Hydrogeochemistry of fluoride in shallow groundwater of the abandoned Yellow River delta, China

Lai Zhou, Shuangshuang Zheng, Di Chen, Xunke Yuan, Mengsheng Lu, Qiyan Feng and Xueqiang Zhu

ABSTRACT

Fluorosis is the most widespread and serious endemic disease in the abandoned Yellow River flooding delta of East China. One of the important causes of fluorosis is drinking high-fluorine groundwater. In this study, 313 groundwater samples were collected in the central part of the flooding delta to address the chemistry of high-fluoride groundwater, and 33 core samples were collected from one borehole of 150 m depth to analyse the vertical distribution characteristics of total fluorine and water-soluble fluorine. The fluorine concentration in groundwater ranges from 0.2 to 6.7 mg/L, and 72.8% of the samples have fluorine above the China maximum permissible limit of 1.0 mg/L for drinking water. These 313 samples can be divided into nine hydrochemical subtypes, and over 77% of the samples belong to the bicarbonate types. High-fluorine groundwater (over 3.0 mg/L) is generally alkaline water with high HCO_3^- and low Ca^{2+}. The concentration of water-soluble fluorine decreases gradually with the increase of formation depth, and that in vertical sediment is negatively correlated with Ca^{2+} and Cl^-, but positively correlated with HCO_3^-. According to the calculation by PHREEQC package, MgF^+ and CaF^+ are the dominant species controlling the endemic fluorosis of the study area.

Key words | abandoned Yellow River flooding delta, fluorine, hydrogeochemical characteristics, shallow groundwater aquifer

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HIGHLIGHTS

- The hydrogeochemical characteristics of fluoride in shallow groundwater in the abandoned Yellow River Delta were analyzed.
- The fluorine in the groundwater are positively correlated with HCO_3^- and negatively correlated with Ca^{2+}.
- High fluorine concentration (over 3.0 mg/L) generally occurs in the alkaline groundwater.
- MgF^+ and CaF^+ are considered to be the main species controlling endemic fluorine poisoning.

INTRODUCTION

As an essential element of the human body, inadequate or excessive intake of fluorine can lead to some health problems. A small amount of fluorine has beneficial effects on teeth by hardening enamel and reducing the incidence of tooth decay (Fung *et al.* 1999). However, long-term exposure of high-dose fluorine in drinking water (higher than 1.5 mg/L) may lead to dental fluorosis or enamel mottling (Pendrys 2000). In addition, excessive fluorine concentration (3.0 mg/L) may lead to skeletal fluorosis and loss of mobility (Dar *et al.* 2011). More than 41 million people in 1,325 different counties in China suffered from dental fluorosis and skeletal fluorosis (An *et al.* 2006). The World Health Organization (WHO) has established guide lines limiting the safe fluorine concentrations in drinking water to 1.5 mg/L (WHO 2011). The maximum concentration of fluorine in China's Drinking Water Standard (GB14848-2017) is 1.0 mg/L, which is used as the reference value in this study.

High fluorine in groundwater has attracted great attention in many countries, such as India (Reddy *et al.* 2010), China (Guo & Wang 2005; Zhu *et al.* 2007; He *et al.* 2013), Korean Peninsula, Sri Lanka (Young *et al.* 2011), East and North Africa (Gaciri & Davies 1993), Britain (Dagmar 1952) and the western United States (Levy *et al.* 1999). Fluorine in groundwater mainly comes from weathering and erosion of fluorine-bearing minerals, which mainly orginate from igneous rocks (Breiter & Kronz 2004; Breiter *et al.* 2006; Lukkari & Holtz 2007; Reddy *et al.* 2010). Apatite [Ca$_5$(PO$_4$)$_3$F] and fluorite [CaF$_2$] are the most common fluorine-bearing minerals, biotite [K(Mg,Fe)$_3$-AlSi$_3$O$_{10}$(F,OH)$_2$], amphibole [(Ca,Na)$_2$–3(Mg,Fe,Al)$_5$(Al,Si)$_8$O$_2$(OH,F)$_2$] and soil mainly composed of clay minerals, such as vermiculite [(MgFe,Al)$_3$(Al,Si)$_4$O$_{10}$(OH)], kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$] and montmorillonite [(Na,Ca)$_{0.33}$(Al,Mg)$_2$(Si$_4$O$_{10}$)(OH)$_2$–nH$_2$O], are also the main sources of fluorine (Zhu *et al.* 2007). The dissolution rate of fluorine-bearing minerals is generally very slow (Gaus *et al.* 2002), so the concentration of fluorine in groundwater does not only depend on the solubility of these mineral phases, but specific hydrogeochemical environment also plays an important role in the enrichment of fluorine in groundwater. For example, high alkalinity and low calcium are beneficial to the formation of high fluorine (Maheshwari 2006; Guo *et al.* 2007). Mutual reaction of evaporation and ion exchange have been invoked to explain increased fluorine levels in shallow groundwater, such as those observed in Northern China (Liu & Zhu 1991).

The study area is located in the middle of the abandoned Yellow River delta plain in Jiangsu, Shandong and Henan provinces of China. It is estimated that approximately 2.19 million people are exposed to high-fluorine groundwater above China's Drinking Water Standard and are at serious risk of endemic fluorosis. According to the local health survey, 28.2% of 830,000 residents suffer from severe and moderate fluorosis. Since drinking high-fluorine shallow groundwater has considerable impact on human health, delineating high-fluorine groundwater zones and understanding how hydrogeochemical factors affect fluorine enrichment are extremely important for water resource management and human health in the abandoned Yellow River flooding delta. The main objectives of this study are to: (1) identify the extent of fluorine concentrations in different types of groundwater; (2) characterize hydrogeochemistry of the regional high-fluorine shallow groundwater in the abandoned flooding Yellow River delta, and (3) assess the dominant geochemical mechanisms and processes controlling high-fluorine shallow groundwater in the study area.

