Geo-chemical processes during the mixing of seawater and fresh water in estuarine regions and their effect on water fluorine levels

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ABSTRACT. Fluorine levels in water significantly affect the quality of creatures’ life and the mixing of seawater with fresh river water changes water characteristics and influences the fluorine levels. However, the current study is mainly focused on groundwater, there’s not much information about the estuary water. The geo-chemical processes that take place when fresh and seawater mix and the effect on fluorine levels have been investigated in the Jiahe estuarine region. The estuarine water has high levels of Fe, Cl, Br, NO3, SO4²-, Na, K, Mg²⁺, Ca²⁺ due to the seawater mixing. The γNa⁺/γCl⁻ ratios are less than those of the standard seawater, while γMg²⁺/γCl⁻ and γCa²⁺/γCl⁻ ratios are higher than those of the standard seawater. Na⁺ and SO4²- strongly shows negative deviation, but Mg²⁺ and Ca²⁺ strongly have positive deviation. These facts indicate an inverse cation exchange. The saturation index (SI) indicates that calcite, magnesite and epsomite are under-saturated, whereas gypsum is over-saturated in No.1-8 samples. Sellaita and fluorite precipitates. Such processes explain the gypsum precipitation and the decreasing concentration of fluorine in the water.

Furthermore, the Mg²⁺ variation due to cation exchange has more contribution to water fluorine variation than Ca²⁺ because of the higher levels of Mg²⁺ and the gypsum precipitation. Such processes are different from those taking place in the intruded groundwater and should be taken into consideration when the water fluorine variation dynamics in estuarine regions are investigated.

Key words – Fluorine, Surface water, Seawater mixing, Cation exchange, Jiahe River.

1. Introduction

Estuaries lie at the transitional area between terrace or ocean and river, where numerous dynamic factors interact (Li et al., 2015; Haddout et al., 2016). The estuarine water has properties of both marine water and river water and hosts both saline and fresh ecosystems (Savenije, 2015). The population in estuarine regions has grown intensively in recent decades although estuaries cover only 0.4% of the total surface of the ocean.
(Seitzinger et al., 2000). Water quality in estuaries is crucial for environmental protection and economic development.

Estuaries receive the entire pollution load from various sources as terrestrial runoff, transported sediments, underlying bedrock and atmospheric deposition (Li et al., 2013; Gopal et al., 2018). Moreover, human intervention causes changes in estuarine water quality, such as urban settlements, industrial discharge, agriculture activities, ports and aquaculture (Xu et al., 2018; Barletta et al., 2019). The complex physicochemical process and explosive anthropogenic disturbance have frequently led to severe aquatic pollution and recently attracted global attention in estuary regions.

Fluorine is an essential element for biological life and the deficiency or excessive intake is harmful to liver, kidney, thyroid, blood sugar etc. This causes poor growth, a high death rate, tissue malformation and metabolic disturbance (Xue et al., 2016). The semi-static toxicity bioassays also have confirmed the bioaccumulation of fluorine ion and its effect on fish embryo development (Shi et al., 2009). Such malfunctioning consequently affects the life quality of both humans and other life forms in estuary regions. Unfortunately, the aquatic pollution in estuary regions is mainly focused on nutrient loads, persistent organic pollutants, heavy metals, micro-plastics, carbon oxide emissions and biomass etc. (Yang et al., 2011; Li et al., 2016; Zhang et al., 2016; Yevences et al., 2017; Zhao et al., 2017; Gopal et al., 2018; Barletta et al., 2019; Yan et al., 2019). Very few researches have been conducted with the aim of assessing fluorine levels of estuarine water.

The mixing of seawater with river water is an important and common phenomenon in estuaries and deeply influences the water geo-chemical process (Haddout et al., 2016; Liu et al., 2017), which is not a process of conservative mixture between seawater and fresh water, but that of complex physical and chemical reactions, such as adsorption and desorption, cation exchange, precipitation and dissolution and even dolomitization (Wu et al., 1994; Ma et al., 2014; Haddout et al., 2016; Abdullah et al., 2016).

