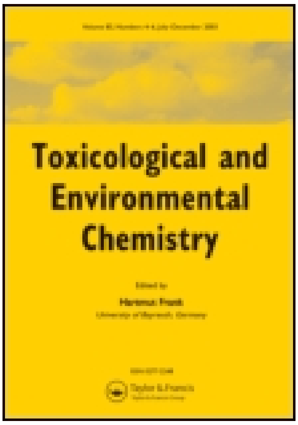


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# Fluorine contents and its characteristics of groundwater in fluorosis area in Laizhou Bay, China

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Fluorine concentration and other parameters in groundwater were assessed and attempts were made to clarify the relationship between fluorine (Fl) and seawater intrusion in coastal area of Laizhou Bay, China by comparing samples in fluorosis and non-fluorosis areas. The water from fluorosis villages reflects the influence of seawater intrusion and higher levels of conductivity (Ec), total dissolved solids (TDS), hardness (TH), $Cl^-$, $Br^-$, $HCO_3^-$, $Li^+$, $Na^+$, $Mg^{2+}$, and $Sr^{2+}$. High Fl concentration was positive correlated with Ec, TDS, $Cl^-$, $Br^-$, $Li^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ and significantly with $Na^+$, $Na^+/Ca^{2+}$, and sodium adsorption ratio. This investigation also observed that seawater intrusion and fluorosis show similar distribution and originating sources. Thus, the special process-seawater intrusion seems to be an important dynamic of Fl enrichment by changing chemical characters and enhancing Fl release ability. Moreover, the water treated by bone coal adsorption still maintains high risk of Ec, $Na^+$, and TDS, even though Fl was within the safe limit. This study indicates that in Laizhou Bay, together with other coastal areas, seawater intrusion is a cause for concern when examining mechanism underlying fluorosis occurrence and developing integrated treatment technology.

**Keywords:** groundwater; fluorine; seawater intrusion; Laizhou Bay

## Introduction

The effects of fluorine (Fl) on humans have been extensively studied (WHO 1984; Slooff et al. 1989). The deficiency or surplus of Fl in humans body may produce adverse health problems or diseases, such as dental and skeletal fluorosis, dental caries, or osteoporosis (Wang and Li 2002; Zheng et al. 2005; Dhiman and Keshari 2006; Chen et al. 2011).

The occurrence and development of endemic fluorosis originates from high Fl content in air, soil, and water, of which water is perhaps the major contributor. Laizhou Bay, in the northern coastal region of Shandong province, China, is characterized by the universal drinking water endemic fluorosis, and more than 640,000 people displayed dental or skeletal fluorosis (Han 1997). Moreover, endemic fluorosis is spreading and new fluorosis areas have appeared in recent years (Yun et al. 2005; Gao, Wang, Zhu et al. 2007).

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The characteristics and confounding factors attributed to high Fl groundwater in this area remain unknown.

The Fl concentration in groundwater is largely governed by the presence of other environmental conditions. 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 (Meng et al. 2002). Seawater intrusion might alter groundwater properties, such as $Na^{+}$, $HCO_3^{-}$ concentrations, hardness (TH), total dissolved solids (TDS), conductivity (Ec), and alkali pH (Zhang et al. 2001; Zhang and Dai 2001; Nin, Yu, and Jiang 2005). However, a series of studies on Fl sources and confounding factors for fluorosis in various aquifers indicated that there is a close relationship between high Fl and soft, alkaline groundwater that is depleted in $Ca^{2+}$ and enriched in $Na^{+}$ (Robertson 1986; Whittemore et al. 1993; Kierdorf and Kierdorf 2000; Woo et al. 2000; Earle and Krogh 2004; Heikens et al. 2005; Nordstrom, Ball, and McCleskey 2005; Chae et al. 2006, 2007; Walna, Kurzyca, and Siepak 2007). Therefore, changes in groundwater properties due to seawater intrusion and its relationship with Fl enrichment need to focus on dynamics of high Fl in this region or other coastal areas. On this basis, groundwater samples in fluorosis areas, non-fluorosis areas, and fluorosis areas with bone-coal adsorption treatment along Laizhou Bay were gathered with the following objectives: (1) compare groundwater properties in fluorosis areas and non-fluorosis areas and clarify factors affecting Fl enrichment, (2) discuss the relationship between Fl enrichment and seawater intrusion, and (3) reveal the effect of bone coal treatment on other geochemical properties other than Fl ions.



