Environ Geol (2007) 53:795–803
DOI 10.1007/s00254-007-0692-z

ORIGINAL ARTICLE

Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China

Xubo Gao · Yanxin Wang · Yilian Li · Qinghai Guo

Received: 1 December 2006 / Accepted: 12 February 2007 / Published online: 7 March 2007

Abstract Long-term intake of high-fluoride groundwater causes endemic fluorosis. This study, for the first time, discovered that the salt lake water intrusion into neighboring shallow aquifers might result in elevation of fluoride content of the groundwater. Two cross-sections along the groundwater flow paths were selected to study the geochemical processes controlling fluoride concentration in Yuncheng basin, northern China. There are two major reasons for the observed elevation of fluoride content: one is the direct contribution of the saline water; the other is the undersaturation of the groundwater with respect to fluorite due to salt water intrusion, which appears to be more important reason. The processes of the fluorine activity reduction and the change of Na/Ca ratio in groundwater induced by the intrusion of saline water favor further dissolution of fluorine-bearing mineral, and it was modeled using PHREEQC. With the increase in Na concentration (by adding NaCl or Na_2SO_4 as Na source, calcium content kept invariable), the increase of NaF concentration was rapid at first and then became slower; and the concentrations of HF, HF_2^-, CaF^+, and MgF^+ were continuously decreasing. The geochemical conditions in the study area are advantageous to the complexation of F^- with Na^+ and the decline of saturation index of CaF_2, regardless of the water type (Cl–Na or SO_4–Na type water).

Keywords Fluoride · Groundwater · Hydrogeochemistry · Salt lake · Northern China

---

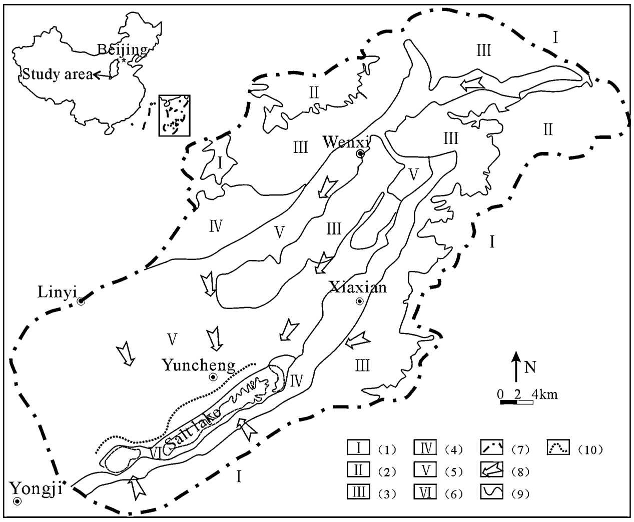
X. Gao · Y. Wang (✉) · Y. Li · Q. Guo
School of Environmental Studies and MOE Laboratory
of Biogeology and Environmental Geology,
China University of Geosciences,
Wuhan 430074, People's Republic of China
e-mail: yx.wang@cug.edu.cn

Introduction

Long-term intake of high-fluoride ground water is the major reason for endemic fluorosis that affects millions of people worldwide (Yiamouyiannis and Burk 1976; Frencken 1992; Jacobsen et al. 1993; Choubisa et al. 1995; Cauley and Murphy 1995). A lot of efforts have been made to understand the occurrence and genesis of high-fluoride groundwater (Banks et al. 1995; Gizaw 1996; Frengstad et al. 2001; Botha and Van Rooy 2001; Carrillo-Rivera et al. 2002; Shanker et al. 2003; Y. Wang and S. L. Shvartsev 2006, submitted data; Tu et al. 2006). As a representative case of endemic fluorosis, the impact of high-fluoride groundwater on human health in Yuncheng basin, Shanxi Province, northern China (Fig. 1), has been a major concern for environmental and medical scientists for decade (Zhang 1993; Cao et al. 1997; Lu et al. 2004). The results of hydrogeological survey show that the shallow groundwater in an area of over 3,156 km^2 at Yuncheng contains fluoride higher than the maximum concentration level (MCL) concentration (1.0 mg/L), occupying 50.8% of the total basin area. In Linyi County where endemic fluorosis is the most serious, there are 13 villages where 22% of villagers have lost the labor capability due to fluorosis.

One of the most distinctive geologic features of the Yuncheng basin is the existence of salt lake. The major mineral phases of the salt lake are mirabilite ($Na_2SO_4 \cdot 10H_2O$), halite, and astrakhanite ($MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$). As can be seen from Table 1, the total dissolved solids (TDS)-values of the lake water ranges from 9.02 to 268.1 g/L (g/L = 1 kg/m^3), with sulfate and chloride as the dominant anions and sodium as the dominant cation.

Inside the basin, shallow groundwater in Quaternary aquifers flows toward the salt lake (Fig. 1). In the central parts of the basin where the sediments become finer,



(1)-(6) Hydrogeological zones: (1)bedrock; (2)high land; (3)hilly loess region; (4)piedmont plain; (5)alluvial plain; (6)salt lake; (7)boundary of the study area; (8)flow path of groundwater; (9)boundary of different landforms;(10)delineated frontier of saline water intrusion

Fig. 1 A simplified hydrogeology map of Yuncheng basin

groundwater flow was retarded, which was advantageous for the enrichment of fluoride in the groundwater. Since 1990s, under the impact of over-exploitation of groundwater, intrusion of the saline water from the salt lake into the shallow aquifers to its north has been observed (Yun 2001).

