Impacts of seawater intrusion on the fluorine content in groundwater: a case study in Shandong province, China

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Abstract—**Endemic fluorosis can be caused by the drinking water with high-fluorine content. The groundwater with high-fluorine was observed in coastal regions of Shandong province, China. In this study, two sets of ten-year monitoring data from the coastal wells were analyzed. The groundwater properties are characterized by a mixture of seawater and freshwater, resulting in increasing of Na^+, HCO_3^-, pH, hardness, salinity and decreasing of Ca^{2+}. It is found that fluorine contents in groundwater are closely associated with high Na^+, HCO_3^-, pH, hardness, salinity and low Ca^{2+}. Seawater intrusion, especially the paleo-seawater intrusion, can greatly change the groundwater fluorine-releasing conditions under the rock-water interaction and cause the high fluorine in the groundwater. Thus, the geological process, seawater intrusion should be noticed when we study the fluorosis in coastal areas.**

Keywords- Groundwater; Coastal zone; Fluorine; Water quality; Seawater intrusion; Human health; Geochemistry

I. INTRODUCTION

Fluorine, as one of indispensable trace elements, plays an important role on balancing the body functions. The deficiency or surplus of fluorine in human body can cause some healthy problems or diseases, such as, macular teeth, fluorosis of bone, dental caries, osteoporosis etc [1-3]. There are different fluorine sources, such as industrial aerosols [4], coal-burning [3], brick tea [5], fluorine-bearing ore rock [6], water [7-8]. But fluoride exposure from drinking water was focused by most studies because it is the easiest pathway to quantify for a community served by a public water supply.

In the northern coastal region of Shandong province, China, more than 6,000 thousand people were involved into the fluorosis symptom over the last decades [9]. The previous studies showed that the groundwater in fluorosis regions of Shandong was characterized by the high fluorine level with a range of 1.0 -20.0 mg/L [10], which greatly exceed the safety standard（≦1.0mg/L).

One of the most distinctive geologic features in the fluorosis regions of Shandong province is the existence of seawater intrusion, including modern seawater intrusion and paleo-seawater intrusion [11]. Seawater intrusion can change groundwater properties, such as, Na^+, HCO_3^- concentrations, hardness, total dissolved solid, conductivity and alkali pH etc [12-13]. However, a series of studies on fluorine sources and forming factors in various aquifers indicated that there is a close relationship between high fluoride and soft, alkaline groundwater that is depleted in Ca^{2+} and enriched in Na^+ [8,14-17]. Therefore, it is logical that variation evoked by seawater intrusion is favor of groundwater fluorine enrichment. Also, a similar process to seawater intrusion, salt lake water intrusion, had been found and confirmed by experiments to elevate of groundwater fluoride content due to the undersaturation with respect to fluorite [18].In fact, [19] also found high proportion of fluorosis in the coastal region of Liaoning province, China. These indications make us consider the impact of seawater intrusion on fluorosis and we can not refrain from considering carefully seawater intrusion when discussing the groundwater high fluorine in coastal regions. Previous scholars occasionally pointed that seawater intrusion may be a predisposing factor of fluorosis in Shandong coastal regions when considering the possible adverse effect [9,20]. However, there is no distinct convincible proof and explanation which can confirm the hypothesis. Thus, it is important to understand how the seawater intrusion can increase the fluorine level in the groundwater by geochemical processes in coastal regions.

In this paper, two wells characterized by fluorosis and seawater intrusion in Gaomi district of Shandong province were carefully selected, and the ten-year monitoring data were gained to explore the relationship between seawater intrusion and fluorine enrichment. It is a primary study to explain the effect of seawater intrusion on fluorine enrichment and evoke people's attention in coastal areas. The aims are to: 1) observe the dynamic variation of fluorine contents and discuss their relationship with geochemical properties; 2) discuss the mechanism of groundwater fluorine enrichment and its potential relationship with seawater intrusion.

II. METHODS AND MATERIALS

A.. Study area

Two wells are respectively situated in Jiangzhuang town (No.717) and Damujia town (No.718), Gaomi district, Shandong province, China (Fig.1).

Gaomi district is one of severe fluorosis areas in Shandong province. There are 253216 people with the characters of macular teeth and 15302 people with fluorosis of

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bone, respectively accounting for 46.64% and 2.46% of the total local population. Jiangzhuang Town and Damujia Town, located in the north of Gaomi district, are the most serious [21].