## Sampling and analysis methods

### *Sampling*

All samples were obtained from Tushan Town, Laizhou city, located in the northern of Shandong Province. The town locally suffers from seawater intrusion as a result of short distance from Bohai Sea, mainly characterized by the paleo-seawater intrusion. Seawater intrusion is sporadic. Six villages in this town were identified in this area (Figure 1). These villages are located nearby and almost have the same water sand layer, which excludes the effect of sandy rocks on groundwater properties. People in three villages, namely Huibu Town, Jiaojiazhuangzi, and Lvjiaji, suffer from dental fluorosis, especially the elderly. Individuals in two villages of Xiaohuibu and Taipingzhuang have no fluorosis symptoms. The water in another village of Zhuodong is treated by bone coal adsorption. More than five samples in every village were obtained randomly.

### *Analytical methods*

Groundwater was collected in precleaned liter polyethylene containers. Samples were kept at low temperature and sent to lab immediately, and all samples are divided into two groups. One group was used to analyze pH, Ec, TDS, total hardness (TH), $CO_3^{2-}$, and $HCO_3^{-}$ within 48 h. Ec, pH, TDS, hardness, and mineralization was determined with DDS-320 conductivity meter; $CO_3^{2-}$ and $HCO_3^{-}$ were determined by 0.01 mol $L^{-1}$ HCl titration with helianthin B and *phenolphthalein* indicators. The other group was frozen for following ion chromatography of $F^{-}$, $Cl^{-}$, $Br^{-}$, $Na^{+}$, $Li^{+}$,$Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$.

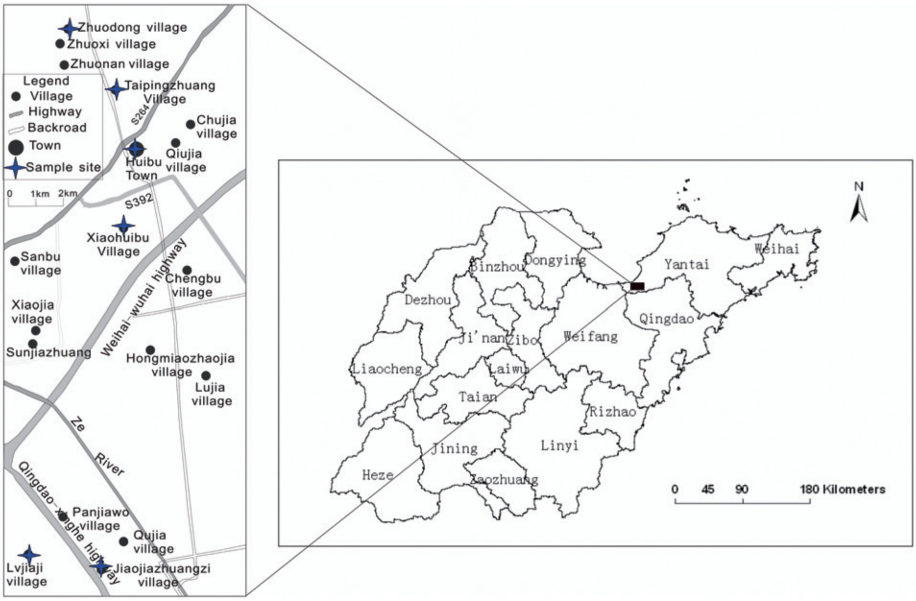


Figure 1. Map of sampling sites.

## Results and discussions

### *Groundwater fluorine contents and fluorosis*

The values of groundwater Fl content and other geochemical characteristics are presented in Table 1. On comparing the results with the limits prescribed by the National Sanitary Standard for drinking water (GB5749-85), it was observed that Fl content in the villages of Huibu Town, Jiaojiazhuangzi, and Lvjiaji exceeded the limits (less than 1 ppm), whereas those in the other three villages fell under the prescribed safe limits.