MATERIALS AND METHODS

Study area

The study area is defined by latitudes 34°05″ and 36°15″N and longitudes 114°35″ and 117°35″E. It is located in the middle part of the abandoned Yellow River delta (Figure 1(a) and 1(b)). Over 80% of the study area is entirely underlain by the flooding sediments of the abandoned Yellow River with average depth of 45 m. The area comprises important rivers of Nansi Lake, Yi River, Shu River, Si River, Sui River and An River. The study area belongs to warm temperature zone and semi-humid monsoon section, and the average annual rainfall is around 800 mm. The strata
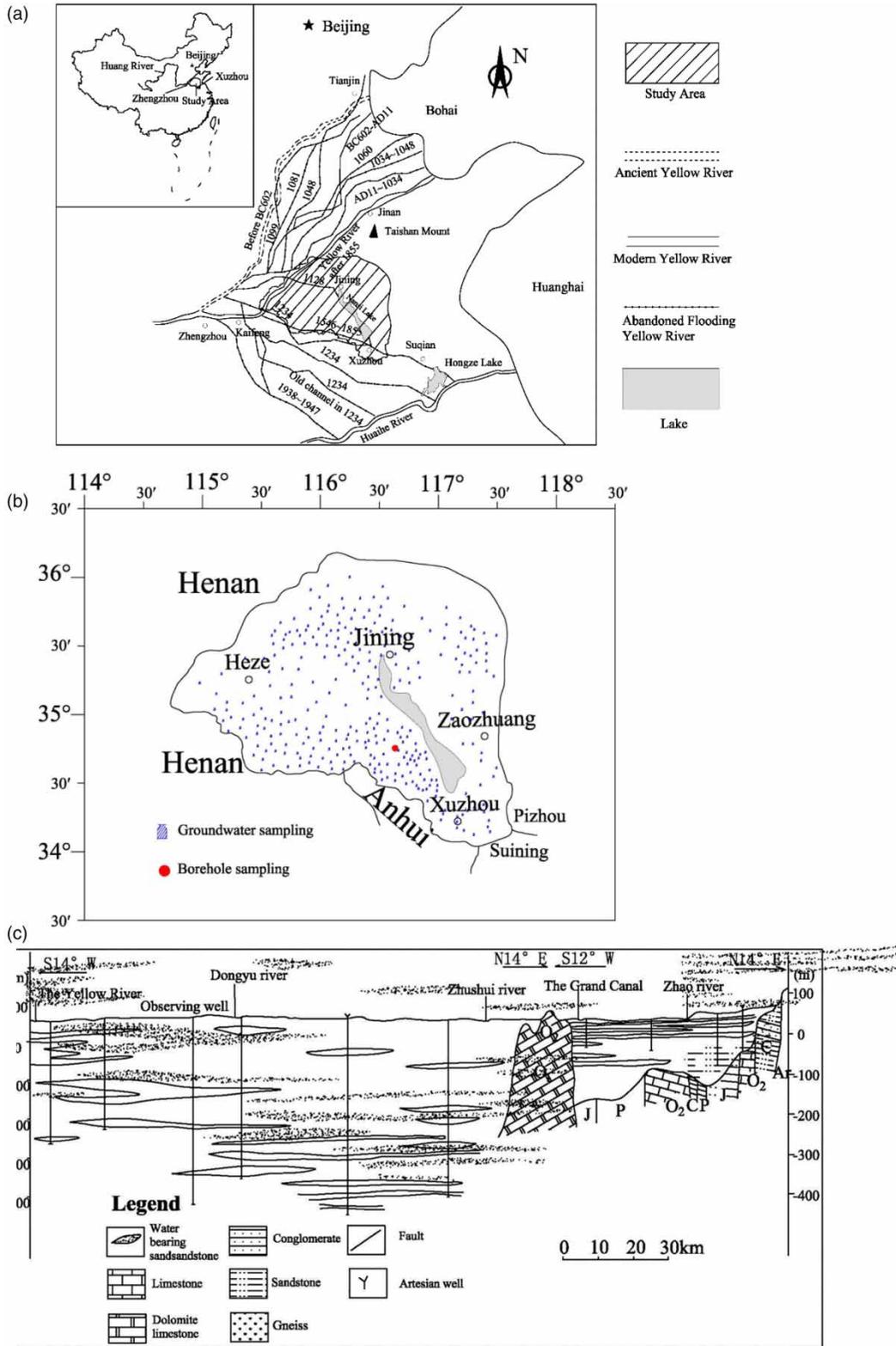
Figure 1 │ (a) A simplified map of the study area, showing the course changes and flooding delta of the Yellow River; (b) the marked sample locations; (c) schematic cross-section of Heze to Jining, the piedmont alluvial plain of the abandoned Yellow River.

from bottom to top are Archean Taishan Group, Upper Proterozoic Tumen Group, Paleozoic Cambrian, Ordovician, Carboniferous, Permian, Mesozoic Jurassic, Cenozoic Tertiary and Quaternary. Among them, mica, amphibole, apatite and tourmaline are the loading minerals of fluorine in Archaean and Proterozoic strata, and the fluorine content in rocks is relatively high. For example, the fluorine content in the Amphiboles of the Precambrian Archaean in Northern Jiangsu is as high as 3,758 mg/kg (Zhang *et al.* 1998). The weathering of rocks results in high-fluorine background values in the soil of the study area.

Many bursts, diversions and deposits of the abandoned Yellow River have resulted in a series of micro-landforms with little difference in elevation, crisscrossing hills, slopes and depressions. These micro-landforms control the infiltration of natural water and the discharge of runoff. Due to long-term atmospheric precipitation and lateral discharge of river water, fluorine in the submerged water in the floodplain of the abandoned old Yellow River with high microgeomorphology, the secondary abandoned river course and the high ground at the top of the crevasse fan has been desalinated, gradually forming a low-fluorine water area (Figure 1(c)). The high potential difference promotes the migration of fluorine and other chemical components from the phreatic water to the low-water and inter-river depression areas. As well, the evaporation results in the relative enrichment of fluorine and other chemical components. In summary, the high-fluorine minerals in the rocks and a high-fluorine accumulation in the phreatic aquifers of the hilly terrains of the abandoned Yellow River alluvial plain reveal that the study area has a high-fluorine geochemical background. Based on the local fluorosis survey, extensive shallow groundwater extraction as drinking water source was found in remote rural areas. Due to daily intake of drinking high-fluorine shallow groundwater, residents in the northeast of Xuzhou, Heze and south of Jining suffer heavily from fluorosis.

Groundwater sample collection and analysis

A total of 313 shallow groundwater samples (7–63 m deep) were collected from hand-pumped and motor-pumped wells in 166 villages of Heze, Jining, Zaozhuang and Xuzhou areas of the abandoned Yellow River flooding delta. Polyethylene bottles of 500 mL were used to contain water, which were rinsed with deionized water and dried before sampling. Before sampling, the wells were pumped for more than 0.5 h. During sampling, all water samples were filtered through 0.45 μm membranes on site. Each filtered water sample was divided into two 500 mL polyethylene bottles in parallel. One of the bottled waters was acidified to pH = 2 with ultra-pure HNO_3 for cation analysis, the other one was used for anion (Cl^-, F^-, SO_4^{2-}, etc.) analysis without adding any reagent. Unfiltered groundwater samples collected into 500 mL bottles were used for determination of alkalinity.