These processes potentially change the water properties and affect water quality. Moreover, the fluorine levels in water are also controlled by these reactions. For example, numerous researches have confirmed that fluorine levels in water are elevated under the conditions of high Na\(^+\) and low Ca\(^{2+}\) (Wang et al., 2015; Singh et al., 2018; Jia et al., 2019). Na-Ca cation exchange upsets the balance between Na\(^+\) and Ca\(^{2+}\) in water and dolomitization, precipitation or dissolution of minerals as limestone, dolomite and gypsum change the Ca\(^{2+}\), Mg\(^{2+}\) levels in water during the mixing in estuaries (Gao et al., 2007). The change of water pH by mixing process may govern the fluorine levels, since OH\(^-\) and F\(^-\) substitute for each other because they have the similar radius and charges (Wang et al., 2015; Chen et al., 2019; Jia et al., 2019). Besides, ion competitive adsorption, common ion effects and other processes during the mixing may also be the cause of water fluorine variation (Singh et al., 2018; Prusty et al., 2018). Unfortunately, such scattered data are only occasionally documented for the groundwater in seawater intrusion areas and there is no any information detailing the fluorine levels in surface water in estuary regions where seawater is mixed.

In this research work, Jiahe estuary, a typical mixing region in Yantai City of China, was selected and the geochemical processes that take place during mixture of seawater with fresh water and their effects on water fluorine levels were investigated in detail. The aims of this research are to: (i) reveal the mixing process by establishing the geo-chemical difference between the mixed water and the non-mixed water of the same river; (ii) relate the fluorine levels to the mixing process; and (iii) analyze the possible dynamics of fluorine levels in estuarine regions.

2. Sample site and analysis methods

2.1. Study area and water sampling

The Jiahe river springs from the mountains in the middle of Jiaodong Peninsula, with a length of 143 km and catchment area of 2296 km\(^2\). The river is affiliated with Yantai City. It has two branches: the Outer Jiahe and the Inner Jiahe. The Outer Jiahe starts in Qixi City and runs through Fushan District, whereas the Inner jiahe rises in Haiyang County and runs through Mouping District. The two branches join in Fushan District and drain into the Yellow Sea (Fig. 1). The river is surrounded by the Economic Developing Zone, which has a dense population and various industries. The Jiahe River is the main resource for drinking and irrigation water.

Fourteen water samples were collected along the river and they were orderly labeled from No. 1 at the coast to No. 14 in the upstream direction, among which, No. 9 leaks before analyses could be performed (Fig. 1). The water was collected using pre-cleaned polycarbonate barrels and was sent to the laboratory on the same day. A dam was built to hold back the seawater between sampling sites 9 and 10, thus, samples from sites 1-9 indicate mixed water and those from 10-14 indicate non-mixed river water.
2.2. Analytical method

The water samples were divided into two parts; one was used to analyze the salinity, HCO$_3^-$ and CO$_3^{2-}$ within 2 days and the other one was frozen for further analysis of F, Cl, Br, NO$_3^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$. A DDS-320 conductivity meter was used to analyze the salinity. 0.01 mol/L HCl titration was used to determine HCO$_3^-$ and CO$_3^{2-}$ with helianthin B and naphthalene indicators. ICS-90 ion chromatography by Dionex was performed to analyze F, Cl, Br, NO$_3^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$.

Quality control (QC) was tested by testing parallel samples and standard samples and the relative error was less than 5%.

3. Results

3.1. Geo-chemical characteristics and fluorine levels of the water

The geo-chemical properties of water in the Jiahe River are presented in Table 1 and the difference between No. 1-8 and No. 10-14 is well revealed. The water samples of No. 1-8 are classified as Na-Cl type, with the dominate cation of Na$^+$ and anion of Cl$^-$. While those of No. 10-14 belong to Ca (Mg)-HCO$_3$ type, with the main cation of Ca$^{2+}$ (or Mg$^{2+}$) and anion of HCO$_3^-$ (Fig. 2). The samples of No. 1-8 obviously have higher levels of F, Cl, Br, NO$_3^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$ than those of No. 10-14. This implies a significant mixture of No. 1-8.
with seawater. The NO$_3^-$ in No. 1-8 shows lower levels than that in No. 10-14. This may be due to the fact that NO$_3^-$ mainly originates from human activities as discharge, agriculture, faeces or fertilizer etc. (Saccon et al., 2013); the No. 10-14 is closer to the city center. The HCO$_3^-$ levels do not show a significant difference between No. 1-8 and No. 10-14.