In the study area, the fluoride content of most shallow groundwater samples ranges between 0.5 and 3.0 mg/L, showing an increasing trend from loess highland and piedmont plain to the alluvial plain and further to the boundary of saline water and fresh water in the north side of the salt lake. It can be seen from Fig. 2 that the TDS-value of groundwater northwest of the salt lake is higher than 4.0 g/L, with a concomitant increase in fluoride concentration above 3.0 mg/L (up to 6.4 mg/L). The increase of TDS-values clearly reflects the impact of saline water intrusion. But are there any relationships between the increase of TDS-values and that of fluoride for these waters? The major objective of this paper is therefore to understand the relationships, based on the hydrogeochemical studies in the area.

Sampling and analysis

Sixty-one groundwater samples were collected from Yuncheng basin from August 2003 to October 2004. Before the sampling, the groundwater was pumped over 1 h. Locations of samples are shown in Fig. 2. When sampling, all water samples were filtered through 0.45 μm membranes on site. Samples were collected in two new 350 mL polyethylene bottles. For cation analysis, reagent-quality HNO_3 was added to one of these polyethylene bottles until pH of samples reached 1. These bottles had been rinsed with deionized water twice before sampling. Unstable hydrochemical parameters including water temperature, pH, and electrical conductivity (EC) were measured in situ using portable Hanna EC and pH meter that had been calibrated before use. Alkalinity was measured on the sampling day using the Gran titration method. Concentration of fluoride and other anions of the samples were determined using ion chromatography (IC) (Dionex 120, Dionex, Sunnyvale, CA, USA). The lower detection limit of the instrument for F^-, Cl^-, and SO_4^{2-} was 0.02, 0.02, and 0.04 mg/L, respectively, with the recovery between 95.4 and 102.3%, RSD between 1.10 and 2.46%. The cation contents were analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (IRIS Intrepid II XSP, Thermo Elemental, Madison, WI, USA). Its recovery was between 97.1 and 105.3%, RSD <3%, and the lower detection limit of the instrument for K^+, Na^+, Ca^{2+}, and Mg^{2+} 0.04, 0.317, 0.115, and 0.010 mg/L, respectively.

Results and discussion

Hydrochemical types

The water samples were plotted onto the Piper diagram (Fig. 3). It can be seen that the samples on the north of the salt lake fall into areas I, II, and III; the samples from south side of the salt lake in area IV; the salt lake sample and the samples of near bank marsh land salt water in area V. The samples from the recharge regions fall into area I, with HCO_3^- as the predominant anion and Na^+ and Ca^{2+} as the predominant cations. The samples collected in the

Table 1 Hydrochemistry of the Yuncheng salt lake water (in mg/L except TDS)

Sampling site	K	Na	Ca	Mg	HCO_3^-	Cl^-	SO_4^{2-}	TDS (g/L)
East part	15.50	1,530.7	43.92	669.1	284.5	1,737.2	4,031.6	9.02
West part	8.50	3,543.2	192.6	546.0	273.1	2,948.5	5,819.5	13.4
Center	7.10	46,438	3.52	28,066	4.80	138,566	55,036	268.1
South part	702.4	17,988	327.6	7,834.0	702.7	32,018	23,584	82.9

