relevant parameters for the Monte Carlo health risk assessment model

Parameter	Meaning	Children	Adults
$RfD_{\mathrm{oral}}(\mathrm{F}^-)/[\mathrm{mg}\cdot(\mathrm{kg}\cdot\mathrm{d})^{-1}]$	F^- oral reference dose	0.06	0.06
$RfD_{\mathrm{oral}}(\mathrm{NO_3^-})/[\mathrm{mg}\cdot(\mathrm{kg}\cdot\mathrm{d})^{-1}]$	$\mathrm{NO_3^-}$ oral reference dose	1.60	1.60
$c_i(\mathrm{F}^-)/(\mathrm{mg}\cdot\mathrm{L}^{-1})$	Average pollutant concentration	0.68	0.68
$c_i(\mathrm{NO_3^-})/(\mathrm{mg}\cdot\mathrm{L}^{-1})$	Average pollutant concentration	23.01	23.01
$IR/(\mathrm{L}\cdot\mathrm{d}^{-1})$	Drinking-water frequency	0.70	1.50
$EF/(\mathrm{d}\cdot\mathrm{a}^{-1})$	Exposure frequency	365.00	365.00
ED/a	Exposure duration	6.00	30.00
BW/kg	Average body weight	15.00	65.00
AT/d	Averaging time	2190.00	10950.00

Table 1 Testing and analytical methods for hydrochemical parameters

Tab. 1 Testing and analytical methods for hydrochemical parameters

Parameter	Method	Detection limit
pH	DDBJ-350 portable multi-parameter instrument	0.01 (dimensionless)
$\mathrm{TDS}/(\mathrm{mg}\cdot\mathrm{L}^{-1})$	DDBJ-350 portable multi-parameter instrument	1.00
$\mathrm{Na}^+/(\mu\mathrm{g}\cdot\mathrm{L}^{-1})$	Inductively coupled plasma optical emission spectrometry	5.00

Parameter	Method	Detection limit
$K^+/(mg \cdot L^{-1})$	Inductively coupled plasma optical emission spectrometry	0.02
$Ca^{2+}/(mg \cdot L^{-1})$	Inductively coupled plasma optical emission spectrometry	0.01
$Mg^{2+}/(mg \cdot L^{-1})$	Inductively coupled plasma optical emission spectrometry	0.01
$HCO_3^-/mg \cdot L^{-1}$	Titration	5.00
$SO_4^{2-}/(mg \cdot L^{-1})$	Ion chromatography	0.10
$NO_3^-/mg \cdot L^{-1}$	Ion chromatography	0.01
$Cl^-/mg \cdot L^{-1}$	Ion chromatography	0.01
$F^-/mg \cdot L^{-1}$	Ion chromatography	0.01

2 Results and Analysis

2.1 Hydrochemical Characteristics of Water Bodies in the Irrigation District

As shown in Table 3, the pH values of all samples ranged from 7.35 to 9.41, and the mean values for canal water, Yellow River water, and groundwater were 8.56, 8.45, and 7.92, respectively, indicating that the water bodies in the study area were weakly alkaline. The TDS of all water samples varied substantially (418-30000 $mg \cdot L^{-1}$; $C_v = 128\%$). Among them, 37.07% of the samples were fresh water (TDS < 1000 $mg \cdot L^{-1}$), 26.97% were brackish water ($1000 \leq$ TDS $<$ 3000 $mg \cdot L^{-1}$), 30.34% were saline water ($3000 \leq$ TDS < 10000 $mg \cdot L^{-1}$), and 5.62% were salt water ($10000 \leq$ TDS < 50000 $mg \cdot L^{-1}$)[23]. For canal-water samples, the proportions of fresh water, brackish water, saline water, and salt water were 46.15%, 28.21%, 20.51%, and 5.13%, respectively; among the Yellow River water samples, only one sample was brackish water, and its

Table 3. Statistical summary of hydrochemistry in the irrigation areas on the south bank of the Yellow River in Hangjin Banner