The fluorine levels in No. 1-8 are 0.88-1.15 mg/L, indicating mixing with seawater (which has an average fluorine level of 1.3 mg/L). The fluorine levels in No. 10-14 are 0.35-0.6 mg/L. All samples are within the water fluorine limits recommended by the World Health Organization (1.5 mg/L), while No. 1-5 samples slightly exceed the allowed standard for drinking water in China (1.0 mg/L).

Compared with the reported data from neighboring groundwater which also suffers from serious seawater intrusion in PZ and TS town (Table 1), concentrations of Na$^+$, Cl$^-$, Br$^-$, HCO$_3^-$ are obviously higher. The concentrations of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and SO$_4^{2-}$ in estuary water are approximately 10, 20, 15, 10 times of intruded groundwater respectively, which may be the two reasons: the higher ratios of seawater mixture in estuary water and the higher adsorption ability of soil in groundwater.

### 3.2. Cation exchange during the mixing process

The Deviations of ion concentrations are always used to define the chemical processes and reactions. Taking into account that Cl$^-$ is stable (Appelo and Postma, 1993), Cl$^-$ always acts as a conservative tracer (Tellam, 1995). The deviations of ion concentrations are calculated by the following formula (Kouzana et al., 2009):

\[
\Delta C_i = C_{i, sample} - C_{i, init}
\]

for the deviation of ion concentration:

\[
f_{sea} = \frac{C_{i, sample} - C_{i, f}}{C_{i, sea} - C_{i, f}}
\]

for the mixture ratio with seawater:

\[
C_{init} = f_{sea} C_{i, sea} + (1 - f_{sea}) C_{i, f}
\]

for the theoretical levels of each ion.

\[
C_{cl, sea} \text{ is the Cl}\text{-level of seawater, } C_{cl, f} \text{ is the seawater Cl}\text{-level, } f_{sea} \text{ is the mixing ratio, } C_{i, sample} \text{ is the ion level of samples, } C_{i, sea} \text{ is the ion level of standard seawater, } C_{i, f} \text{ is the ion level in fresh water and is referenced to No. 14 sample, } C_{i, init} \text{ is the deviation of ion concentration.}

### Notes

TABLE 1

Geo-chemical composition of water in the Jiahe River estuary and its comparison with other water analyses

|         | F      | HCO$_3^-$ | Cl$^-$ ($\times 10^4$) | Br$^-$ | NO$_3^-$ | SO$_4^{2-}$ | Na$^+$ ($\times 10^4$) | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ |
|---------|--------|-----------|------------------------|--------|-----------|-------------|------------------------|-------|-----------|-----------|
| No.1    | 1.15   | 133.7     | 1.841                  | 63.78  | 4.96      | 2296        | 1.004                  | 379.1 | 1312      | 468.5     |
| No.2    | 1.30   | 141.1     | 1.825                  | 63.38  | 6.58      | 2275        | 0.997                  | 369.7 | 1324      | 471.0     |
| No.3    | 1.07   | 146.1     | 1.613                  | 55.72  | 4.04      | 1999        | 0.881                  | 330.4 | 1170      | 400.1     |
| No.4    | 1.11   | 142.3     | 1.659                  | 57.00  | 4.69      | 2059        | 0.905                  | 339.4 | 1205      | 399.5     |
| No.5    | 1.22   | 143.6     | 1.522                  | 52.09  | 9.90      | 1882        | 0.832                  | 312.9 | 1111      | 383.9     |
| No.6    | 0.97   | 142.3     | 1.532                  | 52.29  | 9.16      | 1893        | 0.837                  | 315.5 | 1121      | 387.1     |
| No.7    | 0.97   | 147.3     | 1.455                  | 49.97  | 5.08      | 1796        | 0.795                  | 293.7 | 1078      | 374.0     |
| No.8    | 0.88   | 116.3     | 1.421                  | 48.65  | 6.52      | 1753        | 0.780                  | 287.5 | 1057      | 350.5     |
| No.9    | 0.60   | 117.6     | 0.0043                 | 0.85   | 13.12     | 68.60       | -                     | 4.79  | 21.24     | 1.14      |
| No.10   | 0.40   | 190.6     | 0.0033                 | 0.54   | 17.40     | 66.37       | -                     | 4.33  | 19.15     | 4.25      |
| No.11   | 0.45   | 133.7     | 0.0082                 | 1.65   | 12.12     | 74.65       | 0.0031                | 12.96 | 27.79     | 16.15     |
| No.12   | 0.35   | 151       | 0.0031                 | 1.64   | 62.08     | -           | -                     | 4.60  | 19.49     | 12.87     |
| No.13   | 0.36   | 151       | 0.0026                 | 1.92   | 56.03     | -           | -                     | 4.47  | 17.61     | 18.04     |
| No.14   | 0.32   | 151       | 0.0026                 | 1.92   | 56.03     | -           | -                     | 4.47  | 17.63     | 18.04     |