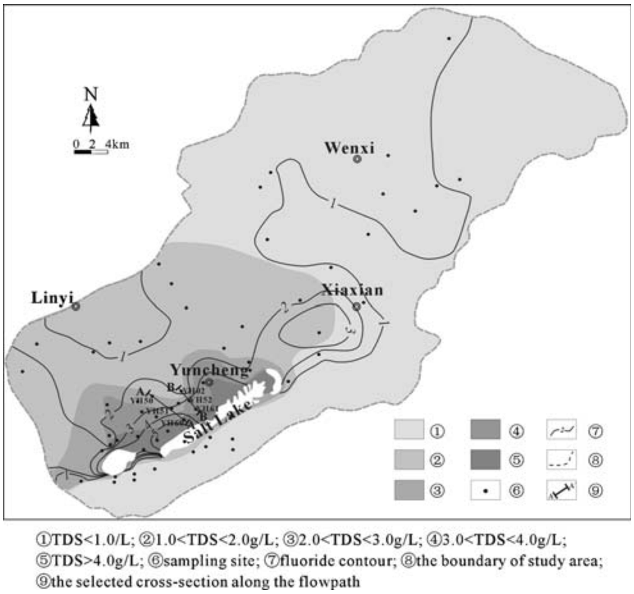


Fig. 2 Sampling sites and TDS and fluoride contour map of shallow groundwater

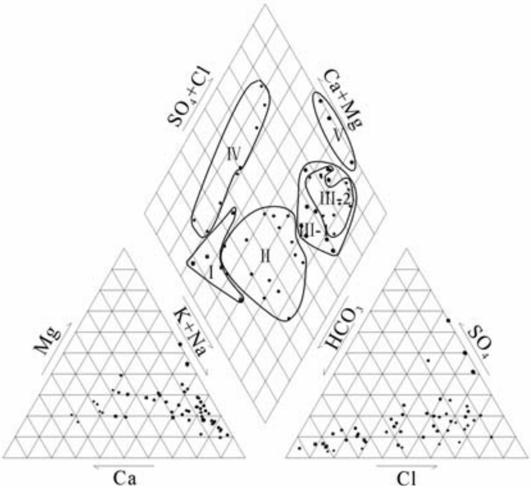


Fig. 3 Trilinear plot of shallow groundwater samples that are grouped into four areas (I–IV) according to their hydrogeological settings. The salt lake water and the near bank marsh salt water fall in area V

flow-through regions belong to HCO_3–Na–Ca, HCO_3–Na–Mg, HCO_3–SO_4–Na, and HCO_3–SO_4–Na–Mg waters. The samples from the discharge regions are located in area III, with Na^+ as the major cation and SO_4^{2-} and Cl^- as the dominant anions. Two sub-areas can be delineated inside the area III (Fig. 3): III-1 and III-2. For samples in sub-area III-1, the dominant anion is HCO_3^- and the main hydrochemical types are HCO_3–SO_4–Na–Mg, HCO_3–SO_4–Cl–Na, HCO_3–SO_4–Na, and HCO_3–SO_4–Cl–Na–Mg. Samples in the sub-area III-2 are possibly affected by salt water intrusion, with Cl^- and SO_4^{2-} as the dominant anions, and their hydrochemical types are mainly SO_4–Na, SO_4–Cl–Na–Mg, and SO_4–Cl–Na. It is interesting to see that samples from the south side of the salt lake contain Ca^{2+} as the dominant cation and have monotonous increase in sulfate concentration, with HCO_3^- and then SO_4^{2-} as the dominant anions. Since the groundwater from area IV has the TDS-values <1 g/L, it can be inferred that there is no saline water intrusion south of the salt lake. The intrusion is therefore the result of over-exploitation of groundwater northwest of the lake, in the more densely populated and fast developing regions of Yuncheng basin.

Hydrochemical evidences of salt water intrusion

Before 1990s, there had been hydrodynamic equilibrium between the shallow groundwater of the Yuncheng basin and the salt lake water, and the latter being recharged by the former. In recent years, however, intrusion of salt water into shallow groundwater has been detected (Yun 2001). Long-term over-exploitation of groundwater in the north side of the salt lake resulted in the occurrence of a depression cone in the area between Yongji city and Yuncheng city.

It can be seen from Fig. 2 that groundwater TDS increases from the recharge area to the discharge area, with the highest close to the salt lake. The high-TDS region (TDS > 4.0 g/L) is located in the northwestern side of the salt lake, stretching north to the urban district of Yuncheng city, where there are four samples with TDS more than 5.0 g/L. It was reported by the water conservancy bureau of Yuncheng city to the authors that the TDS of shallow groundwater in the East Street of the Yuncheng city was once as high as 15.7 g/L. Such abnormal TDS level is clearly an indication of the effect of salt water intrusion.

Under the impact of intrusion of salt water that contains Na^+, K^+, and Cl^- with high contents, the content of Ca^{2+} in the groundwater may increase due to cation exchange. It can be seen from Fig. 4 that the (Ca + Mg)/(K + Na) ratio (in meq/L) decreases with the increase of Cl^- content when the chloride concentration is lower than 1 g/L, and that the ratio then increases when the concentration is higher than 1 g/L. This may result from cation exchange between Ca^{2+}

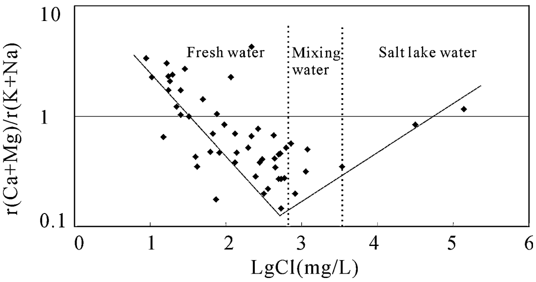


Fig. 4 *r*(Ca–Mg)/*r*(K–Na)–Cl *dot* plot of samples in study area

or Mg^{2+} sorbed by the mineral phase in the aquifer matrix and Na^+ in the groundwater added by salt water intrusion:

$$(\mathrm{Ca}_{1-x}\mathrm{Mg}_x)(\mathrm{sorbed}) + 2\mathrm{Na}^+ \rightarrow 2\mathrm{Na}^+(\mathrm{sorbed}) + (1-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+}, \tag{1}$$

where x is the relative stoichiometry.