The fluorosis in the six villages was also investigated. Fluorosis was present in the villages of Jiaojiazhuangzi and Lvjiaji, especially in the elderly people. Fluorosis occurred in Huibu Town but with a mild situation because of the recent water renovation projects. Although the water in Zhuodong village showed safe Fl content after treatment, fluorosis still prevailed due to the historical drinking of polluted groundwater. In fact, although the villages are located within short distances, Fl content showed a wide range. The distribution of fluorosis in this area also appears discontinuous. Generally, the range of Fl concentration is associated with dental and skeletal fluorosis.

### *Groundwater quality parameters between fluorosis and non-fluorosis areas*

The observed properties are given in Table 1. The three villages with super-standard Fl content showed significantly higher levels of the determined properties except pH compared to Taipingzhuang and Xiaohuibu villages on the whole, especially the Jiaojiazhuangzi and Lvjiaji villages. However, Zhuodong village still maintained high content of determined properties although Fl content was within safe limits as a result of bone coal adsorption. In addition, pH showed a reverse variation trend and people in fluorosis villages displayed lower pH than those in Taipingzhuang and Xiaohuibu villages.

Table 1. Statistical groundwater fluorine contents and other geochemical properties.

| | $F^-$ | pH | Ec | TDS | TH | $Cl^-$ | $Br^-$ | $HCO_3^-$ | $Li^+$ | $Na^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zhuodong | 0.48 | 7.387 | 3326 | 1.683 | 1011.38 | 771.35 | 1.99 | 0.003503 | 0.016 | 163.06 | 51.62 | 309.70 | 9.51 |
| | (0.22) | (0.286) | (1722.9) | (0.856) | (83.76) | (533.11) | (1.28) | (0.001152) | (0.0068) | (89.31) | (36.86) | (173.64) | (0.89) |
| Taipingzhuang | 0.63 | 7.608 | 1430 | 0.715 | 540.17 | 218.61 | 0.28 | 0.00347 | 0.0127 | 80.75 | 28.78 | 168.86 | 5.44 |
| | (0.17) | (0.136) | (193.8) | (0.969) | (87.36) | (90.28) | (0.78) | (0.00085) | (0.0040) | (14.58) | (4.84) | (27.15) | (1.95) |
| Xiaohuibu | 0.27 | 7.593 | 1371.6 | 0.691 | 479.45 | 144.87 | 0.39 | 0.003908 | 0.0065 | 40.25 | 31.69 | 134.36 | 3.66 |
| | (0.03) | (0.135) | (260.2) | (0.136) | (–) | (43.26) | (0.13) | (0.00096) | (0.0012) | (3.80) | (6.13) | (21.47) | (–) |
| Huibu Town | 1.19 | 7.506 | 1619.5 | 0.810 | 608.27 | 216.31 | 0.36 | 0.003936 | 0.0089 | 88.88 | 43.27 | 172.25 | 8.15 |
| | (0.50) | (0.0566) | (129.2) | (0.064) | (51.54) | (18.15) | (0.10) | (0.001142) | (0.0008) | (12.83) | (1.94) | (20.19) | (3.97) |
| Jiaojiazhuangzi | 1.25 | 7.266 | 2513.5 | 1.256 | 866.79 | 412.84 | 0.76 | 0.004391 | 0.0254 | 161.71 | 45.20 | 272.59 | 11.83 |
| | (0.39) | (0.090) | (377.5) | (0.187) | (120.18) | (76.21) | (0.18) | (0.002385) | (0.0079) | (29.19) | (9.91) | (37.92) | (5.85) |
| Lvjiaji | 1.21 | 7.288 | 2882 | 1.444 | 957.70 | 510.64 | 0.77 | 0.005194 | 0.0369 | 182.10 | 62.27 | 280.85 | 21.97 |
| | (0.29) | (0.0936) | (374.5) | (0.187) | (109.53) | (61.86) | (0.11) | (0.002592) | (0.0047) | (54.08) | (9.52) | (35.65) | (2.73) |

Notes: Concentration in ppm except pH, Ec in $\mu S\,cm^{-2}$, and $HCO_3^-$ in $mol\,L^{-1}$. Values in parentheses indicate SD.