Water temperature (T), pH and electron conductivity (EC) were measured *in situ* using a portable Hanna EC and pH meter, respectively, that was calibrated before use. Alkalinity (as HCO_3^-) was determined by using a Gran titration on the same day of sampling. Within 2 weeks of sampling, all groundwater samples were analysed for cation (Na^+, K^+, Ca^{2+} and Mg^{2+}) by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 80000, Perkin Elmer), anions (SO_4^{2-}, Cl^-) were analysed by ion chromatography (IC) (ICS-1500, Dionex) and fluorine was analysed by ion selective electrode (ISE) at the Advanced Center as well as Central Laboratory of Environmental Science and Engineering in China University of Mining and Technology, Xuzhou. In the analysis of samples, 5% of the repeated sample was added. The error of repeated sample is less than 5%. Analytical precisions as reported by commercial laboratories were better than 10%.

Sediment sample collection and analysis

Quaternary sediment was sampled from one borehole of 150 m depth to analyse the lithology. The borehole is located in the Pei County, northwest of Xuzhou, where waterborne fluorosis is severe (Figure 1). Thirty-three core samples were collected at intervals of 3.5–5 m, immediately packed in polyethylene bags, sealed in PVC pipes. According to the Chinese Standard method of GB/T14506.12, the total fluorine and water-soluble fluorine in the sediments were determined by ISE with alkali fusion (Jha *et al.* 2008). The water-soluble fluorine was extracted with water and the total fluorine was extracted with alkali melting method, and the total ion intensity regulating buffer solution

was added to the extract, and measured by the fluorine ion selective electrode method. Other water-soluble ions in groundwater samples were determined by the same analysis method.

RESULTS AND DISCUSSION

Distribution of fluorine in shallow groundwater

A statistical summary of the analytical results (minimum, maximum, mean and median) for each water-quality characteristic of 313 shallow groundwater samples are listed in Table 1. Concentrations of F^- in the shallow groundwater samples varied from 0.21 to 6.91 mg/L with a mean value of 1.68 mg/L ($n = 313$, Table 1). 72.8% of the shallow wells had F^- concentrations above 1.0 mg/L (Chinese MCL level).

A better understanding of F^- spatial distribution in groundwater in abandoned the Yellow River delta is of great significance for clarifying the causes of F^- enrichment in groundwater and preventing endemic fluorosis. The spatial variation of F^- concentration in shallow groundwater is shown in Figure 2. It can be seen that the F^- concentration

in the northwest of Jining and Zaozhuang areas, which is a small part of the Piedmont Highlands in the study area, is less than 1.0 mg/L. Generally speaking, the high flow rate of groundwater in the Piedmont Highlands will cause the fluorine to be lost more easily (Kim & Jeong 2005). In the northwest of Jining and Zaozhuang regions, the groundwater flow rate is high and the residence time is short, so the interaction time between groundwater and minerals is short, which leads to the low concentration of most elements (including F^-) in groundwater.

The concentration of F^- in most shallow groundwater in the study area is more than 1.0 mg/L. The high-fluorine areas are mainly distributed in the intersection areas between the abandoned Yellow River alluvial plain and piedmont alluvial plain of Heze, alluvial plain depression areas of Jiaxiang and Cao counties of Heze, Fei, Pei counties and Tongshan district of Xuzhou, where the groundwater flow is generally slow due to low hydraulic gradient and abundant fine-grained sediments. The concentration of F^- of shallow groundwater in these areas ranged from 2.0 to 4.0 mg/L, or even exceeding 6.5 mg/L in some proportion of groundwater samples. This implied that groundwater was more enriched in elements available during the groundwater

Table 1 | Hydrochemical parameters of shallow groundwater in the abandoned Yellow River flooding delta ($n = 313$)

| Parameters	Max	Min	Mean	Median
Well depth	63	7	39	35
Temperature (°C)	15.2	7.8	11.1	10.2
pH	9.20	6.40	7.49	7.50
EC (ms/cm)	12.440	0.125	2.031	1.768
TDS (mg/L)	6,086.26	125.54	1,120.43	862.01
TH (mg/L)	2,791.72	30.30	591.93	542.36
F^- (mg/L)	6.91	0.21	1.68	1.39
K^+ (mg/L)	58.12	0.11	2.36	0.69
Na^+ (mg/L)	1,373.86	3.15	185.63	111.38
Ca^{2+} (mg/L)	472.88	8.20	100.24	83.21
Mg^{2+} (mg/L)	474.45	3.66	58.75	48.00
Cl^- (mg/L)	2,053.62	5.77	152.84	103.55
SO_4^{2-} (mg/L)	2,125.50	2.47	236.39	95.45
HCO_3^- (mg/L)	1,186.17	0.38	524.71	503.68
CO_3^{2-} (mg/L)	47.66	N.D.	2.82	1.53

N.D., not detected.
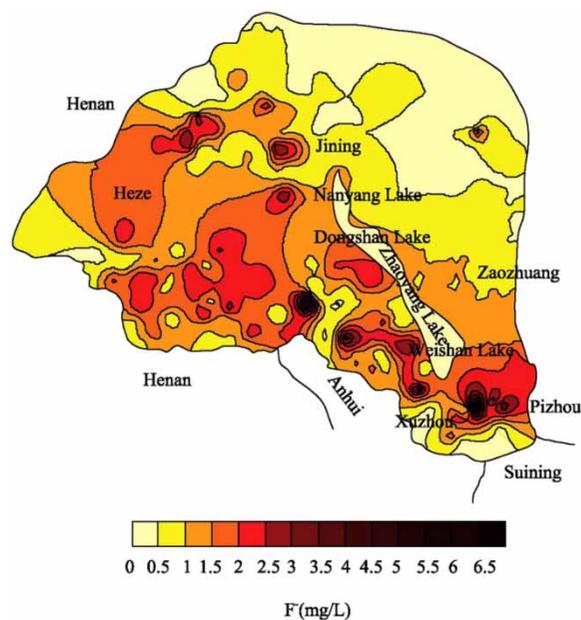
Figure 2 | F^- concentration distribution of the shallow groundwater in abandoned Yellow River flooding delta.

regime and flow path (Khair *et al.* 2015). Therefore, the high concentration of F⁻ in groundwater was enriched.