Also, as a result of short distance away Bohai Sea and Yellow Sea, Gaomi district has a worse seawater intrusion, mainly the paleo-seawater intrusion. Brine water, salt water, and their mixture with fresh water are widely distributed. Comparing with modern seawater intrusion, paleo-seawater intrusion is obviously characterized by higher contents of Na^+, Mg^{2+}, K^+, Cl^-, SO_4^{2-} and HCO_3^- [12,22].

B.. Data source

The two wells were monitored as observation stations for water quality, and the groundwater was gathered and analyzed every year. Ten-year data from 1990 to 2000 (exclusive of 1993) were documented in public by [23]. Several properties were determined, including F^-, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, pH, hardness and salinity. The results were listed in Table Ⅰ. Generally, the samples can be classified into two groups according to observation time: summer (May and June) and autumn (Sep and Oct).

Figure 1. The sketch map of Gaomi district and wells

TABLE I. GROUND WATER FLUORINE CONTENTS AND OTHER PROPERTIES OF TWO OBSERVATION STATIONS IN GAOMI DISTRICT

stations	Sampling time	F^-	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	Total Hardness	pH	Salinity
Jiangzhuang Town (N0.717)	Sep-90	2.8	367.28	42.08	26.61	168.76	643.76	76.5	7.3	1330.92
	May-91	3.2	249.6	73.95	66.11	241.43	552.84	9.13	8.19	1382.51
	Oct-92	4.25	540.27	51.1	43.88	180.81	782.24	6.16	7.5	1781.19
	Oct-94	2	162	123.28	48.31	255.59	314.99	506.91	7.3	1170.12
	May-95	3	50.8	174.71	64.98	324.62	185.3	704.06	7.6	1043.24
	Oct-96	2.3	933.6	187.52	54.65	111.82	420.03	693.35	7.2	1734.25
	Jun-97	4	392	47.89	15.56	116.76	744.83	183.65	8.41	1508.95
	Sep-98	2.4	245.6	171.24	54.81	307.77	463.48	653.36	6.5	1666.11
	Jun-99	2.6	146.88	56.41	43.87	122.72	452.54	320.36	6.7	947.62
	Oct-00	2.2	285.67	72.07	48.11	162.6	586.28	379.12	7	1433.55
Damujia Town (No.718)	Sep-90	5	1055	123.25	225.78	1366.68	1026.97	24.73	7.18	4531.99
	May-91	3.6	990	344.89	244.63	1742.16	1555.55	37.34	7.95	5654.69
	Oct-92	3.5	1080.77	230.86	287.98	1483.77	910.98	35.21	7.12	4904.23
	Oct-94	1.5	448	243.72	221.12	1217.24	561.44	1497.2	7.5	2966.36
	May-95	3.2	436	155.78	281.38	1240.23	476.61	1547.24	7.4	3029.92
	Oct-96	3	970	114.28	256.97	1092.75	993.31	1343.6	7.2	4817.71
	Jun-97	1.6	788	446.99	0.62	918.26	734.77	1118.39	7.85	4136.34
	Sep-98	3.4	860	165.62	218.72	1094.95	895.67	1315.13	6.8	4574.59
	Jun-99	4	990.3	136.93	288	1180.61	1092.8	1527.72	6.5	4984.34
	Oct-00	2.2	811.53	95.95	174.95	735.44	864.65	956.33	7.1	3906.22

Note: Concentration in mg/l except pH, and the data from [23].

C.. Data analysis method

The software Excell and Spss.10 are used to analyze the relationship between fluorine and other geochemical properties.

III. RESULTS

A. Fluorine content characteristics for 10 years

Fig.2 shows the fluorine contents in the two monitoring wells from 1990 to 2000. The fluorine content of Jiangzhuang Town station almost keeps stable and the average fluorine content reaches 2.88mg/L, with a maximum of 4.25mg/L in Oct, 1992 and a mix of 2.2mg/L in Oct, 2000. Damujia Town station has fluorine contents varying from 1.5mg/L in Oct, 1994 to 5.0mg/L in Sep, 1990, with an average of 3.1mg/L. The observed fluorine contents in the two wells are both much higher than 1.0mg/L, the national drinking water standard (GB-5749-85). It is not strange the reported fluorine contents in Gaomi district go beyond 1.0mg/L. [24]found groundwater in Gaomi district generally has fluorine content of 5.0mg/L and even of 18.0mg/L.

No distinction can be obviously seen (Table Ⅰ) between the fluorine contents in summer and autumn, or between two stations. This means fluorine contents have little seasonal influence such as temperature, rainfall, evaporation.