Note: Units are in mg/L and $^*$ is after Wang et al. (2015) - Means below the detection line.
TABLE 2

The ratio of seawater mixing and the exchanged ions in the Jiahe River

| Sample No. | Mixing ratio | △Na⁺ | △K⁺ | △Mg²⁺ | △Ca²⁺ | △Br⁻ | △HCO₃⁻ | △SO₄²⁻ | △F  |
|-----------|--------------|------|-----|-------|-------|------|--------|--------|-----|
| No. 1     | 93.44        | -6.52| 0.37| 7.26  | 4.21  | 0.038| -0.3   | -5.58  | -0.01|
| No. 2     | 92.65        | -5.84| 0.21| 9.07  | 4.49  | 0.039| -0.18  | -5.57  | -0.001|
| No. 3     | 81.87        | -5.37| 0.26| 7.87  | 3.05  | 0.03 | -0.09  | -5.3   | -0.008|
| No. 4     | 84.18        | -5.74| 0.27| 8.32  | 2.58  | 0.028| -0.16  | -5.33  | -0.007|
| No. 5     | 77.25        | -4.5 | 0.27| 7.95  | 3.16  | 0.022| -0.13  | -5.15  | 0.003|
| No. 6     | 77.74        | -4.93| 0.24| 8.19  | 3.22  | 0.02 | -0.15  | -5.2   | -0.011|
| No. 7     | 73.84        | -4.46| 0.12| 8.84  | 3.33  | 0.023| -0.07  | -5.03  | -0.008|
| No. 8     | 72.07        | -3.01| 0.13| 8.97  | 2.5   | 0.021| -0.58  | -4.94  | -0.012|
| No. 10    | 0.08         | -    | -0.002| 0.21  | -0.86 | 0.003| -0.55  | 0.21   | 0.013|
| No. 11    | 0.04         | -    | -0.007| 0.09  | -0.7 | -0.0003| 0.65  | 0.2   | 0.002|
| No. 12    | 0.29         | -1.36| 0.19| 0.54  | -0.15 | 0.012| -0.28  | 0.23   | 0.005|
| No. 13    | 0.02         | -    | 0.001| 0.13  | -0.26 | -    | 0.00   | 0.11  | -0.001|
| No. 14    | 0.00         | -    | 0.00 | 0.00  | -    | 0.00  | 0.00   | 0.00  | -    |

Notes: the units are in meq/L except the mixing ratio in %
Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) plotted against Cl\(^-\) during mixing of river water with seawater in the estuarine region of No. 1-8 samples (the drawn line represents the standard seawater).