Parameter	Maximum value / ($mg \cdot L^{-1}$)	Minimum value / ($mg \cdot L^{-1}$)	Mean value / ($mg \cdot L^{-1}$)	Standard deviation (SD)	Coefficient of variation (C_v) / %
pH	9.41	7.35	8.26	0.40	4.90
TDS	30000.00	418.00	3148.43	4020.28	128
K^+	279.40	0.00	14.32	31.93	223
Ca^{2+}	444.50	0.02	78.80	57.69	73
Na^+	6404.00	0.14	509.54	834.93	164
Mg^{2+}	977.00	0.02	89.18	123.07	138
Cl^-	8616.00	0.03	544.04	1070.05	197
SO_4^{2-}	5093.00	0.12	406.80	617.91	152
HCO_3^-	1917.54	0.00	425.98	298.43	70
F^-	7.27	0.00	0.68	0.94	139
NO_3^-	381.51	0.00	23.01	60.12	261

The remainder were freshwater. Among the groundwater samples, the proportions of freshwater, brackish water, saline water, and brine were 12.82%, 30.77%, 48.72%, and 7.69%, respectively. According to ionic abundance, the cation concentrations in irrigation-channel water and groundwater decreased in the order $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, whereas those in Yellow River water decreased in the order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. The anion concentrations in irrigation-channel water and groundwater decreased in the order $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$, whereas those in Yellow River water decreased in the order $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$.

The main nitrogen compound in surface water and groundwater in the irrigation areas on the south bank of the Yellow River in Hangjin Banner was NO_3^-, with a maximum concentration of 381.50 $mg \cdot L^{-1}$ and a mean concentration of 23.01 $mg \cdot L^{-1}$. In the Standard for Groundwater Quality (GB/T 14848-2017), the acceptable limit for NO_3^- is 20.00 $mg \cdot L^{-1}$; statistical analysis showed that 15.73% of the samples exceeded this limit [24].

F^- is another important pollutant of concern [25]. In the study area, F^- concentrations ranged from 0.00 to 7.27 $mg \cdot L^{-1}$, with a mean of 0.68 $mg \cdot L^{-1}$. Among the samples, 20.22% had F^- concentrations exceeding the groundwater Class III water-quality standard of 1.00 $mg \cdot L^{-1}$ specified in the Standard for Groundwater Quality (GB/T 14848-2017) [24].

2.2 Cluster analysis of water bodies in the irrigation area

SOM can cluster, reduce the dimensionality of, and visualize data to identify water-quality characteristics and pollution causes, and can also analyze ion correlations to assist in source tracing. In this study, 11 variables from 89 samples were used as the input data for SOM calculation, namely K^+, Na^+, Ca^{2+}, Mg^{2+},

Cl^-, HCO_3^-, SO_4^{2-}, NO_3^-, F^-, TDS, and pH, and an 8×6 neuron pattern was determined. The color-gradient distributions of Na^+ with Cl^-, Mg^{2+}, and SO_4^{2-} were relatively consistent, with ion concentrations gradually increasing from top to bottom (Fig. 2a), indicating that they share the same source mechanism or migration pathway. This may be attributable to the influence of water-rock interaction, such as the dissolution of minerals including halite and gypsum. Secondly, Na^+ and SO_4^{2-} showed similar patterns, whereas the color-gradient distributions of Ca^{2+} and HCO_3^- displayed different patterns, suggesting that they may be affected by cation exchange. In addition, the concentration patterns of NO_3^- and F^- were similar and increased from left to right, indicating that NO_3^- and F^- in the study area have similar sources.

As shown in Table 4, the 89 samples were divided into three clusters, each exhibiting different hydrochemical compositions and source characteristics (Fig. 2b).

(a) SOM visualization topology maps of 11 variables

TDS; pH; K^+; Na^+; Ca^{2+}; Mg^{2+}; SO_4^{2-}; Cl^-; HCO_3^-; NO_3^-; F^-

(b) SOM clustering pattern map

Note: Fig. a shows the SOM visualization topology maps of 11 hydrochemical parameters in the study area; neuron colors from blue to red correspond to parameter values from low to high. Fig. b is the SOM clustering pattern map; the red solid lines are cluster boundaries, dividing the sampling sites into three classes, C1, C2, and C3. Among them, ZD1-ZD39 are irrigation-channel water sampling sites, ZD40-ZD50 are Yellow River water sampling sites, and ZD51-ZD89 are groundwater sampling sites.

Fig. 2 SOM classification results

Table 4 Davies-Bouldin Index (DBI) for different clusters

Tab. 4 Davies-Bouldin Index (DBI) for different clusters

Cluster	1	2	3	4	5	6	7
DBI	NaN	0.9565	**0.7013**	1.0333	0.7066	0.7366	0.7172

Note: Bold font indicates the optimal solution. When the number of clusters is 1, the computational conditions for the Davies-Bouldin Index cannot be satisfied; the corresponding DBI value is marked as NaN (Not a Number), indicating that no valid calculation result is available.