Another evidence of the mixing between the salt water and the shallow groundwater is the variation of calcium and sulfate ion concentration in the groundwater (Fig. 5). The reason for the y-axis-value (Ca-0.33 HCO_3^-) is that the sources of Ca include dissolution of gypsum, calcite, and dolomite. To find out the contribution of gypsum dissolution, that of calcite and dolomite has to be excluded by considering the following overall reaction:

$$\mathrm{CaCO_3} + \mathrm{CaMg(CO_3)_2} + 3\mathrm{CO_2} + 3\mathrm{H_2O} = 2\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + 6\mathrm{HCO_3^-} \tag{2}$$

As shown in Fig. 5, when the concentration of SO_4^{2-} is higher than 10 mmol/L, the water samples are located far from the gypsum dissolution line, indicating that the main source of SO_4^{2-} in groundwater is not the dissolution of gypsum. Since these samples commonly have elevated TDS-values, saline water intrusion should be the major source for the additional SO_4^{2-}.

Modeling of fluorine species change due to salt water intrusion

In order to reveal the geochemical processes responsible for fluoride enrichment in the shallow groundwater before and after the intrusion of salt water, geochemical modeling was done. First of all, the activity coefficient was calculated using PHREEQC Interactive 2.8 (Parkhurst and Appelo 1999). When the ion intensity of solution is smaller than 0.1 mol/L, the activity coefficient is calculated by Debye–Hückel equation. When the ion strength is >0.1 mol/L and lower than 0.5 mol/L, it could be calculated by the Davies equation. It can be seen from Fig. 6 that the activity coefficient of fluoride decreases from above 0.90 to 0.71. To accurately evaluate the contribution of activity coefficient change to the fluorine content in the groundwater, the following equation was used for the calculation of F^- concentration change:

$$\Delta[\mathrm{F}^-] = \frac{C_0 r_0}{r_1} - C_0, \tag{3}$$

where Δ [F^-] is the change in F^- concentration, C_0 the concentration of F^- before mixing, r_0 the activity coefficient before mixing, and r_1 is the activity coefficient after mixing.

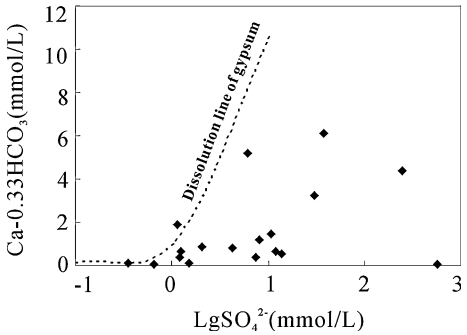


Fig. 5 Sulfate versus (Ca-0.33 HCO_3^-) plot showing the impact of gypsum dissolution on the hydrochemistry of the groundwater samples from Yuncheng. Samples with additional sources of sulfate are located away from the dissolution line, especially when the sulfate content is higher than 10 mmol/L

Along the groundwater flow path, two cross-sections (Fig. 2, Table 2; cross-section A–A′: YH50, YH51, YH60; and cross-section B–B′: YH02, YH52, YH61) were selected to study the effect of activity coefficient on fluoride concentration. The premise is that YH51, YH60 or YH52, YH61 can be obtained by the mixing of fresh water YH50 or YH02 and the salt water. Along the cross-section A–A′, the fluoride concentration of YH50 is taken as C_0 to calculate Δ [F^-]-values of YH51 and YH60. Along the cross-section B–B′, fluoride concentration of YH02 is taken as C_0 to calculate Δ [F^-]-values of YH52 and YH61. The computed results indicate that the concentration change of fluoride in the groundwater ranges between 0.020 and 0.334 mg/L due to activity coefficient decline (Table 3). This means the F^- activity coefficient decline does have effect on fluoride concentration change. But it is not the predominant factor.

Due to difference in solubility between sodium fluoride and calcium fluoride, the fluoride content increases with the increase of Na/Ca ratio in groundwater (Krainov and Zakutin 1994; Krainov and Petrova 1976). The same pattern has been found in the study area (Fig. 7).

In modeling the effect of Na^+ concentration increase on fluoride enrichment, the content of calcium was kept

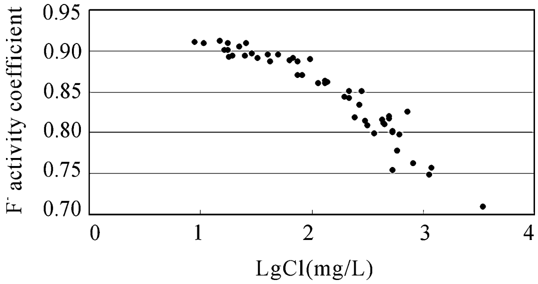


Fig. 6 Fluoride activity coefficient versus Cl plots of groundwater samples from Yuncheng

Table 2 Two cross-sections selected for the study of salt water and fresh water mixing at Yuncheng

Cross-section	Sample	pH	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	SO_4^{2-}	HCO_3^-	F^-
A–A′	YH50	7.9	24	0.0	63.2	392	278.3	297.8	543.1	2.70
	YH51	7.7	40.1	1.4	131.3	714	439.6	835.7	805.5	3.10
	YH60	7.7	88.2	2.8	183.6	1,680	537.1	3,230	689.5	6.40
B–B′	YH02	8.0	28.14	1.01	93.14	406.9	194.6	506.9	507.5	1.75
	YH52	7.5	50.1	1.7	124	384	267.6	677.2	448.5	3.10
	YH61	7.7	91.2	6.4	321	1,440	1,200	2,267	790.2	4.40
Salt lake groundwater		8.0	280	31.2	621	7,020	8,050	5,424	183.0	10.33