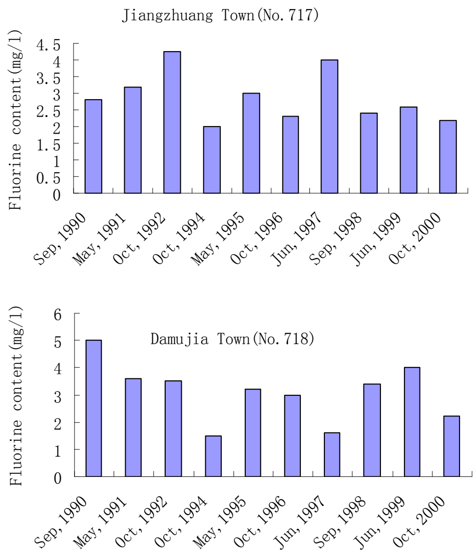


Figure 2. Fluorine contents of two stations from 1990 to 2000

B. Hydro-geochemical characteristics

The water samples were plotted onto the Piper diagram (Fig.3). It can be seen that the groundwater in Damujia station is Na-Cl type, with Na^+ as the predominant cation and Cl^- as the predominant anion. This means that Damujia station water has the typical characteristics of serious seawater intrusion. For the samples in Jiangzhuang station, the dominant anion is HCO_3^- and the main hydro-chemical types are Na-HCO_3. Generally, the water types are different from the local natural freshwater (HCO_3.Cl-Ca.Mg or HCO_3.Cl-Ca).

The Cl^- concentrations in Damujia station have high levels, ranging from 700mg/L to 1500mg/L. Such levels sharply exceed the local normal freshwater content of 60-80mg/L [25], and the groundwater suffers from severe intrusion and has a quick Cl^- increasing. Those in Jiangzhuang station have relatively low Cl^- contents of 110-320mg/L, and part of them has exceeded the safe standard (200mg/L). Such phenomena show the water in Jiangzhuang has a mild intrusion, and this maybe indicates the intrusion is just at the initial stage and has a slow increasing because of adsorption effect [26]. Such abnormal Cl^- contents in the two wells are clearly an indication of the effect of seawater intrusion.

Under the impact of intrusion, Na^+, HCO_3^-, salinity and hardness have high contents (Table Ⅰ). These results are accordant with the numerous investigations in seawater intrusion areas and show evidence of intrusion [12,22]. Ca^{2+} concentrations in Jiangzhuang station are about 40-200mg/L, and those in Damujia station are much higher due to possibly cation exchange between Ca^{2+} or Mg^{2+} sorbed by the mineral phase in the aquifer matrix and more Na^+ in the groundwater added by seawater intrusion [12,18,22].

Moreover, the groundwater types and Cl^- contents in the two wells show that intrusion in Damujia station is much more serious than that in Jiangzhuang station. Furthermore, groundwater in Damujia station has a higher Mg/Ca value and a lower SO_4/Cl than those in Jiangzhuang station, which also can illustrate that Jiangzhuang station is just at the initial stage while Damujia station is at maturity stage. Clearly, Na^+, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, hardness and salinity of groundwater in Damujia station are much higher than those in Jiangzhuang station. These data illustrate that seawater intrusion increase contents of Na^+, Mg^{2+}, Cl^-, HCO_3^-, hardness and salinity.

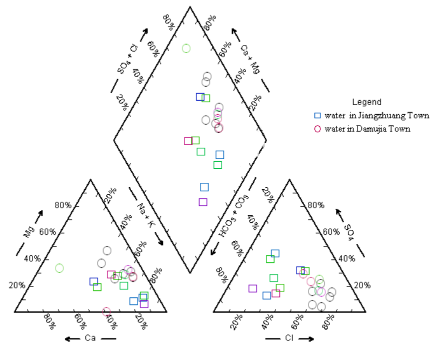


Figure 3. Piper diagram of the two wells

C. Relationship between fluorine contents and geochemistry

Fluorine contents and their relationship with other geochemical properties are shown in Fig.4 and Fig.5.

Na ions elevate fluorine contents due to two reasons: higher solubility of NaF than CaF_2, and the priority to combine with Na to Ca or Mg ions [18]. Na ions in Damujia town station show a positive correlation with fluorine contents (Fig.4). But in Jiangzhuang town station, the sample in 1995, with fluorine content of 3.0mg/L and the lowest Na^+ concentration of 50.8mg/L, deviates from the linear trend as an exception. Similarly, the Na-F relationships in Jiangzhuang also show a positive correlation if the sample in 1995 is excluded. Generally, the tendency of Na-F positive relationships in the two wells indicates such a fact that Na ions are responsible for the fluorine variation.