A total of 67 samples (75.28%) were classified as C1 (cluster 1), including 36 canal-water samples, 10 Yellow River water samples, and 21 groundwater samples. The concentrations of TDS and major ions were very low, while the concentrations of Ca^{2+} and HCO_3^- were relatively higher than those of the other major ions. This indicates that the hydrochemical composition of the C1 samples is mainly controlled by water–rock interaction dominated by carbonate or silicate dissolution. In addition, the overall NO_3^- concentration in the C1 samples was relatively low, while the F^- concentration in some samples exceeded the Class III water-quality standard. Spatially, the C1 samples were mainly distributed in groundwater recharge areas or in areas with favorable flow conditions, where groundwater renewal is rapid and anthropogenic pollution has little influence; thus, they represent the regional background hydrogeochemical conditions.

Nineteen samples (21.35%) were identified as C2 (cluster 2), including 1 canal-water sample and 18 groundwater samples. The TDS and major-ion concentrations of this group were relatively high, and the NO_3^- and F^- contents far exceeded the Class III water-quality standard. By contrast, only 3 samples (3.37%) were classified as C3 (cluster 3), including 2 canal-water samples and 1 groundwater sample. This group had the highest concentrations of TDS, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}, suggesting that its hydrochemical composition is mainly controlled by evaporite dissolution or the input of high-salinity water.

Further analysis in combination with the Piper diagram shows (Fig. 3) that the hydrochemical types of the samples in cluster C1 are relatively complex. The main hydrochemical types are Ca-HCO_3 and Na-HCO_3, which can be classified as "moderate NO_3^- and F^-, Ca · Na-HCO_3-type water." The C2 and C3 samples are concentrated in type II and type IV regions; their main hydrochemical types are Na-SO_4 type and Na-Cl type, respectively, and they are classified as "high NO_3^- and F^-, Na-SO_4 · Cl-type water" and "high-salinity, Na-SO_4 · Cl-type water."

2.3 Hydrogen and oxygen isotope characteristics of water bodies in the irrigation area

As shown in Fig. 2b, class C1 includes most canal-water samples and all Yellow River water samples, and is categorized as surface water. Class C2 is mainly composed of groundwater samples and is regarded as groundwater. Class C3 is relatively special, consisting of a mixture of 2 canal-water samples and 1 groundwater sample, and belongs to a transitional mixed-type sample group. From the distribution characteristics of isotope composition (Fig. 4), the vast majority of water-sample points are located to the lower right of the Global Meteoric Water Line (GMWL), showing an overall relatively concentrated distribution pattern. This indicates that the water bodies in the study area are mainly derived from atmospheric precipitation and are affected by evaporation during recharge [26]. The δD and δ^{18}O values of surface-water and groundwater samples show a distinct overlapping region, indicating that surface water and groundwater in the study area

Fig. 3 Piper diagram of different clusters in the irrigation areas on the south bank of the Yellow River in Hangjin Banner

Legend in Fig. 3: C1, C2, C3; I: SO_4 · Cl-Ca · Mg; II: HCO_3-Na; III: HCO_3-Ca · Mg; IV: SO_4 · Cl-Na.

Fig. 4 Relationship between δD and δ^{18}O of different clusters and water bodies in the irrigation areas on the south bank of the Yellow River in Hangjin Banner

(Figure labels: GMWL; C1, C2, C3; canal water, Yellow River water, groundwater; x-axis: δ^{18}O/‰; y-axis: δD/‰.)

There is a common recharge source or a close hydraulic connection between them[^27]. On the one hand, during infiltration, surface water mixes with groundwater, causing its isotopic characteristics to shift toward those of groundwater. On the other hand, groundwater discharge may also affect the isotopic composition of surface water. This further confirms the transformation between surface water and groundwater in the study area and their mutual influence on water quality. In C1, one groundwater sample deviates markedly from the GMWL; its δ^{18}O and δD values, -2.26‰ and -37.30‰, respectively, are significantly higher than those of the other samples, indicating that it was strongly affected by evaporation. During evaporation, light isotopes preferentially escape, resulting in increased δ^{18}O and δD values in the remaining water body.