Table 3 Change in F^- activity coefficient and corresponding fluoride concentration change along cross-section A–A′ and B–B′

Cross-section and sample number	Cross-section A–A′			Cross-section B–B′		
	YH50	YH51	YH60	YH02	YH52	YH61
$[F^-]$ (mg/L)	2.70	3.10	6.40	1.75	3.10	4.40
F^- activity coefficient	0.851	0.812	0.754	0.843	0.834	0.758
$[F^-]$ (mg/L)		0.131	0.334		0.020	0.198

constant, the balance solution was made up of pure water and fluorite, and 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, and 0.2 mol Na (by adding Na_2SO_4/NaCl) was added in turn, and the concentration of different species of fluorine was calculated using PHREEQC.

From Figs. 8 to 9, it can be seen that with the increase in Na concentration, the increase of NaF concentration was rapid at first and then became slower; and the concentration of HF, HF_2^-, and CaF^+ was continuously reducing. In other words, fluorine complexes in the solution gradually were transformed into more soluble NaF. The reduction of CaF^+ content also helps to reduce the saturation index (SI)-values of CaF_2. As shown in Fig. 10, keeping the total fluorine content invariable, the SI-value of fluorite drops rapidly to be more negative; i.e., the solution becomes more undersaturated with respect to fluorite. In addition, the different Na source (NaCl or Na_2SO_4) also has effects on the concentration of different fluorine species in the solution. For the solution that takes NaCl as the source of sodium, its NaF content is obviously lower than the one that has Na_2SO_4 as the sodium source. The same trend applied to the decrease in the contents of HF, HF_2^-, and CaF^+. It can be explained that in the latter solution, SO_4^{2-} and Ca^{2+} interact and produce $CaSO_4$ and $CaHSO_4^-$. This helps to reduce the concentration of Ca^{2+} and to lower down SI-value of CaF_2.

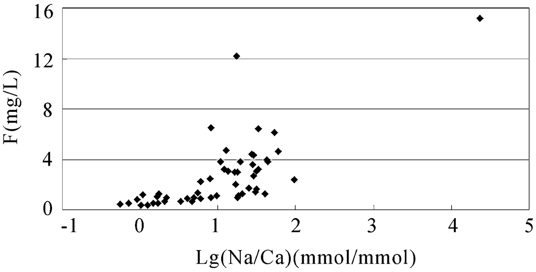


Fig. 7 Fluoride concentration versus Na/Ca ratio plot of groundwater samples from Yuncheng

Based on the discussion of ideal solution, the real samples YH50 and YH02 were used as the initial solution to discuss the effect of increased sodium content on the distribution of different fluorine species, with the total quantity of calcium kept invariable. The result was illustrated in Figs. 11,12,13,14,15.

From Figs. 8,9,10,11,12,13,14,15, it can be concluded that in the solution with increased Na/Ca ratio (due to sodium content increase and calcium content kept invariable), the chemical conditions are advantageous to the complexation of F^- with Na^+, regardless of the water type (Cl–Na or SO_4–Na type water). And the decrease of the concentration of MgF^+ and CaF^+ favors the occurrence of undersaturated state of the solution. This can be explained using the following equation:

$$Mg^{2+} + F^- = MgF^+ \ (\text{Lg k} = 1.820), \tag{4}$$

$$Ca^{2+} + F^- = CaF^+ \ (\text{Lg k} = 0.940), \tag{5}$$

$$Na^+ + F^- = NaF \ (\text{Lg k} = -0.240), \tag{6}$$

where k is balance constant.

As compared with Ca^{2+} and Mg^{2+}, the complexation of Na^+ with F^- needs lower energy, and therefore occurs

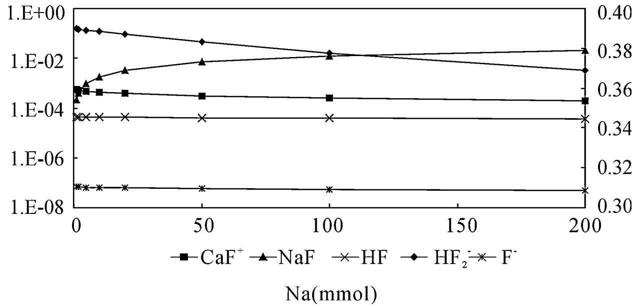


Fig. 8 The concentration change of different fluorine species when different amount NaCl is added into the initial solution (the balance solution of pure water and fluorite). The *right vertical axis* is F^- concentration in mmol/L

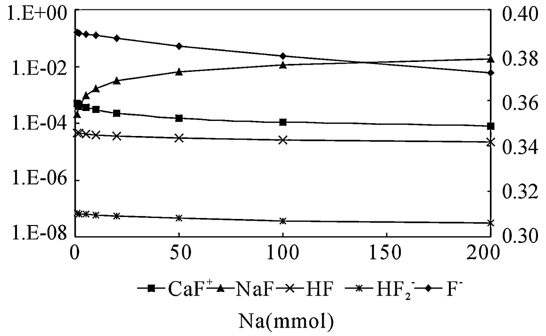


Fig. 9 The concentration change of different fluorine species with different amount Na_2SO_4 added into the initial solution (the balance solution of pure water and fluorite). The *right vertical axis* is F^- concentration in mmol/L