The groundwater properties also indicate seawater intrusion in this area. According to seawater intrusion grade prescribed by the China Geological Survey (DD2008-03), $Cl^-$, $Br^-$, and TDS in Jiaojiazhuangzi and Lvjiaji villages, respectively, exceed their limits ($250\,mg\,L^{-1}$, $0.55\,mg\,L^{-1}$, and $1\,mg\,L^{-1}$), which indicates groundwater in these villages is mixed with paleo-seawater. Groundwater in Huibu Town also showed a slight intrusion with relative low content of $Cl^-$, $Br^-$, and TDS. Groundwater in Zhuodong village displayed the highest content of $Cl^-$, $Br^-$, and TDS despite bone coal adsorption and indicates a serious seawater intrusion.

The relative proportion of sodium, calcium, and magnesium is expressed as sodium adsorption ratio (SAR) and calculated by the following equation, which is a standard equation (Biswas and Mukherjee 1987):

$$SAR = Na^+/[(Ca^{2+} + Mg^{2+})/2]^{1/2},$$

where concentrations are in $me\,L^{-1}$. The SARs in Jiaojiazhuangzi, Lvjiaji, and Zhuodong villages are more than the limits ($\geq 2$), indicating seawater intrusion, and SAR in Huibu Town is less than 2 but more than in Xiaohuibu and Taipingzhuang villages, which illustrates that seawater intrusion is relatively slight in this village.

The difference in groundwater quality properties in the investigated villages indicates that seawater intrusion is associated with Fl enrichment. The high Fl content and seawater intrusion are in conjunction with each other, and display similar distribution. The content of properties such as TDS, Ec, $Na^+$, and $Cl^-$ are distinguishable between fluorosis and non-fluorosis areas. In contrast, seawater intrusion results in high levels of these properties. Thus, geochemical indicators potentially suggest the geological process-seawater intrusion is an important factor affecting Fl enrichment in Laizhou Bay.

The correlation matrix of Fl with other constituents is shown in Table 2; however, the samples in Zhuodong village were not included because of the effect of bone coal treatment on other geochemical characteristics. Positive correlation of Fl with Ec, TDS, $Cl^-$, $Br^-$, $Li^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and significant with $Na^+$ and SAR was found. Similar results were observed in other districts with high Fl groundwater (Krainov and Zakutin 1994; Kierdorf and Kierdorf 2000; Gao, Wang, Li et al. 2007) and our investigation is in agreement with their findings. Besides, alkaline is helpful for Fl enrichment and Fl is seldom detected in water having a pH value $<7$ (Wang and Cheng 2001), groundwater pH in this area was above 7. However, pH showed a negative correlation with Fl, which is different from findings (Gupta, Doshi, and Paliwal 1986; Frengstad, Banks, and Siewers 2001; Zhang, Fu, and Zhang 2004). This indicates that pH is not the predominant dynamics of Fl enrichment. The correlation matrix in the mass suggests that Fl enrichment is associated with increase in properties evoked by seawater intrusion.

### *Fluorine enrichment and its relationship with seawater intrusion*

Fluorine predominantly originates from Fl-bearing rocks, with small proportion of other sources such as seawater, air, or human activities (Fuge 1988; Lahermo, Sandstrom, and Malisa 1991). Rocks determine groundwater Fl content from two aspects: Fl from the rock itself (Rao and Devadas 2003) and Fl due to release (Dowgiatto 2000; Woo et al. 2000; Smedley et al. 2002). Groundwater properties, such as pH, $Na^+$, $Cl^-$, and TDS, change because of the mixing of seawater resulting in the acceleration of Fl-releasing ability. $Na^+$ and $Na^+/Ca^{2+}$ seem to increase owing to seawater intrusion (Wu et al. 1994; Zhang and Peng 1998; Lamia, Abdalah, and Mennoubi 2009). Such a process promotes Fl solubility

Table 2. The correlation matrix of groundwater fluorine with other characteristics.