2.4 Enrichment mechanisms and influencing factors of fluoride and nitrate in irrigation-area water bodies

In general, water-rock interaction, acidity-alkalinity, and anthropogenic inputs are the main factors influencing F^- and NO_3^- in water bodies[^28]. The coefficients of variation C_v of F^- and NO_3^- concentrations are 139% and 261%, respectively (Table 3), indicating large fluctuations in concentration; this phenomenon suggests that they are jointly affected by multiple factors. Based on this result, this study adopts a method combining PCA with ion ratios, aiming to identify the key factors regulating the contents of F^- and NO_3^- in water bodies. For the 89 groups of water samples collected in the study area, 11 physicochemical indicators were likewise selected as analytical objects, and eigenvalues were extracted using the PCA method. The KMO and Bartlett' s test of sphericity results (KMO = 0.63, $P < 0.05$) confirmed that PCA was suitable for the data analysis in this study[^20]. As shown in Table 5, the three principal factors with eigenvalues greater than 1 cumulatively explain 82.58% of the total variance, and the spatial distribution characteristics of each factor score are shown in Fig. 5.

Table 5 Factor loadings of PCA results

Factor	F1	F2	F3
pH	-0.47	-0.56	0.33
TDS/($mg \cdot L^{-1}$)	**0.96**	-0.13	0.09
K^+/($mg \cdot L^{-1}$)	**0.57**	0.46	0.09
Ca^{2+}/($mg \cdot L^{-1}$)	**0.80**	-0.17	-0.45
Na^+/($mg \cdot L^{-1}$)	**0.95**	-0.17	0.15
Mg^{2+}/($mg \cdot L^{-1}$)	**0.96**	-0.15	0.01

Factor	F1	F2	F3
$Cl^-/(mg \cdot L^{-1})$	**0.95**	-0.26	0.07
$SO_4^{2-}/(mg \cdot L^{-1})$	**0.97**	-0.18	0.05
$HCO_3^-/(mg \cdot L^{-1})$	**0.70**	0.49	0.35
$F^-/(mg \cdot L^{-1})$	0.05	**0.64**	0.48
$NO_3^-/(mg \cdot L^{-1})$	0.20	0.47	**-0.70**
Eigenvalue	6.30	1.61	1.19
Explained variance	57.30	14.62	10.84
Cumulative variance contribution rate/%	57.30	71.92	82.58

Note: Bold type indicates loadings with absolute values >0.5.

2.4.1 Water-rock interaction

The contribution rate of factor F1 to the total variance reaches 57.30% (Table 5). Among them, the absolute factor loadings of Ca^{2+}, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, and TDS all exceed 0.80, indicating that F1 may reflect hydrochemical changes caused by water-rock interaction[^29]. Areas with higher F1 scores (values >1) are concentrated in the central part of the study area (Fig. 5a). The samples in this area are mainly from C2 and C3, indicating that the hydrochemical characteristics of groundwater and surface water in the study area are significantly affected by water-rock interaction, and that this influence is particularly pronounced in the C2 and C3 samples.

Generally, water-rock interaction has a relatively weak effect on NO_3^- concentrations in groundwater and surface water, whereas it has a stronger influence on F^- concentrations[^30]. In various water-rock interaction processes, the dissolution and precipitation of Ca^{2+} exert significant regulatory control over the occurrence state of F^-. This is because calcite, dolomite, and fluorite all contain Ca^{2+} as a key component, and the solubilities of the three minerals show a significant coupled relationship[^31]. The saturation indices (SI) of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4$), and fluorite (CaF_2) indicate that the two carbonate minerals are saturated or supersaturated ($SI \geq 1$) (Fig. 6a), whereas halite, gypsum, and fluorite tend to dissolve. When calcite or dolomite is supersaturated, precipitation readily occurs, which directly consumes Ca^{2+} in the water body; according to the principle of dissolution equilibrium, this change promotes the dissolution process of fluorite (Equations 3-5), facilitating the release of F^-.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \tag{3}$$

$$Ca^{2+} + Mg^{2+} + 4HCO_3^- \rightarrow CaMg(CO_3)_2 + 2H_2O + 2CO_2 \tag{4}$$

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

$$Ca^{2+} + 2NaX = 2Na^+ + CaX_2 \quad (6)$$

(a) F1 factor
F1 factor score: −0.70–1.00; 1.01–1.45. Scale: 0–20 km.

(b) F2 factor
F2 factor score: −0.72–1.00; 1.01–2.54. Scale: 0–20 km.

(c) F3 factor
F3 factor score: 0.00–1.00; 1.01–7.55. Scale: 0–20 km.