Ca ions generally have a decreasing tendency with the increasing of fluorine contents in both stations, and Mg ions show no direct correlation with fluorine contents. The limitation of fluorine content in water is usually restricted by CaF_2 solubility [26-27], and a negative correlation between Ca^{2+} and F^- appears when solution is saturated [28].The observed results also show the fluorine contents of the two stations are both affected by Ca ions, although the correlation isn't significant possibly due to ion exchange.

HCO_3^- is positively correlated with fluorine contents in the two stations, and the tendency that fluorine contents increase with HCO_3^- concentrations is clear. HCO_3^- is carefully considered by a series of studies when fluorine enrichment mechanism is discussed. Especially, the following reactions occur under the condition of adequate Na^+ and HCO_3^- ions [27,29-30]:

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2$$

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$

Obviously, this reaction can release more CaF_2 in rocks and dissolve more solid-phase CaF_2 in water. The observed results of the two stations imply that HCO_3^- concentration deeply affects the rock-water interaction and changes the releasing of fluorine-bearing minerals of wall rocks.

pH plays an important role in maintaining groundwater fluorine contents. Seawater intrusion causes alkalic water and certainly is helpful for fluorine enrichment in groundwater. The pH of Jiangzhuang town station shows a positive correlation with fluorine contents. The higher the pH is, the higher the groundwater fluorine contents are. But there is no such a positive correlation in Damujia station, and we still can't judge the accurate reasons only from the observed value. Specially, pH in 1998 and 1999 are distinctly low. Possibly, other properties have greater contribution to fluorine contents than pH, and individual factor of pH can't significantly explain fluorine contents.

Multitude studies have researched that high conductivity, TDS, salinity and hardness are favorable to enrich fluorine [17-18,31-33]. The total hardness of the two stations sharply varied during the ten years. It has low values ranging from several to dozens mg/L from 1990 to 1993, but it increases to about 30-100 times in the next years. The driving force is still ill-defined. But the salinity in Damujia station shows positive correlation with fluorine contents, and such relationship between salinity and fluorine also occurs in Jiangzhuang whether in summer or autumn (Fig. 6). Obviously, the higher salinity in the two stations is, the higher fluorine contents are.

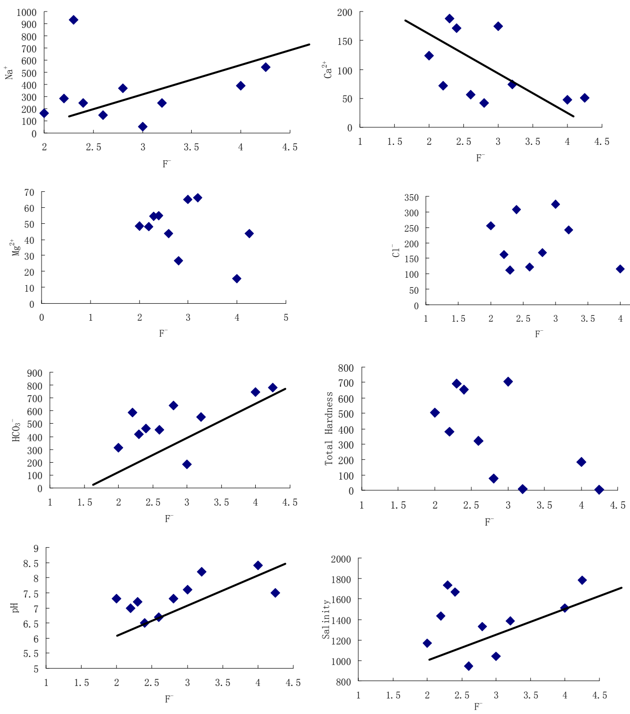
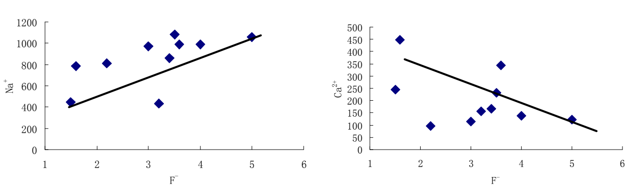


Figure 4. Scatter diagrams of fluorine and other geochemistry in Jiangzhuang Town