Aqueous geochemistry of the shallow groundwater

Aqueous chemical type

As shown in Table 1, pH ranged from 6.40 to 9.20, indicating water in the study area to be slightly acidic to mildly alkaline. The total dissolved solids in groundwater range from 125.54 to 6,086.26 mg/L with a mean value of 1,120.43 mg/L. Reasons for these high values cannot easily be explained, but could be the results of residential pollution (Zhu *et al.* 2018). Total hardness ranges from 30.30 to 2,791.72 mg/L with a mean value of 591.93 mg/L. Calcium ranges from 8.20 to 472.88 mg/L with a mean value of 100.24 mg/L. Magnesium ranges from 3.66 to 474.45 mg/L with a mean value of 58.75 mg/L. Sodium ranges from 3.15 to 1,373.86 mg/L with a mean value of 185.63 mg/L. Potassium ranges from 0.11 to 58.12 mg/L with a mean value of 2.36 mg/L. These mean values are less than standard values of Chinese MCL level. Bicarbonate in the water ranges from 0.38 to 1,186.17 mg/L with a mean value of 524.71 mg/L. Sulfate ranges from 2.47 to 2,125.50 mg/L with a mean value of 236.39 mg/L. Chloride ranges from 5.77 to 2,053.62 mg/L with a mean value of

152.84 mg/L. A well at Jinxiang, Hezeng area has the highest chloride value of 2,053.62 mg/L with the high sulfate value of 1,940.28 mg/L. Few of the water sources have elevated levels of sulfate with corresponding elevated levels of nitrate. Such water sources may have been polluted.

According to Figures 3 and 4, shallow groundwater hydrochemical type demonstrates complex classification. A total of 313 samples can be divided into nine hydrochemical
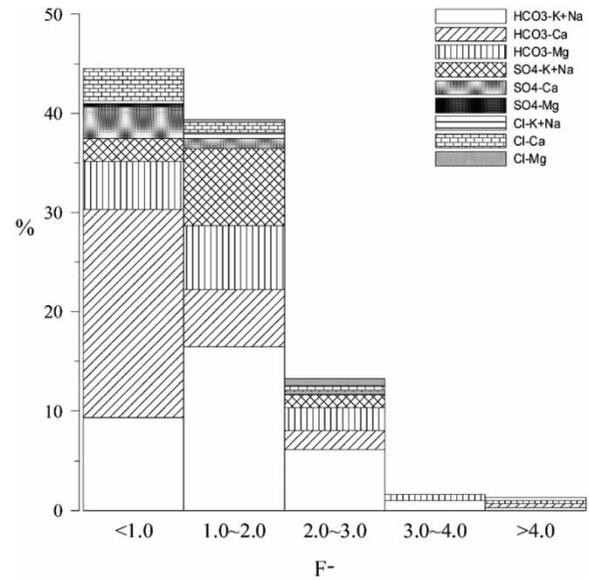

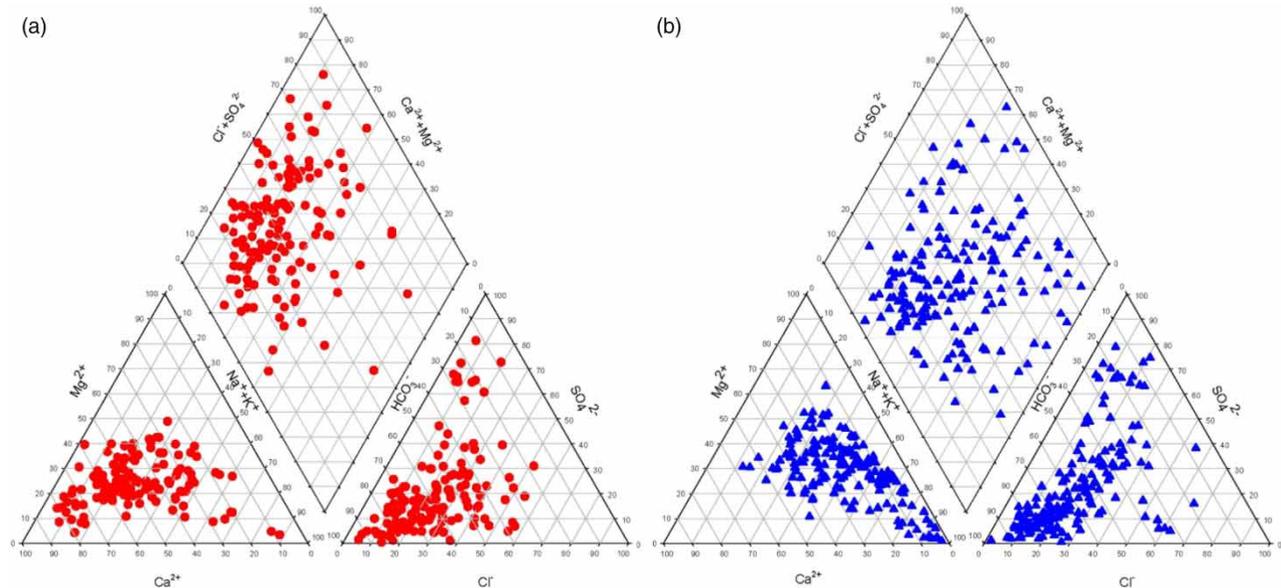Figure 4 │ Chemical type classification of the shallow groundwater.

Figure 3 │ Piper diagram for groundwater samples from abandoned Yellow River flooding delta: (a) F⁻ <1.0 mg/L and (b) F⁻ >1.0 mg/L.

subtypes, respectively, including HCO_3-K + Na, HCO_3-Mg, HCO_3-Ca, SO_4-K + Na, Cl-K + Na, SO_4-Ca, SO_4-Mg, Cl-Ca and Cl-Mg. A majority of the samples (over 77%) belong to the bicarbonate types, i.e., HCO_3-K + Na, HCO_3-Mg, HCO_3-Ca, etc. Figure 3 shows that predominant water type for the water samples is HCO_3-K + Na, SO_4-K + Na, HCO_3-Mg, HCO_3-K + Na, SO_4-K + Na and HCO_3-Mg. The samples collected from southern and eastern mountain areas was Ca-HCO_3, Ca-Na-HCO_3 or Mg-Ca-HCO_3 types. For the shallow groundwater from flow through and discharge area it is Na-HCO_3, Na-SO_4-Cl or Mg-Na-SO_4-Cl type. The predominant water type for the intermediate and deep groundwater is of Na/Ca/Mg-Ca-HCO_3 type.