Legend:
Land-use types in Hangjin Banner: cropland; forest; grassland; water area; bare land; wetland; impervious surface.
Groundwater types: C1; C2; C3.
River.

Note: F1 denotes water-rock interaction; F2 denotes the alkaline aquatic environment; F3 denotes anthropogenic input. Circle size is positively correlated with the factor score: the higher the factor score, the larger the circle radius. Higher scores for F1, F2, and F3 indicate that the corresponding factor has a more pronounced influence on groundwater chemistry.

Fig. 5 Spatial distribution of factor scores in the irrigation areas on the south bank of the Yellow River in Hangjin Banner

In addition, cation exchange can also affect the increase in F^- concentration. Specifically, Ca^{2+} in the water exchanges with Na^+ adsorbed on the surfaces of clay minerals, consuming Ca^{2+} in the water and thereby increasing the F^- concentration in groundwater and surface water (formulas 5-6). Generally, if $(Na^+ + K^+ - Cl^-)$ and $(Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-)$ exhibit a linear relationship with a slope close to -1, cation exchange may have occurred [32]. As shown in Fig. 6b, the vast majority of samples conform to the above linear relationship, confirming the contribution of cation exchange to the increase in F^- concentrations in groundwater and surface water.

It can be seen from Fig. 5a that the C2 samples (water with high NO_3^- and F^-) and C3 samples (high-salinity water) are mainly closely associated with water-rock interaction, indicating that water-rock interaction is one of the driving factors for high NO_3^-, F^-, and salinity in groundwater and surface water in the study area. In addition, higher F1 scores are distributed in the central part of the study area, indicating strong water-rock interaction in this region.

2.4.2 Alkaline aquatic environment

The variance contribution of the F2 factor is 14.62%. The pH value has the highest loading on this factor and is its dominant indicator. Considering that both surface water and groundwater in the study area are generally weakly alkaline (Table 3), the F2 factor can therefore represent the alkaline aquatic environment.

Areas with relatively high F2 factor scores (>1) are distributed throughout the entire study area (Fig. 5b), indicating that the alkaline aquatic environment is a pervasive factor regulating the contents of NO_3^- and F^- in groundwater and surface water in the study area.

In alkaline or weakly alkaline water environments, an increase in OH^- concentration can promote the chemical reaction process represented by formula (7), thereby facilitating the dissolution of CaF_2. The reason for this phenomenon is that the ionic radii of OH^- and fluoride ions (F^-) are relatively similar; fluorine-bearing minerals can undergo ion exchange, with OH^- replacing F^-, thereby releasing F^- into the water [33]. In addition, the adsorption capacity of silicate minerals for F^- is significantly correlated with water pH. Related studies have shown that this adsorption capacity reaches its peak within the pH range of 5.00–6.50 [34]. The pH values of water samples from the irrigation areas on the south bank of the Yellow River in Hangjin Banner range from 7.35 to 9.41, which exceeds the zero charge point (ZCP) of aquifer minerals, causing the surfaces of mineral solids to exhibit neutral or negatively charged characteristics [35]. Under these pH conditions, the key processes affecting the hydrochemical characteristics of groundwater and surface water in the study area include two aspects: first, promoting the dissolution of silicate minerals such as muscovite and biotite; and second, inhibiting the adsorption of F^- on mineral surfaces. The specific reactions are shown in formulas (8) and (9) [36]. Therefore, the competitive adsorption effect between OH^- and F^- affects the F^- concentration in groundwater and surface water

(a) Relationship between saturation index (SI) and total dissolved solids (TDS)

Axis labels: SI; TDS/$(\mathrm{mg \cdot L^{-1}})$
Legend: $\mathrm{SI_{calcite}}$; $\mathrm{SI_{dolomite}}$; $\mathrm{SI_{gypsum}}$; $\mathrm{SI_{halite}}$; $\mathrm{SI_{fluorite}}$

(b) Relationship between $(\mathrm{Ca^{2+} + Mg^{2+}}) - (\mathrm{SO_4^{2-} + HCO_3^-})$ **and** $(\mathrm{Na^+ + K^+ - Cl^-})$

Axis labels: $(\mathrm{Ca^{2+}+Mg^{2+}})-(\mathrm{SO_4^{2-}+HCO_3^-})/(\mathrm{meq \cdot L^{-1}})$; $\mathrm{K^+ + Na^+ - Cl^-}/(\mathrm{meq \cdot L^{-1}})$
Legend: C1; C2; C3