| | $F^-$ | pH | Ec | TDS | TH | $Cl^-$ | $Br^-$ | $HCO_3^-$ | $Li^+$ | $Na^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | SAR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $F^-$ | 1 | | | | | | | | | | | | | |
| pH | −0.464** | 1 | | | | | | | | | | | | |
| Ec | 0.39* | −0.821** | 1 | | | | | | | | | | | |
| TDS | 0.387* | −0.821** | 1** | 1 | | | | | | | | | | |
| TH | 0.199 | −0.804** | 0.978** | 0.978** | 1 | | | | | | | | | |
| $Cl^-$ | 0.388* | −0.756** | 0.882** | 0.883** | 0.865** | 1 | | | | | | | | |
| $Br^-$ | 0.493** | −0.702** | 0.757** | 0.758** | 0.731** | 0.781** | 1 | | | | | | | |
| $HCO_3^-$ | 0.14 | −0.206 | 0.276 | 0.277 | 0.314 | 0.269 | 0.185 | 1 | | | | | | |
| $Li^+$ | 0.344* | −0.709** | 0.843** | 0.843** | 0.814** | 0.881** | 0.665** | 0.299* | 1 | | | | | |
| $Na^+$ | 0.472** | −0.794** | 0.919** | 0.917** | 0.865** | 0.827** | 0.663** | 0.208 | 0.753** | 1 | | | | |
| $Mg^{2+}$ | 0.401* | −0.681** | 0.798** | 0.799** | 0.797** | 0.751** | 0.556** | 0.289 | 0.746** | 0.652** | 1 | | | |
| $Ca^{2+}$ | 0.361* | −0.79** | 0.95** | 0.948** | 0.978** | 0.856** | 0.71** | 0.236 | 0.799** | 0.897** | 0.685** | 1 | | |
| $Sr^{2+}$ | 0.05 | −0.614** | 0.678** | 0.682** | 0.687** | 0.773** | 0.533** | 0.349* | 0.761** | 0.631** | 0.76** | 0.598** | 1 | |
| SAR | 0.52** | −0.748** | 0.841** | 0.84** | 0.755** | 0.773** | 0.612** | 0.185 | 0.689** | 0.982** | 0.564** | 0.82** | 0.572** | 1 |

Notes: **Correlation is significant at the 0.01 level (one-tailed).
*Correlation is significant at the 0.05 level (one-tailed).

due to the following reason: NaF has higher solubility than $CaF_2$, and $Na^+$ is more reactive on combining with $F^-$ than $Ca^{2+}$ and $Mg^{2+}$. Several experiments confirmed that Fl increased with increasing $Na^+$ and $Na^+/Ca^{2+}$ (Krainov and Petrova 1976; Krainov and Zakutin 1994; Gao, Wang, Li et al. 2007). Tang and Wang (2005) noted that the released Fl from rocks increased with $(Na^++K^+)/Ca^{2+}$. Gao, Wang, Li et al. (2007) observed that NaF complexes increased and HF and $CaF^+$ decreased when more $Na^+$ mix into water. Hyndman (1985) and Faure (1991) reported that in areas with underlying intrusive igneous rocks, the rocks are not only enriched in Fl-bearing minerals, but also their plagioclase composition is typically high in albite, the sodium-rich end-member; and consequently, the water in contact with these rocks allows for higher Fl concentration when equilibrium is attained. All these observations indicate the importance of $Na^+$ and $Ca^{2+}$ in maintaining Fl balance. The Fl maximum concentration is generally restricted by $CaF_2$ (Apambire, Boyle, and Michel 1997; Cronin et al. 2000; Saxena and Ahmed 2003) and a negative correlation between $F^-$ and $Ca^{2+}$ often occurs in the saturation state (Ozsvath 2009). Further, an alkaline condition due to seawater intrusion results in low $Ca^{2+}$ and is therefore beneficial for Fl enrichment. Our investigation showed that high Fl groundwater is closely associated with $Na^+$. However, $Ca^{2+}$ does not decrease with the increasing Fl but displayed a positive correlation. This may be due to exchange of $Na^+$–$Ca^{2+}$ complex (Wu et al. 1996; Xue et al. 1997; Zhang et al. 2001; Lu, Chen, and Hu 2004). However, $Na^+/Ca^{2+}$ still showed a positive correlation with Fl content suggesting that $Na^+$ variation due to seawater intrusion may be a main contributor to Fl in this area.