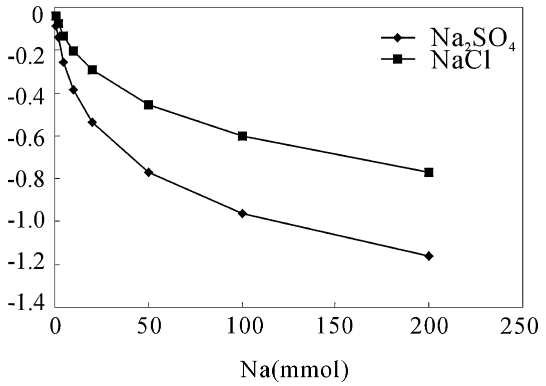


Fig. 10 The change of SI of fluorite with different amount of NaCl/Na_2SO_4 added into the initial solution

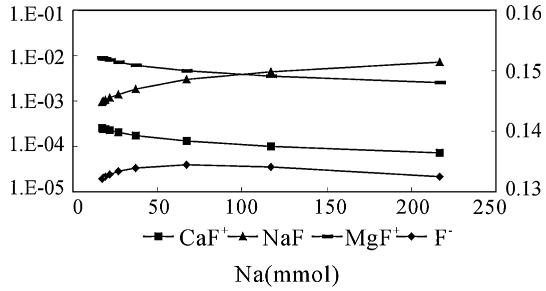


Fig. 11 The concentration change of different fluorine species in the solution when different amount of Na_2SO_4 was added into sample YH50. The *right vertical axis* is F^- concentration in mmol/L

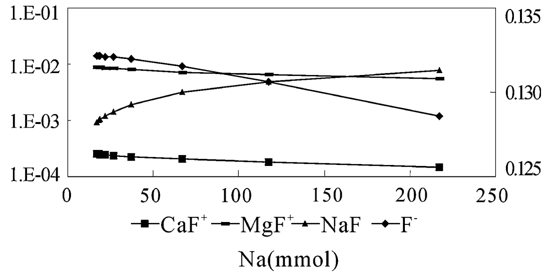


Fig. 12 The distribution of different fluorine species in the solution when different amount NaCl adding into sample YH50. The *right vertical axis* is F^- concentration in mmol/L

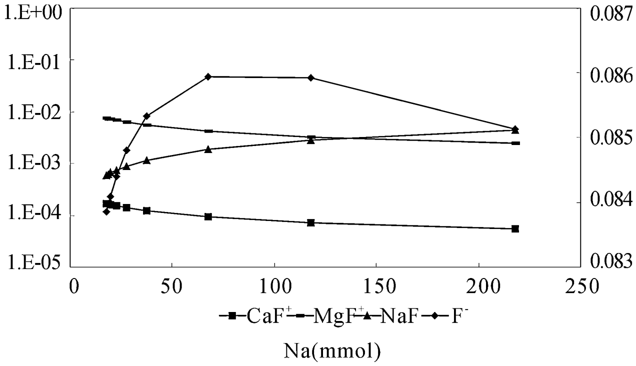


Fig. 13 The distribution of different fluorine species in the solution when different amount Na_2SO_4 adding into sample YH02. The *right vertical axis* is F^- concentration in mmol/L

preferentially. When sodium is added into the solution, NaF will be formed preferentially. Since the solubility of NaF is very high (42 g/L), this is favorable to the release of more fluorine into the solution. It is interesting to note that there are differences in the change of F^- when sodium from different sources (NaCl or $NaSO_4$) was added: when NaCl was the source for added sodium, the F^- concentration gradually declined; and when Na_2SO_4 as the source, the F^- concentration first increased and then declined for sodium concentration over 50–70 mmol/L (Fig. 13). But the SI-value of CaF_2 keeps decreasing, regardless of the type of sodium source.

Determination of possible intrusion frontier of salt water

As a kind of analysis method, inverse hydrogeochemical simulation can be used to delineate the chemical reaction

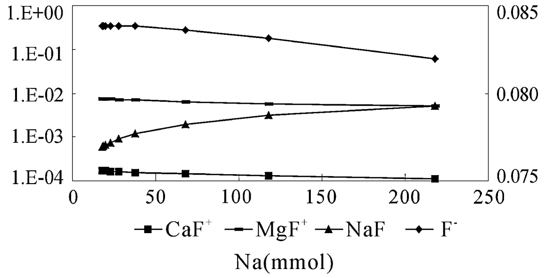


Fig. 14 The concentration change of different fluorine species in the solution with different amount of NaCl added into sample YH02. The *right vertical axis* is F^- concentration in mmol/L