(c) Relationship between $\mathrm{NO_3^-/Na^+}$ **and** $\mathrm{Cl^-/Na^+}$

Axis labels: $\mathrm{NO_3^-/Na^+}/(\mathrm{meq \cdot L^{-1}})$; $\mathrm{Cl^-/Na^+}/(\mathrm{meq \cdot L^{-1}})$
In-figure labels: agricultural activities; carbonate and silicate salts; sewage;

evaporation
Legend: C1; C2; C3

Fig. 6 Relationships among hydrochemical components in the irrigation areas on the south bank of the Yellow River in Hangjin Banner

played an important driving role in the increase.

$$CaF_2 + 2OH^- \rightarrow Ca(OH)_2 + 2F^- \tag{7}$$

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^- \tag{8}$$

$$KMg_3[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow KMg_3[AlSi_3O_{10}][OH]_2 + 2F^- \tag{9}$$

Different chemical forms of nitrogen can likewise undergo mutual transformation under specific acid–base conditions (Eqs. (10) and (11))

27

. This transformation property is closely related to the sensitivity of nitrifying bacteria to changes in pH. The optimal pH range for nitrification is 6.00–8.50

37

; when the pH is below 6.00 or above 8.5, the nitrification reaction rate decreases significantly. In this study, the mean pH of groundwater and surface water in the irrigation area on the south bank of the Yellow River in Hangjin Banner was 8.26 (Table 3), within the optimal range for nitrification. Therefore, the alkaline aquatic environment in the study area is conducive to the formation of NO_3^-.

In summary, the above analysis indicates that the alkaline aquatic environment has a significant influence on the occurrence characteristics of F^- and NO_3^- in groundwater and surface water in the study area, and is one of the dominant factors controlling F^- and NO_3^- concentrations in groundwater and surface water in the irrigation area on the south bank of the Yellow River in Hangjin Banner.

$$2NH_4^+ + 3O_2 \xrightarrow{\text{nitrifying bacteria}} 2NO_2^- + 2H_2O + 4H^+ \tag{10}$$

$$2NO_2^- + 2O_2 \xrightarrow{\text{nitrifying bacteria}} 2NO_3^- \tag{11}$$

2.4.3 Anthropogenic input

Factor F3 explained 10.84% of the total variance. Among its loadings, the absolute factor loading of NO_3^- exceeded 0.60, while that of F^- approached 0.50, indicating that F3 may characterize anthropogenic input processes. Areas with relatively high F3 scores (values >1) were concentrated in the western part of the study area (Fig. 5c). Samples in this area were dominated by C2, indicating that the formation of "high-NO_3^- and high-F^--type water" is closely related to anthropogenic input.

The ratios of NO_3^-/Na^+ and Cl^-/Na^+ are commonly used to identify the impacts of agricultural activities and sewage discharge on groundwater

38

. As shown in Fig. 6c, C2 samples are mainly distributed between the agricultural-activity end member and the sewage end member, indicating that inputs from human activities are indeed the dominant factor responsible for the high NO_3^- and F^- concentrations in groundwater and surface water in the study area. The study found that the high-score area of F3 is concentrated in the western part of the study area, reflecting the more pronounced influence of human activities on groundwater and surface water in this region (Fig. 5c). Therefore, nitrate and fluoride pollution in groundwater and surface water in this area may be associated with human activities such as agricultural irrigation return flow and sewage discharge.

2.5 Human health risk assessment

The non-carcinogenic risk assessment based on cumulative probability curves shows that the distributions of the hazard quotient (HQ) for F^- and NO_3^- among different water bodies in the study area differ significantly for adults and children (Fig. 7). An HQ > 1 indicates an unacceptable non-carcinogenic risk

39

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In terms of water-body type, the overall risk level exhibits a gradient of groundwater > canal water > Yellow River water. The non-carcinogenic risks of F^- and NO_3^- in Yellow River water are both at extremely low levels. The 95th-percentile HQ values for adults and children are 0.21 and 0.44 for F^-, and 0.14 and 0.30 for NO_3^-, respectively. Samples with HQ > 1 are almost absent, so Yellow River water can be regarded as a low-risk water source. In canal water, the risks associated with F^- and NO_3^- increase slightly; the proportions of adults with HQ > 1 are respectively