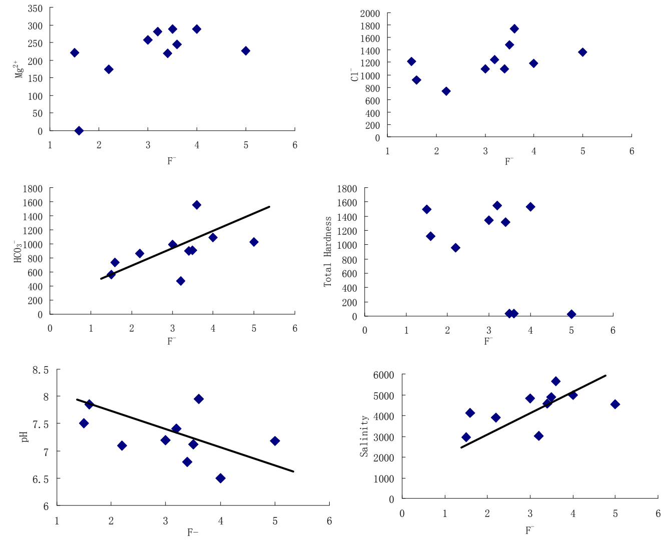


Figure 5. Scatter diagrams of fluorine and other geochemistry in Damujia Town

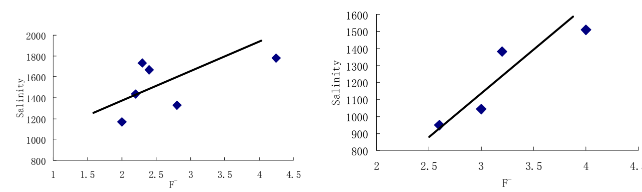


Figure 6. Scatter diagrams of fluorine and salinity of Jiangzhuang Town in different seasons

IV. DISCUSSION

A. *Fluorin enrichment factors due to seawater intrusion*

As far as the fluorosis in Shandong province, a series of reports mainly focused on epidemiological investigation, geological distribution, water improvement measures and fluorine-fixing methods [34-35]. There are still no unambiguous explanations about high fluorine groundwater, and not to say the fluorine sources and its enrichment dynamics. [23] stated that clastic rocks and volcanic rocks of Cretaceous Qingshan Formation, and clastic rocks of Wangshi Formation are higher in fluorine level and dissolution coefficients, and considered these rocks as fluorine sources. But the data showed that the fluorine contents of these rocks is 180-740ppm， which are equal to or even lower than the average fluorine contents of rocks. Moreover, fluorosis distribution isn't matched with these rocks.

In fact, not only in Gaomi district, but also other palaces in Shandong province, superstandard fluorine groundwater was found, such as typical Guangrao, Pingdu, Changyi, Shouguang, Jining, Heze, Dezhou, Laizhou and so on [34-36]. Such a distribution is approximately in accord with seawater intrusion, especially with the paleo-seawater intrusion, and bitter salt groundwater always occurs in endemic areas.

Seawater has a fluorine level of about 1-1.3mg/L, which is slightly higher than the fresh water. It is reported that about 40% sea water mixed into fresh water in serious intrusion areas. Therefore, the groundwater fluorine contents shouldn't reach such a high level if they just simply mix, and the fluorine-releasing conditions and dynamics [15] during rock-water interaction should be noticed.

Obviously, Na ions increase sharply and Ca ions decrease when seawater intrudes. A series of field work and experiments have confirmed that fluorine increases with the increasing of Na ions and Na/Ca [18]. Furthermore, Ca ions can restrict fluorine dissolution. [37] experimented that fluorine released from rocks increases with $(Na^{+}+K^{+})/Ca^{2+}$. [18]even observed that complexes as NaF increase and those as HF, CaF^{+} decrease when Na ions are added into water. [38]reported in high-fluorine groundwater areas with intrusive magma, the rocks are not only enriched in fluorine-bearing minerals, but also their plagioclase composition is typically high in albite. All these indicate the importance of Na ions in maintaining fluorine balance.

HCO_3^{-} can improve CaF_2 dissolubility and release more fluorine ions from the insoluble minerals, and such phenomena were discovered during the investigation of high fluorine groundwater in India, Mexico etc [29-30]. [39] also found that CO_3^{2-} and HCO_3^{-} can promote CaF_2 dissolubility. [27] statistics that fluorine contents are positively correlated with HCO_3^{-} and 85% high fluorine groundwater has HCO_3^{-}/Ca^{2+} ratio of 0.8-2.3. [40] found that groundwater fluorine contents are positively related with $(HCO_3^{-}+SO_4^{2-})/Ca^{2+}$ in Hetao district, Inner Mongolia.