Figure 4 indicates that groundwater with F^- content >1.0 mg/L is mainly distributed in the HCO_3-K + Na, SO_4-K + Na water types. However, groundwater with F^- content less than 1.0 mg/L is mainly concentrated in HCO_3-Ca, HCO_3-K + Na and HCO_3-Mg water forms. Figure 4 shows that the content of F^- in HCO_3-Ca water varies from 0 to 7.0 mg/L, mainly in the range of <1.0 mg/L; while the F^-

content of HCO_3-K + Na water varies from 0 to 6.0 mg/L, and most from 1.0 to 4.0 mg/L; and the F^- content of HCO_3-Mg water varies from 0 to 4.0 mg/L, and most of the samples are >1.0 mg/L; the F^- content of SO_4-K + Na water varies from 0 to 3.0 mg/L, and most of the samples are concentrated in the range of >1.0 mg/L.

Correlation between F^- and geochemical parameters

Figure 5(a) shows that the correlation between F^- content and pH in shallow groundwater is not obvious; probably because the factors affecting F^- content are complex and pH is not the main factor. The content of F^- in acidic water with pH < 7.0 is mostly less than 1.0 mg/L, while the high fluorine samples ($F^- > 3.0$ mg/L) were mostly found in alkaline water with pH > 7.5, indicating that F^- is easier to dissolve and aggregate in alkaline water.

The correlation between F^- content and $Na^+ + K^+$ is not obvious, but with the increase of the ratio of $Na^+ + K^+$ to Mg equivalent in cations, the concentration of F^- tends
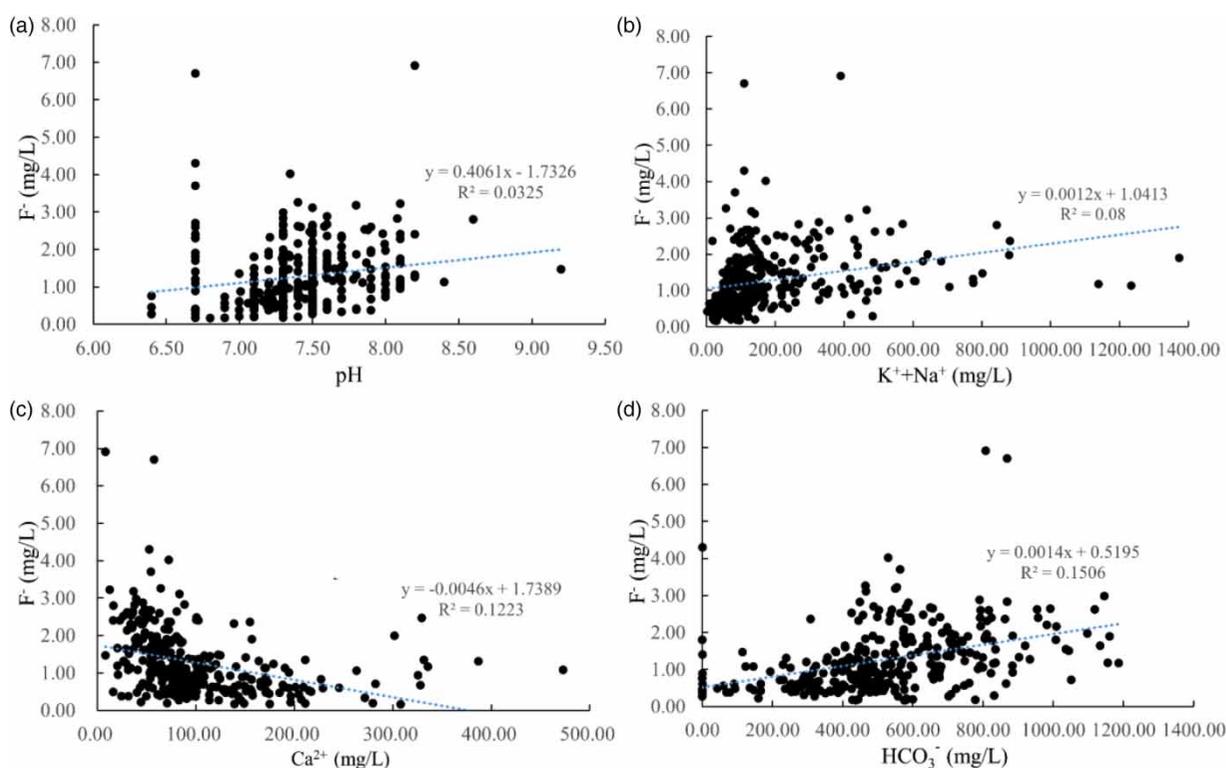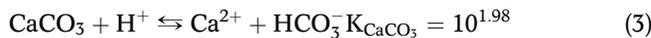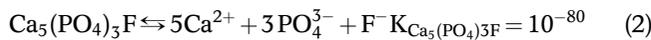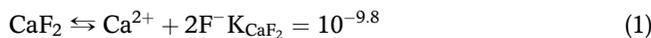

Figure 5 | Correlation between fluorine and other aqueous chemical parameters: (a) F^- versus pH of groundwater samples; (b) F^- versus $Na^+ + K^+$ of groundwater samples; (c) F^- versus Ca^{2+} of groundwater samples; (d) F^- versus HCO_3^- of groundwater samples.

to increase (see Figure 5(b)). The Pearson's correlation coefficient between fluorine and $Na^+ + K^+$ is 0.283, and means significant correlation, which can also prove the point. Figure 5(c) shows a negative correlation between F^- and Ca^{2+} indicating that Ca^{2+} has a considerable inhibitory effect on the migration and enrichment of F^- in water. Figure 5(d) shows that the correlation between HCO_3^- and F^- is positive, and the content of F^- increases with the increase of HCO_3^- in water when pH changes slightly. The Pearson correlation coefficient results in Table 2 also support the above conclusions.