Figure 7

(a) Cumulative probability of non-carcinogenic risk of F^- in canal water

- y-axis: Cumulative probability / %
- x-axis: $HQ(F^-)$
- Acceptable risk; Unacceptable risk
- Children: $95\% = 0.97$; children $(4.38\%) > 1$; mean $= 0.36$
- Adults: mean $= 0.18$; $95\% = 0.47$; adults $(0.00\%) > 1$
- Legend: Adults; Children

(b) Cumulative probability of non-carcinogenic risk of $\mathrm{NO_3^-}$ in canal water

- y-axis: Cumulative probability / %
- x-axis: $HQ(\mathrm{NO_3^-})$
- Acceptable risk; Unacceptable risk
- Children: $95\% = 1.73$; children $(20.67\%) > 1$; mean $= 0.34$
- Adults: mean $= 0.16$; $95\% = 0.84$; adults $(2.53\%) > 1$
- Legend: Adults; Children

(c) Cumulative probability of non-carcinogenic risk of F^- in Yellow River water

- y-axis: Cumulative probability / %
- x-axis: $HQ(F^-)$
- Acceptable risk; Unacceptable risk
- Children: $95\% = 0.44$; children $(0.01\%) > 1$; mean $= 0.18$
- Adults: mean $= 0.09$; $95\% = 0.21$; adults $(0.00\%) > 1$
- Legend: Adults; Children

(d) Cumulative probability of non-carcinogenic risk of $\mathrm{NO_3^-}$ in Yellow River water

- y-axis: Cumulative probability / %
- x-axis: $HQ(\mathrm{NO_3^-})$
- Acceptable risk; Unacceptable risk
- Children: $95\% = 0.30$; children $(0.00\%) > 1$; mean $= 0.09$
- Adults: mean $= 0.04$; $95\% = 0.14$; adults $(0.00\%) > 1$
- Legend: Adults; Children

(e) Cumulative probability of non-carcinogenic risk of F^- in groundwater

- y-axis: Cumulative probability / %
- x-axis: $HQ(F^-)$
- Acceptable risk; Unacceptable risk
- Children: $95\% = 2.57$; children $(42.00\%) > 1$; mean $= 0.83$
- Adults: mean $= 0.41$; $95\% = 1.26$; adults $(11.66\%) > 1$
- Legend: Adults; Children

(f) Cumulative probability of non-carcinogenic risk of $\mathrm{NO_3^-}$ in groundwater

- y-axis: Cumulative probability / %

- x-axis: $HQ(\mathrm{NO}_3^-)$
- Acceptable risk; Unacceptable risk
- Children: 95% = 5.46; children (51.84%) > 1; mean = 1.15
- Adults: mean = 0.56; 95% = 2.61; adults (35.47%) > 1
- Legend: Adults; Children

Fig. 7 The cumulative probability of non-carcinogenic risk

0.00% and 2.53%, while for children they were 4.38% and 20.67%, respectively; some samples exceeded the acceptable risk threshold. The risk in groundwater was the most pronounced: the proportions of $HQ > 1$ for F^- among adults and children reached 11.66% and 42.00%, respectively, while those for NO_3^- further increased to 35.47% and 51.84%, meaning that more than half of the children' s samples exhibited unacceptable non-carcinogenic risk.

Comparison of population sensitivity showed that the non-carcinogenic risk for children was significantly higher than that for adults. Across all water-body and pollutant scenarios, the mean HQ, 95th-percentile values, and exceedance proportions for children were all markedly higher than those for adults. This indicates that children, as a sensitive population for drinking-water exposure, are more vulnerable to the health risks posed by F^- and NO_3^-, and that targeted protective measures should be implemented in drinking-water safety management.

In terms of pollutant dimensions, in surface water—canal water and Yellow River water—F^- and

The differences in the risk levels of NO_3^- were relatively small, whereas the overall non-carcinogenic risk of NO_3^- in groundwater was higher than that of F^-. This is consistent with the relatively high load of groundwater nitrogen pollution in the region. The above results provide a quantitative basis for risk-based classification and management of water sources in the study area and for safeguarding the safety of children' s drinking water.