Groundwater in intrusion areas always appears alkaline, which makes "surplus" fluorine dissolve in groundwater by decreasing Ca ion concentration. Besides, alkaline water intensifies dissolving of fluorine-bearing silicate minerals. Hydroxide ion can substitute fluorine ion and promote extraction of fluorine in rocks [39]. [41] argues that alkalic groundwater is helpful for desorption of the absorbed fluorine. [42] concluded fluorine content increases with pH by analyzing 1604 water samples in Norway. [17] observed that high pH can liberate fluorine ions absorbed by colloid.

Multitude researches show that high fluorine groundwater is characterized by high conductively, TDS, mineralization and hardness. [27] reported fluorine enriches under conditions of 7.6-8.6 pH, 750-1750us/cm conductivity in Krishna district, Andhra Pradesh, India. [31] summarized that high fluorine groundwater has 7.8-8.8 pH and 530-2680us/cm conductivity by determining 58 samples from 8 states in India. [33] reported that groundwater with fluorine contents of more than 1.0mg/L has the same distribution as mineralization of more than 1.0g/L in fluorosis area in Hebei province, China.

Generally, the geochemical characteristics evoked by seawater intrusion seem to be in favor of fluorine enrichment. Our analysis found that groundwater fluorine contents are closely associated with high Na^{+}, HCO_3^{-}, pH, hardness, salinity and low Ca^{2+}. Such a phenomenon is similar to other researches about the conditions of groundwater fluorine enrichment. Simultaneity, the well water is obviously characterized by seawater intrusion, causing high Na^{+}, HCO_3^{-}, pH, hardness, salinity and low Ca^{2+}. Thus, the special dynamic, seawater intrusion, can logically change fluorine-releasing conditions and elevate groundwater fluorine. Of course, other affecting factors, such as different geological setting, hydrological process, should not be ignored easily.

B. Two types of seawater intrusions

There are two types of seawater intrusions in Shandong province: paleo-seawater intrusion and modern seawater intrusion [10]. Modern seawater intrusion mainly occurs in the north of Laizhou Bay, from the Futou Cliff in west to Shihuzhui in east. Paleo-seawater intrusion occurs in Quaternary alluvial plain from Futou Cliff in east to Guangrao County in west, where brine-water distributes widely [9].

Although geochemical proofs have revealed that brine water mainly origins from ancient seawater evaporation due to historical marine transgression and regression [13], the brine water geochemistry is greatly distinguished from modern seawater. Brine water, salt water and the ancient seawater have the approximate content of Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-} etc, but compared with modern seawater, they have 5-5.9 times of Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-} contents and 3-4.6 times of K^{+}, HCO_3^{-} contents [12,22]. Obviously, paleo-seawater intrusion may be more helpful for fluorine to release from rocks and accumulate in groundwater than modern seawater intrusion.

High fluorine groundwater in Shandong always occurs where seawater mixes into freshwater, and the groundwater is a little bitter and salt. In the north of Laizhou Bay where modern seawater intrudes, fluorosis occasionally occurs in several villages. The main fluorosis distributes where paleo-seawater intrudes, almost accounting for more than 80% fluorosis in Shandong province. Two main fluorosis areas in Shandong province are both characterized by paleo-seawater intrusion. This means paleo-seawater intrusion may be more responsible for fluorosis in Shandong province. In fact, the higher contents of Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, K^{+} and HCO_3^{-} are more helpful for fluorine enrichment in groundwater in brine-water intrusion regions. This may explain why fluorosis often occurs where paleo-seawater intrudes, and does occasionally where modern seawater intrudes.

V. Conclusion

Large area groundwater with high-fluorine was observed in Shandong province, China. In order to analyze fluorine variation dynamic and its sources, two sets of ten-year monitoring data from the coastal wells were analyzed. We found that fluorine contents in groundwater are closely associated with high Na^{+}, HCO_3^{-}, pH, hardness, salinity and low Ca^{2+}, which is similar to other researches about the conditions of groundwater fluorine enrichment. Also, it is found that the groundwater properties are characterized by a mixture of seawater and freshwater, due to which, Na^{+}, HCO_3^{-}, pH, hardness, salinity increase and Ca^{2+} decreases. High fluorine groundwater and seawater intrusion have the same distribution in geography. Thus, Seawater intrusion, together with such other factors as geological setting and hydrological process, should also be noticed when the forming factors of fluorosis in coastal regions are discussed.

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