$HCO_3^-$ was considered as an Fl enrichment mechanism due to the following reactions under the condition of adequate $Na^+$ and $HCO_3^-$ ions (Ramamohana Rao, Suryaprakasa Rao, and Schuiling 1993; Saxena and Ahmed 2001, 2003; Rao and Devadas 2003):

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2$$
$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2.$$

The solubility of $CaF_2$ increased with an increase in $NaHCO_3$, as noted during the investigation of high Fl groundwater in India and Mexico (Ramamohana Rao, Suryaprakasa Rao, and Schuiling 1993; Rao and Devadas 2003). Fan et al. (2008) also found that $CO_3^{2-}$ and $HCO_3^-$ promoted $CaF_2$ solubility. Saxena and Ahmed (2003) noted that Fl content was positively correlated with $HCO_3^-$ and 85% Fl groundwater has $HCO_3^-/Ca^{2+}$ ratio of 0.8–2.3. Zhao et al. (2007) found that groundwater Fl content was positively related with $(HCO_3^- + SO_4^{2-}+)/Ca^{2+}$ in Hetao district, Inner Mongolia. However, $HCO_3^-$ did not show a significant correlation with Fl (Table 2). This may be explained on the basis that there are low bicarbonate concentrations in this area. However, $HCO_3^-$ in fluorosis villages was higher than in non-fluorosis areas indicating that $HCO_3^-$ is not the predominant factor for Fl enrichment.

Seawater intrusion produces alkaline water. $F^-$ and $OH^-$ have the similar ionic radii, which often substitute for each other within minerals, and at high pH $OH^-$ ions displace $F^-$ ions, which are then released to groundwater (Sreedevi, Ahmed, and Made 2006). Thus groundwater with high Fl concentration also has high pH value. Zhang, Fu, and Zhang (2004) indicated that alkaline groundwater is helpful for desorption of the absorbed Fl. Frengstad, Banks, and Siewers (2001) concluded that Fl content increased with pH by analyzing 1604 water samples in Norway. Chae et al. (2007) observed that high pH liberated Fl ions absorbed by colloid. The negative correlation of pH in six villages with Fl reveals that the low bicarbonate and some other dynamics may be contributing Fl to groundwater water. Figure 2 illustrates that Fl increases with increasing pH when Fl is

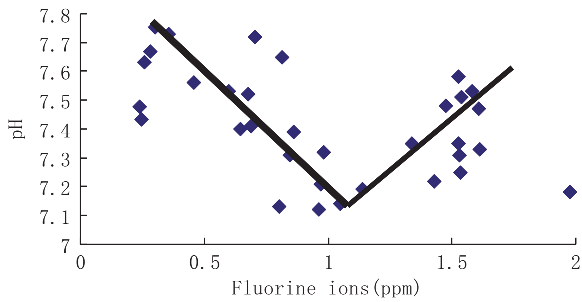


Figure 2. Groundwater fluorine contents and its relationship with pH.

more than 1 ppm in this area. A contrasting tendency occurs when Fl is less than 1 ppm, and this may be the insoluble fluoride which dissolves easily but forms different complex compounds.

Several studies demonstrated that Fl enrichment is favored by high conductivity, TDS, salinity, and hardness (Ahmed et al. 2002; Chae et al. 2006; Valenzuela-Vasquez et al. 2006; Gao, Wang, Li et al. 2007; Zhang et al. 2007; Jiang 2008). Saxena and Ahmed (2001) reported that Fl enriches under the conditions of pH 7.6–8.6, 750–1750 $\mu S\,cm^{-1}$ conductivity in Krishna district, Andhra Pradesh, India. Ahmed et al. (2002) noted that high Fl groundwater has pH 7.8–8.8 and 530–2680 $\mu S\,cm^{-1}$ conductivity in 58 samples from eight states in India. Jiang (2008) found that groundwater with Fl content of more than 1 $mg\,L^{-1}$ has the same distribution as mineralization of more than 1 $L^{-1}$ in fluorosis area in Hebei province, China. Similar results were observed in these areas and positive correlation of Fl with Ec and TDS. Similar to $HCO_3^-$, TH did not appear to have a significant relationship with Fl.