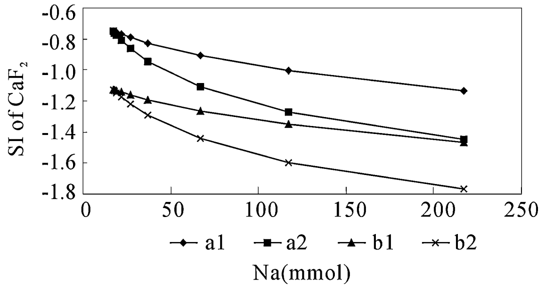


Fig. 15 The change of SI of fluorite with different amount of NaCl/Na_2SO_4 added into the sample YH50 and YH02. *a*1 and *a*2 are, respectively, the mixing solution of sample YH50 with NaCl and Na_2SO_4; *b*1 and *b*2 are, respectively, the mixing solution of sample YH02 with NaCl and Na_2SO_4

that occurs during the evolution process of groundwater. Many studies indicated that, during the course of salt water and fresh water mixing, besides the machinery mixing, the dissolution and precipitation reaction and the cation exchange adsorption might also happen. From this the mixing model was built as follows:

$$\begin{aligned} & \mathrm{a\,CaCO_3} \downarrow/\uparrow, \\ & \mathrm{b\,CaMgCO_3} \downarrow/\uparrow, \\ & x\%\mathrm{Fresh\ Water} + y\%\mathrm{Salt\ Water} + \rightarrow \mathrm{c\,CaSO_4 \cdot H_2O} \uparrow, \\ & \mathrm{d\,CaF_2} \downarrow/\uparrow, \\ & \mathrm{2Na^- + Mg_rCa(1-r)X} \Leftrightarrow \mathrm{dMg^{2+} + (1-r)Ca^{2+} + 2NaX}, \\ & \Rightarrow \text{Mixing water}, \end{aligned} \tag{7}$$

where *x*, *y* are the mixing percentage of fresh water and salt water, respectively; a, b, c, d are the amounts of minerals participating in reaction; and r is the relative stoichiometry.

Cross-sections A–A′ and B–B′ are still used for the mixing model calculations. The premise of mixing simulation is that the chemistry of samples YH51 and YH60 and that of YH52, and YH61 is formed as the result of mixing of fresh water YH50 and YH02, respectively, with the salt lake groundwater.

The simulation result indicates (Table 4) that the major hydrogeochemical reaction is the precipitation of calcite and the dissolution of dolomite, gypsum, and fluoride during the mixing. Cation exchange also plays an important role when the mixing proportion of salt water is high. Mixing promoted the dissolution of minerals in the aquifer. The increase of fluorine content in the groundwater, first, originates from the fluorine in the salt water, second, attributes to the dissolution of fluoride-bearing minerals. In this process, the total Ca content gradually increases because of the cation exchange and the dissolution of gypsum, though the precipitation of calcite consumes a large amount of Ca^{2+} simultaneously. And the Na/Ca ratio rises instead of falling because of the input of massive sodium for mixing. As discussed above, the increase of Na/Ca ratio may induce a more undersaturated state with respect to CaF_2, and consequently an increase in fluoride content of the water.

Using the mixing model, the contribution of fluorine from salt water was calculated to change from 0.064 to 1.013 mg/L (Table 4). Similarly, the possible proportion of salt water in shallow groundwater was calculated (Table 5) to be between 0.5 and 11.8%. To delineate the intrusion boundary, a proportion of 1.0% was used as the limit value. In other words, the proportion is higher than 1.0%, the water sample is classified as intrusion-impacted and in this way the frontier of saline water intrusion delineated, as shown in Fig. 1.

Conclusions

The following conclusions can be drawn from the present study.

1. The salt lake water intrusion into neighboring shallow aquifers can result in elevation of fluoride content of the groundwater. There are two major reasons for the observed elevation of fluoride content: one is the direct contribution of the saline water; the other is the undersaturation of the groundwater with respect to fluorite due to salt water intrusion, which appears to be more important.
2. With the intrusion of saline water, the reduction of fluorine activity favors further dissolution of fluorine-bearing mineral, contributing 0.02–0.33 mg/L to the elevation of fluoride content.
3. Modeling of Na/Ca ratio change in groundwater using PHREEQC show that with the increase in Na concentration (by adding NaCl or Na_2SO_4 as Na source, calcium content kept invariable), the rate of NaF concentration was rapid at first and then became slower; and that the concentrations of HF, HF_2^-, CaF^+, and MgF^+ were continuously decreasing. The reduc-

Table 4 Mixing of fresh water and salt water and the phase mole transfers during mixing

Water sample number	Fractions of shallow groundwater (%)	Fractions of salt water (%)	Fluorine contributing from salt water (mg/L)	Mixed solution	Phase mole transfer (plus means dissolution, negative means precipitate) mmol	
					CO_2(g)	Gypsum
YH50	98.02	1.97	0.097	YH51	2.48	4.47
	96.80	3.10	0.237	YH60	1.46	28.82
YH02	99.25	0.75	0.064	YH52	–0.23	1.11
	88.16	11.81	1.013	YH61	2.78	11.84

Water sample number	Mixed solution	Phase mole transfers (plus means dissolution, negative means precipitate) (mmol)					
		Calcite	Dolomite	Fluorite	KX	NaX	CaX_2
YH50	YH51	–2.47	2.34	0.00	0.02	8.11	–4.06
	YH60	–7.16	4.23	0.09	0.05	49.11	–24.58
YH02	YH52	–3.18	1.29	0.03	–0.03	–2.45	1.24
	YH61	–11.32	6.91	0.04	0.04	13.28	–6.66