The correlation between fluorine and other hydrochemical components in shallow groundwater is closely related to the equilibrium of dissolution-precipitation reaction in groundwater. The reaction equations are as follows:

$$CaF_2 \leftrightarrows Ca^{2+} + 2F^- \quad K_{CaF_2} = 10^{-9.8} \tag{1}$$

$$Ca_5(PO_4)_3F \leftrightarrows 5Ca^{2+} + 3PO_4^{3-} + F^- \quad K_{Ca_5(PO_4)3F} = 10^{-80} \tag{2}$$

$$CaCO_3 + H^+ \leftrightarrows Ca^{2+} + HCO_3^- \quad K_{CaCO_3} = 10^{1.98} \tag{3}$$

The dissolved product of $Ca_5(PO_4)_3F$ is relatively small, so CaF_2 may be one of the mineral phases that restrict the dissolution of F^- in groundwater. According to the results of groundwater chemical test, the Ca^{2+} content in most water samples is probably in the order of dozens, so the saturated concentration of F^- should be at least in the dozens. However, the fluorine content in most groundwater is far less than 10 mg/L, and it is generally difficult to reach the saturation of CaF_2. Therefore, the content of F^- in groundwater is not determined by fluorite minerals alone. The precipitation-dissolution equilibrium equations of CaF_2 and $CaCO_3$ can be obtained simultaneously:
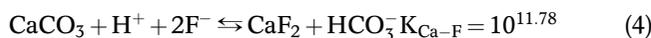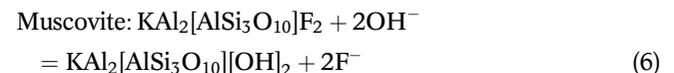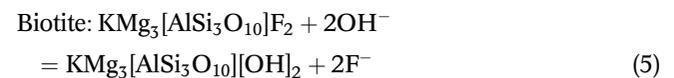
$$CaCO_3 + H^+ + 2F^- \leftrightarrows CaF_2 + HCO_3^- \quad K_{Ca-F} = 10^{11.78} \tag{4}$$

Table 2 | Pearson's correlation coefficients between fluorine and other aqueous chemical parameters

	pH	$K^+ + Na^+$	Ca^{2+}	HCO_3^-
F^-	0.180**	0.283**	−0.350**	0.388**

**At 0.01 level, the correlation is significant.

The equilibrium constant is $K_{Ca-F} = [HCO_3^-]/[H^+][F^-]^2$. From this formula, the reason could be revealed that F^- content increases with HCO_3^- content. Furthermore, F^- content increases with the increase of pH, that is, F^- is more concentrated in HCO_3^- type alkaline water. The above four equations also show that CaF_2 will dissolve under certain conditions, resulting in the increase of F^- concentration in water and the simultaneous dissolution of Ca^{2+}. The dissolved Ca^{2+} partially separates from the water body in the form of $CaCO_3$ precipitation. The other part participates in the displacement reaction of $Na^+ + K^+$ on the surface of clay minerals due to ion exchange or reduction potential reduction in water (Rafique *et al.* 2009). Because most K^+ is adsorbed by clay minerals under natural conditions, it can be understood that high fluorine groundwater is mostly distributed in HCO_3-Na type water. In addition, HCO_3-Na shallow groundwater is often alkaline and contains OH^-. At the same time, granitoid rocks or their weathering products in this region are rich in high-fluorine minerals. Therefore, OH^- in water will displace F^- in high-fluorine minerals in large quantities when they combine with HCO_3-Na water. For example, the reaction equations of shallow HCO_3-Na water with biotite and muscovite are shown in Equations (5) and (6) (Guo *et al.* 2007). These reactions further promote the accumulation of fluorine in shallow groundwater.

$$Biotite: KMg_3[AlSi_3O_{10}]F_2 + 2OH^- = KMg_3[AlSi_3O_{10}][OH]_2 + 2F^- \tag{5}$$

$$Muscovite: KAl_2[AlSi_3O_{10}]F_2 + 2OH^- = KAl_2[AlSi_3O_{10}][OH]_2 + 2F^- \tag{6}$$

Vertical variation of water-soluble fluorine

Vertical distribution characteristics of water-soluble fluorine

Water-soluble fluorine, pH and main water-soluble chemical components of 33 sediment profile samples were tested (Figure 6). Figure 6 shows that the concentration of water-soluble fluorine ranges from 5.99 mg/kg to 31.66 mg/kg, with an average of 11.73 mg/kg. With the increase of formation depth, the content of water-soluble fluorine
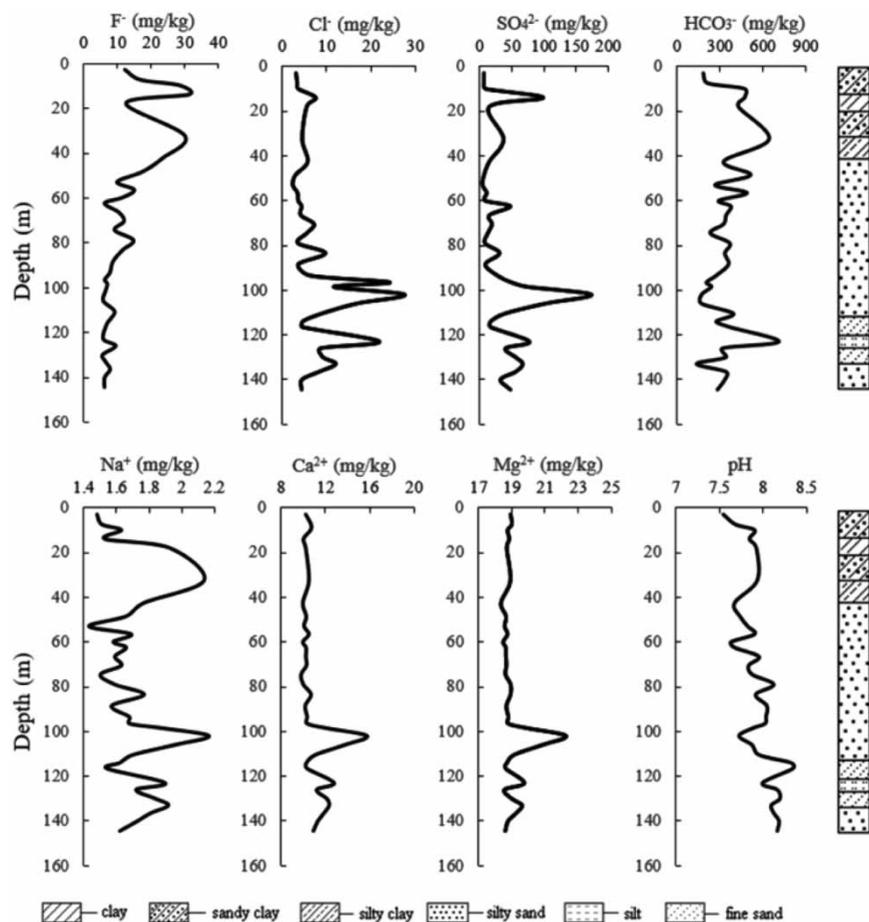
Figure 6 │ Contents of water-soluble fluorine and main chemical components in geologic profile of sediment.

decreases gradually. The water-soluble fluorine content reached 31.66 mg/kg and 30.23 mg/kg in the two high-value areas of 6–14 m and 25–50 m, respectively. And water-soluble fluorine content below 80 m was less than 10 mg/kg.