Various studies on Fl sources and forming factors in several aquifers also indicated that there is a close relationship between high Fl and soft, alkaline groundwater that is depleted in $Ca^{2+}$ and enriched in $Na^+$ water (Robertson 1986; Whittemore et al. 1993; Kierdorf and Kierdorf 2000; Woo et al. 2000; Earle and Krogh 2004; Heikens et al. 2005; Nordstrom, Ball, and McCleskey 2005; Chae et al. 2006, 2007; Walna, Kurzyca, and Siepak 2007). In general, our investigation found that the water in fluorosis region is characterized by seawater intrusion, which results in higher levels of $Na^+$, $Na^+/Ca^{2+}$, $HCO_3^-$, TDS, Ec, and TH and such changes are favorable for groundwater Fl enrichment. Thus the special process-seawater intrusion may be responsible for fluorosis in Laizhou Bay by changing groundwater properties and enhancing Fl ion release.

In fact, our investigation in Laizhou Bay found seawater intrusion and fluorosis distribution in the same manner, both characterized by spots and discontinuity in space. The high Fl water often tastes a little bitter due to the mixture of seawater, and as more seawater intrudes, the more serious fluorosis is. Further, not only in Laizhou Bay, but also in other regions, high Fl groundwater occurred in seawater intrusion areas. Kou and Wang (2000) also found high proportion of fluorosis in the coastal region of Liaoning Province, China. A similar process to seawater intrusion, salt lake water intrusions of Yuncheng, Shanxi province of China and Nagar Parker, Sindh province of Pakistan were found and confirmed by experiments to contain elevated groundwater Fl content due to the undersaturation with respect to fluorite (Gao, Wang, Zhu et al. 2007; Tahir et al. 2009), which suggest the effect of seawater intrusion on Fl in coastal areas.

### *Bone coal adsorption and its effect on groundwater quality*

Bone coal adsorption is used to treat high Fl groundwater because of the shortage of water resources in many villages, including Zhuodong villages. The groundwater properties in Zhuodong villages are presented in Table 1. Fluorine content decreased to 0.48 ppm within safe limits after treatment, indicating Fl ions are adsorbed by bone coal. $Cl^-$, $Br^-$, and TDS still have the highest content exceeding the grade limits (DD2008-03), which indicates a serious seawater intrusion. The fact that SAR is less than 2 may be due to $Na^+$ adsorption by bone coal. Ec, TDS, TH, $Cl^-$, $Br^-$, and $Ca^{2+}$ have the highest content, and $Li^+$, $Na^+$, $Mg^{2+}$, and $Sr^{2+}$ are higher than those in non-fluorosis villages and almost equal to those in the three fluorosis villages. This indicates that bone coal shows no specific adsorption of other ions and a single bone coal adsorption is not efficient. Our investigation indicated that such water is still widely being used as drinking water or industrial water in Laizhou Bay and is a potential factor for health risk.

## Summary

A comparison of geochemistry between groundwater in fluorosis and non-fluorosis areas was carried out to determine Fl content characteristics in Laizhou Bay, a region with seawater intrusion, and the following conclusions were drawn:

(1) The groundwater in fluorosis areas is characterized by seawater intrusion by indicators of $Cl^-$, $Br^-$, Ec, TDS, and SAR. The groundwater with high Fl content generally has higher contents of $Na^+$, $Na^+/Ca^{2+}$, SAR, TDS, Ec, and TH. Moreover, the variation of groundwater Fl ions is correlated with Ec, TDS, $Cl^-$, $Br^-$, $Ca^{2+}$, $Mg^{2+}$,and $Li^+$, and significantly correlated with $Na^+$ and SAR, with a tendency to increase with these ions. Data suggest that fluorosis in Laizhou Bay is related to special geological process-seawater intrusion, and the geochemistry evoked by seawater intrusion promotes Fl-releasing ability by changing its related parameters.

(2) Bone coal adsorption was widely used to treat the high Fl groundwater in Laizhou Bay. The result showed that although groundwater bone coal decreased Fl content, high content of $Cl^-$, $Na^+$, $Ca^{2+}$, $Br^-$, TDS, TH, and salinity still maintained. Treatment technology with just bone coal was not sufficient to remove fluorosis.

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