3 Conclusions

Taking the irrigation area on the south bank of the Yellow River in Hanggin Banner as the study object, this study combined self-organizing map neural networks (SOM), principal component analysis (PCA), hydrogen and oxygen isotope tracing, and the Monte Carlo health risk assessment model (MCM) to systematically reveal the spatial enrichment patterns, causal mechanisms, and human health risks of nitrate and fluoride in regional groundwater and surface water. The main conclusions are as follows:

(1) The various water bodies in the study area are generally weakly alkaline (pH 7.35-9.41), and TDS shows significant spatial variation (418-30000 $\mathrm{mg \cdot L^{-1}}$). Under the combined influence of regional hydrogeological conditions and agricultural activities, nitrate (exceedance rate 15.73%)

and fluoride (exceedance rate 20.22%) in the water bodies both show exceedances. Groundwater is the main carrier of these two pollutants, with prominent pollution problems; the Yellow River water is generally of good quality and can serve as a safe regional water-supply source.

(2) Based on the SOM clustering results, the 89 groups of water samples in the study area can be divided into three categories. The C1 category, with the highest proportion, consists of $Ca \cdot Na - HCO_3$-type waters with moderate nitrate and fluoride contents, representing the natural hydrogeochemical background of the region. The C2 category consists of $Na - SO_4 \cdot Cl$-type waters enriched in nitrate and fluoride, with distinct pollution characteristics. The C3 category consists of high-salinity $Na - SO_4 \cdot Cl$-type waters. Hydrogen and oxygen isotope characteristics confirm that both regional surface water and groundwater are mainly recharged by atmospheric precipitation, evaporation is strong, and the hydraulic connection between the two types of water bodies is close.

(3) The PCA results show that water–rock interaction, the alkaline water environment, and anthropogenic inputs are the three dominant factors controlling the enrichment of pollutants in regional water bodies, with a cumulative explained variance of 82.58%. Among them, anthropogenic inputs such as agricultural production are the primary inducement for NO_3^- accumulation; the release and enrichment of F^- are mainly controlled by natural mechanisms such as fluorite dissolution, anion exchange, and competitive adsorption.

(4) The MCM-based assessment results show that the health-risk ranking of the three types of water bodies is groundwater > canal water > Yellow River water. Owing to differences in exposure parameters such as drinking-water intake and body weight, children's health exposure risks from nitrate and fluoride are much higher than those of adults, indicating that children are a sensitive population. Considering regional conditions, groundwater is recommended as the core target of pollution prevention and control, while targeted measures should be implemented to ensure the safety of children' s drinking water.

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Enrichment Characteristics of Nitrate and Fluoride in Groundwater and Surface Water in the Irrigation Areas on the South Bank of the Yellow River in Hangjin Banner, China

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Abstract: The combined pollution of nitrates and fluorides poses a significant threat to the ecological security and human health in arid and semi-arid irrigation districts. However, systematic research on such contamination in the irrigation area along the southern bank of the Yellow River in Hangjin Banner remains limited. To address this gap, 89 water samples were collected from the study area in November 2024, comprising 39 groundwater samples, 39 canal water samples, and 11 Yellow River water samples. Using a combination of self-organizing map (SOM), principal component analysis (PCA), and Monte Carlo simulation (MCM), this study systematically investigated the enrichment characteristics, driving mechanisms, and human health risks of nitrates and fluorides in the water bodies. The results showed that the water in the study area was generally weakly alkaline, with pH values ranging from 7.35 to 9.41 and total dissolved solids (TDS) concentrations between 418 and 30000 $mg \cdot L^{-1}$. Nitrate and fluoride concentrations in some water samples exceeded the Class III water quality limits. SOM analysis classified the 89 water samples into three clusters (C1-C3): C1 represented Ca · Na-HCO_3-type water with moderate nitrate and fluoride levels; C2 was Na-SO_4 · Cl-type water with high nitrate and fluoride enrichment; and C3 was Na-SO_4 · Cl-type water with high salinity. Hydrogen and oxygen isotope tracing confirmed that both surface water and groundwater in the study area were primarily recharged by atmospheric precipitation and were significantly influenced by evaporation. PCA extracted three principal components, namely water-rock interaction (57.30%), alkaline environment (14.62%), and anthropogenic input (10.84%). Among these, anthropogenic input was the dominant factor controlling nitrate enrichment, while water-rock interaction and the alkaline environment jointly drove fluoride release. The health risk assessment indicated that groundwater posed the highest health risk in the study area, and the non-carcinogenic risk to children was significantly higher than that to adults. In summary, priority should be given to the prevention and control of nitrate and fluoride pollution in groundwater, with a particular focus on ensuring the safety of drinking water for children.

Keywords: irrigation areas on the south bank of the Yellow River in Hangjin Banner; water quality; self-organizing map neural network; principal component analysis; health risk assessment

Note: Figure translations are in progress. See original paper for figures.