Vertical distribution of water-soluble fluorine in sediments is mainly influenced by stratum parent material, lithology, climate and hydrological conditions in the area. The Quaternary sediments in the study area mainly come from the northern Taiyi uplift area. The fluorine content of Archaean and Proterozoic metamorphic rocks and migmatites in Taiyi area is abnormally high. The fluorine content of Archaean amphibolite is 3,758 mg/kg and that of Sinian shale is 5,214 mg/kg. Holocene (Q4) in this area is composed of yellow alluvium, alluvial lake sediment and lake-marsh sediment, in which fluorine content can be as high as 743 mg/kg, 1,050 mg/kg and 585×10^{-6} mg/kg,

respectively (Zhang *et al.* 1998). The annual evaporation in this area is about twice that of rainfall, mostly in flooded lowlands and inter-river depressions, so the evaporation concentration is an important reason for the accumulation of fluorine in shallow groundwater (Liao 1992). The Yellow River flooding, rainwater leaching and groundwater migration are the hydrological conditions for the distribution of water-soluble fluorine in Quaternary strata. The fluorine content in the upper Quaternary is higher than that in the deep Quaternary because of the accumulation of fluorine by multi-flooding. The alkaline characteristics of the strata in this area are more conducive to rainwater leaching and infiltration of water-soluble fluorine (Li & Wang 1992). The sand particles of phreatic aquifer in the study area are coarse, with less clay content, loose structure and good permeability. The bottom is lake-marsh silty clay. The clay aquifer blocks the vertical runoff of groundwater

and adsorbs water-soluble fluorine, which makes water-soluble fluorine easy to accumulate. For these reasons, water-soluble fluorine reached two peaks of 31.66 and 30.23 mg/kg in the Quaternary phreatic aquifer (Q4) floor (12–14 m) and confined aquifer (Q3) floor (32–34 m). The water-soluble fluorine content reached its peak at the depth of 10–20 m rather than at the surface of the soil, which is similar to the results of Babulal *et al.* (2003). The accumulation of fluorine in the Yellow River flooded sediments below 35 m decreased, while the leaching and infiltration of rainwater were greatly weakened, the downward migration of water-soluble fluorine was weakened, and the vertical water-soluble fluorine content in the sediment layer showed a downward trend. The content of water-soluble fluorine in sediments below 90 m is stable within 10 mg/kg. The fluorine content of groundwater in this layer is not high, and the vertical migration of fluorine by groundwater is correspondingly weakened. The water-soluble fluorine in this layer is mainly produced by mineral dissolution, so its content is relatively stable. Throughout the vertical distribution of water-soluble fluorine in the whole sedimentary layer, the overall trend is downward. The average content of water-soluble fluorine in 0–45 m formation (22.25 mg/kg) is much higher than that in 45–150 m formation (8.9 mg/kg), which indicates that water-soluble fluorine is easier to accumulate in shallow layers in this area.

Relationship between water-soluble fluorine and pH

With the increase of formation depth, the pH value increases (Figure 6), which is contrary to the decreasing trend of water-soluble fluorine. The correlation analysis of pH and water-soluble fluorine content showed that they were negatively correlated (r = −0.358). This is consistent with the research conclusions of Shao *et al.* (1999), but different from those of Li *et al.* (2003). The adsorption process of fluorine can be affected by pH value (Zhou & Yang 1995). For specific sediment, the maximum adsorption amount of an ion corresponds to the corresponding pH value. Besides pH value, mineral components and particle size of sediment, hydrochemical characteristics and runoff velocity of groundwater could also affect the release of fluorine, which may lead to the result of no strong correlation between water-soluble fluorine and pH in the vertical sediment.

Relationship between water-soluble fluorine and other ions

Table 3 shows that there is a significant negative correlation between F^- and Ca^{2+}. The content of Ca^{2+} in shallow Quaternary strata with high F^- content is lower, while that in lower F^- strata is higher. It is generally believed that Ca^{2+} has an inhibitory effect on the migration and enrichment of F^- in water due to the fact that they are able to form a poorly soluble CaF_2 precipitate. In addition, F^- content is closely related to the lithology and structure of the aquifer: in the strata with coarse grains, large thickness and few layers, F^- content is low and Ca^{2+} content is high; in the strata with fine lithologic grains, many aquifer layers and small thickness, F^- accumulates and Ca^{2+} content are low. F^- is negatively correlated with Cl^- and the content of F^- decreases in strata with higher Cl^- content. In addition, F^- is positively correlated with HCO_3^-. It can be seen from Figure 6 that the content trends of F^- and HCO_3^- are almost the same, especially in the range of 0–100 m. After the relative excess of HCO_3^- in groundwater, the hardness and alkalinity of groundwater are strengthened, and the dissolution and hydrolysis of fluorine salts and fluorosilicates in formation are accelerated. Results show that there is no significant correlation between F^- content and Na^+, Mg^{2+} and SO_4^{2-} content in vertical strata.

Hydrochemical type analysis of sediment solution

The relationship between the distribution of water-soluble fluorine in the vertical strata of Quaternary strata in Pei area of Xuzhou and the hydrochemical types of the extracts was

Table 3 │ Correlation between water-soluble fluorine and other ions in geologic profile of quaternary system

Component	Correlation coefficient r ($n = 33$, df = 31)	Equation
Na^+	−0.056	$y = 15.691 − 2.314x$
Mg^{2+}	−0.268	$y = 59.574 − 2.518x$
Ca^{2+}	−0.378	$y = 35.325 − 2.149x$
Cl^-	−0.352	$y = 14.953 − 0.407x$
SO_4^{2-}	−0.195	$y = 13.198 − 0.039x$
HCO_3^-	0.485	$y = 2.137 + 0.028x$

obtained by using Shukalev classification method (Figure 7). Within 0–90 m, the hydrochemical type of the extract is mainly HCO_3-Mg, and a small amount of $SO_4.HCO_3$-Mg. In the 90–150 m interval, three chemical types of $SO_4.HCO_3$-Mg.Ca, HCO_3-Mg and $SO_4.HCO_3$-Mg alternately appeared in the extract. Generally speaking, the F^- content from high to low is HCO_3-Mg, $SO_4.HCO_3$-Mg and $SO_4.HCO_3$-Mg.Ca.