Data about salt lake groundwater are from Wang et al. (2000); the content of fluorine was calculated using PHREEQC when SI of fluorite equals zero

Table 5 Calculated intrusion proportion of salt water for the samples around the salt lake

Sample number	Fractions of salt water (%)	Sample number	Fractions of salt water (%)	Sample number	Fractions of salt water (%)
YH61	11.8	YH60	3.1	YH8	4.6–7.4
YH58	2.1–3.2	YH59	0.5	YH64	4.6
YH57	0.7–2.1				

tion of CaF^+ and MgF^+ contents helps to reduce the SI-values of CaF_2 to be more negative.

4. With increased Na/Ca ratio due to saline water intrusion, the geochemical conditions of groundwater are advantageous to the complexation of F^- with Na^+, regardless of the water type (Cl–Na or SO_4^-–Na type water). And the decrease of the concentration of MgF^+ and CaF^+ favors the occurrence of undersaturation state of fluorite in the solution.

Acknowledgments The research work was financially supported by National Natural Science Foundation of China (Grant No.40425001) and China Geological Survey (No. CGS-200310400009). The manuscript greatly benefited from the constructive comments from prof. Teng Ma.

References

Banks D, Reimann C, Royset O, Skarphagen H, Saether OM (1995) Natural concentrations of major and trace elements in some Norwegian bedrock groundwaters. Appl Geochem 10(1):1–16

Botha FS, Van Rooy JL (2001) Affordable water resource development in the northern province, South Africa. J Afr Earth Sci 33(3):687–692

Cao X, Zhao W, Wei J (1997) The formation and distribution of fluoride enriched groundwater in Yuncheng Basin, Shanxi Province, China (in Chinese). Shaxi Hydrotech 116(2):30–33

Carrillo-Rivera JJ, Cardona A, Edmunds WM (2002) Use of abstraction regime and knowledge of hydrogeological conditions to control high fluoride concentration in abstracted groundwater: San Luis Potos basin, Mexico. J Hydrol 261:24–47

Cauley J, Murphy P (1995) Effects of fluoridated drinking water on bone mass and fractures: the study of osteoporotic fractures. J Bone Miner Res 10(7):1076–1086

Choubisa SL (2001) Endemic fluorosis in southern Rajasthan, India. Fluoride 34(1):61–70

Choubisa SL, Sompura K, Choubisa DK, Pandya H, Bhatt SK, Sharma OP, Parmar L (1995) Fluoride content in domestic water resources of Dungarpur districts of Rajasthan. Indian J Environ Health 37:154–160

Frencken JE (1992) Endemic fluorosis in developing countries, causes, effects and possible solutions. NIPG-TNO, Leiden, The Netherlands

Frengstad B, Banks D, Siewers U (2001) The chemistry of Norwegian groundwaters: IV. The dependence of element concentrations in crystalline bedrock groundwaters. Sci Total Environ 277:101–117

Gizaw B (1996) The origin of high bicarbonate and fluoride concentration in waters of the Main Ethiopian Rift Valley, East African Rift system. J Afr Earth Sci 22:391–402

Jacobsen SJ, O'Fallon M, Melton LJ (1993) Hip fracture incidence before and after the fluoridation of the public water supply, Rochester, Minnesota. Am J Public Health 83:743–745

Krainov SR, Petrova NG (1976) Fluorine-bearing groundwater, their geochemical characteristics, and the effect on biological processes. Geokhimiya 10:1533–1541

Krainov SR, Zakutin VP (1994) Geochemical and environmental state of groundwater in Russia (the causes and tendencies in the changes of groundwater chemistry). Geokhimiya 3:312–329

Lu X, Zhang S, Zhang J (2004) Surveillance on fluoride during 10 years drinking-water improvement in Yuncheng city. China J End 23(1):53–54

Parkurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US Geological Survey Water-Resources Investigations Report 99–4259 (a report)

Shanker R, Thussu JL, Prasad JM (2003) Geothermal studies at Tattapani hot spring area, Sarguja district, central India. Geothermics 16:61–76

Tu VL, Watkins R, Nguyen GK (2006) Distribution and genesis of high-fluoride groundwaters in Ninh Hoa District, Vietnam. Paper presented at the scientific programs of the 7th international symposium on environmental geochemistry, Beijing, 24–27

Wang Z, Xin X, Chang Y (2000) Formation causes and controlling measures of groundwater quality deterioration in Xiezhou area, Yuncheng City. Earth Sci 25(5):477–480 (in Chinese with English Abstract)

Yiamouyiannis JA, Burk D (1976) Fluoridation of public water systems and cancer death rates in humans. Fed Proc 35:1707

Yun G (2001) Preventive measures against worsening of groundwater quality in Haizhou township (in Chinese). Shanxi Hydraul Eng 2:12–13

Zhang Y (1993) Causes for the rising again of fluoring contents in water in Yuncheng prefecture and determination of effective value of fluorine in water in No.1 endemic area (in Chinese). Hydrogeol Eng Geol 6:53–55