Chemical species with simulation

According to this investigation on the correlation between fluorine concentration and fluorosis, the fluorine concentration in water is less than or slightly greater than 1.0 mg/L and, in some villages, the phenomenon of fluorosis or high prevalence rate still occurs. In the other villages, however, the fluorine concentration in water is higher, even close to 2.0 mg/L, and the fluorosis prevalence rate is very low. Many studies have discussed the relationship between the existence of fluorine in groundwater and human health. Fluorine in groundwater not only exists in the form of simple F^-, but also in complex forms including NaF, CaF^+, MgF^+, etc. It was found that the incidence and severity of endemic fluorosis were positively correlated with the total F^- content in water, its activity and the activity of complexes. The results showed
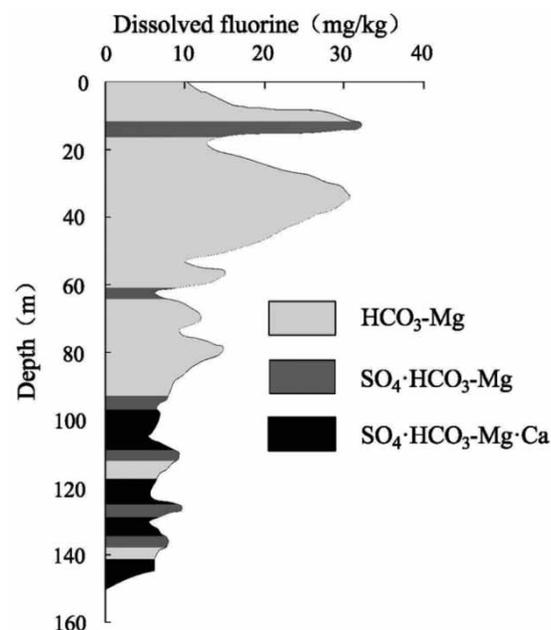

Dissolved fluorine (mg/kg)

Figure 7 │ Hydrochemical types of sediment solution.

Table 4 │ Activity of fluorine and its complexes

Geochemical parameters		F^- (%)	MgF^+ (%)	CaF^+ (%)
F^- (mg/L)	1–2	72.39–96.80	2.14–25.06	0.17–2.71
	2–4	80.49–98.00	1.03–17.87	0.10–2.68
	>4	86.88–92.39	6.99–12.18	0.21–0.55
pH	7–8	72.39–96.01	3.29–25.06	0.24–2.10
	>8	89.68–98.00	1.03–9.67	0.10–2.71
Mineralization degree (g/L)	<1	87.45–97.31	2.06–11.49	0.15–1.18
	1–2	81.43–98.00	1.03–17.05	0.02–0.89
	>2	72.39–93.28	5.46–25.06	0.38–2.71

that the pathogenicity of different forms of endemic fluorosis could be divided into: $\alpha_{NaF^0} > \alpha_{MgF^+} > \alpha_{CaF^+} > \alpha_{F^-} > \alpha_{F_{sum}}$ (Singh *et al.* 1979). Therefore, the simulation calculation of fluorine complexes in groundwater cannot be neglected when investigating the hydrogeochemical origin of endemic fluorosis. In this study, the geochemical simulation software PHREEQC was used to calculate water samples of shallow groundwater in the flood delta of the Yellow River. The calculation results are shown in Table 4.

It can be seen from Table 4 that the composition of fluorine in the shallow groundwater of the study area is mainly in the form of F^-, MgF^+ and CaF^+. The fluorine ion activity (α_{F^-}) accounts for 72.39–98.00% of the total fluorine concentration ($\alpha_{F_{sum}}$), followed by the fluoromagnesium complex activity (α_{MgF^+}) of 1.03 to 25.06%, and the fluorocalcium complex activity (α_{CaF^+}) is the lowest, accounting for 0.10–2.71%. In addition, the calculation results show that with the increase of salinity, the activity percentage of F^- decreases, the activity percentage of MgF^+ and CaF^+ increases. The activity percentage of F^- increases with the increase of pH value. The activity percentage of MgF^+ reaches its maximum at pH 7.0–8.0. The activity of MgF^+ and CaF^+ in shallow groundwater in this area is higher than that in similar geochemical background areas in China (Singh *et al.* 1979). Therefore, MgF^+ and CaF^+ in shallow groundwater are important controlling hydrochemical factors of fluorosis in this area.

CONCLUSIONS

In this study, the F^- and hydrochemical characteristics of groundwater in the flooded area of the Yellow River were analysed. A total of 313 groundwater samples were collected in the central part of the flooding delta to address the chemistry

of high-fluorine groundwater. Thirty-three core samples were collected from one borehole of 150 m depth to analyse the vertical distribution characteristics of total fluorine and water-soluble fluorine. The main conclusions include:

1. The concentration of fluorine in groundwater ranges from 0.2 to 6.7 mg/L, and fluorine in 72.8% of the groundwater samples exceed China's maximum permissible limit of 1.0 mg/L for drinking water. The local people were highly exposed to naturally occurring fluorine in shallow groundwater of the abandoned Yellow River flooding delta. These groundwater samples can be divided into nine hydrochemical subtypes, and the majority of the samples (over 77%) belong to the bicarbonate types, i.e., HCO_3-K + Na, HCO_3-Mg, HCO_3-Ca, etc.

2. The F^- in the groundwater is positively correlated with HCO_3^- and Na^+, K^+ and negatively correlated with Ca^{2+}. The correlation between F^- content and pH in shallow groundwater is not obvious, while groundwater with F^- concentration of over 3.0 mg/L generally occurs in the alkaline environment.

3. The concentration of water-soluble fluorine in 33 sediment samples ranged from 5.99 mg/kg to 31.66 mg/kg, and the content of water-soluble fluorine decreases gradually with the increase of formation depth. The water-soluble fluorine content reached 31.66 mg/kg and 30.23 mg/kg in the two high-value areas of 6–14 m and 25–50 m, respectively and the water-soluble fluorine content below 80 m was less than 10 mg/kg.

4. The content of water-soluble fluorine in vertical sediments is negatively correlated with Ca^{2+}, Cl^- and positively correlated with HCO_3^-, and showed no significant correlation with Na^+, Mg^{2+}, SO_4^{2-} and pH.

5. Activity of different fluorine complex species was quantified using PHREEQC package. According to the calculation, MgF^+ and CaF^+ in the groundwater were dominant species controlling the endemic fluorosis of the abandoned Yellow River flooding delta.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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