The calculated results are shown in Table 2. The seawater mixing ratios of No. 1-8 samples are as high as 72.07-93.44%. The Na\(^+\) and SO\(_4^{2-}\) show a strong negative deviation, whereas Mg\(^{2+}\) and Ca\(^{2+}\) show a strong positive deviation and other ions show only slight deviations. This indicates a deficit of Na\(^+\) and an excess of Ca\(^{2+}\) compared to Cl\(^-\). Thus, an inverse cation exchange is confirmed to occur during the mixing process. Na\(^+\) captured by the exchanger (clay of the substratum), while Mg\(^{2+}\) or Ca\(^{2+}\) is released into estuarine water (Yu et al., 2014). Their \(\gamma_{\text{Na}^+}/(\gamma_{\text{Na}^+}+\gamma_{\text{Cl}^-})\) ratios are less than the standard seawater (0.5), while \(\gamma_{\text{Mg}^{2+}}/\gamma_{\text{Cl}^-}\) and \(\gamma_{\text{Ca}^{2+}}/\gamma_{\text{Cl}^-}\) ratios (in meq/l) decrease with the increasing of Cl\(^-\), which supports that cation exchange becomes less by the mixing with seawater, which is in agreement with previous findings (Gao et al., 2007; Su et al., 2012).

K\(^+\) deviation values are no more than 15 mg/L, which shows that K\(^+\)-Ca\(^{2+}\)(Mg\(^{2+}\)) exchange occurs in the late stage (Wu et al., 1994; Zhang et al., 1998; Su et al., 2012). The numerous previous studies of groundwater cation exchange all found that Na\(^+(\text{K}^+)\)-Ca\(^{2+}\) exchange has priority to Na\(^+(\text{K}^+)\)-Mg\(^{2+}\) exchange (Xue et al., 1998). However, Mg\(^{2+}\) shows larger deviation values than Ca\(^{2+}\) in estuarine water. This may be because Mg\(^{2+}\) levels in estuarine water are 30 times of those in groundwater and the cation exchange process is controlled by the ion concentration. On the other hand, the fact that Ca\(^{2+}\)/Mg\(^{2+}\) in estuarine water is higher than that of the standard seawater (0.33) also indicates the priority of Ca\(^{2+}\) exchange. It can be deduced from Fig. 5 that the (Ca\(^+\)/Mg)(Na/K) ratios (in meq/l) decrease with the increasing of Cl\(^-\), which supports that cation exchange becomes less by the mixing with seawater, which is in agreement with previous findings (Gao et al., 2007; Su et al., 2012).
The fluorine deviation in No. 1-8 samples shows negative values except No. 5 samples, with a range from -0.001 to 0.012 meq/L (-0.02-0.23 mg/L). On average, 15% of the total fluorine was absorbed or precipitated during the mixing of seawater and fresh river water in estuarine regions (Table 2).

3.3. Saturation index (SI) of minerals and variation in fluorine level

The saturation degree of the water with respect to minerals is determined so as to investigate the thermodynamic controls on the water composition using the Piper software. The saturation index (SI) of a mineral is defined by the following equation:

\[ SI = \log \left( \frac{IAP}{Ksp} \right) \]

where, IAP is the ion activity product and Ksp is the solubility product at a certain temperature. If the index is below zero, it means that the water is under-saturated with respect to the particular mineral phase. Such values reflect that the water is from a formation with insufficient amount of the mineral in solution. An index greater than zero indicates that the water is supersaturated with the particular mineral phase and is incapable of dissolving more of the mineral. A central band of 0.4 units along each values represents essential equilibrium to account for possible errors that may have occurred in the measurement of pH, Mg$^{2+}$, and Ca$^{2+}$.

The computed saturation indices of several minerals in estuarine regions are plotted in Fig. 6. All the SI values in No. 10-14 samples are below zero, indicating the water is under-saturated for the minerals. The SI values of calcite (CaCO$_3$), magnesite (MgCO$_3$) and epsomite (MgSO$_4$) in No. 1-8 is under-saturated, indicating these mineral phases did not precipitate. The SI values of gypsum (CaSO$_4$) indicate that gypsum precipitation when seawater mixes with river water. Thus, the negative SO$_4^{2-}$ deviation can be logically explained by this process. Besides, it implies more Ca$^{2+}$ is consumed by precipitation of gypsum, which may result in the less Ca$^{2+}$ deviation than Mg$^{2+}$ deviation. The SI values of fluorite (CaF$_2$) are near zero and within the central band of 0.4 units; those of sellaite (MgF$_2$) are more than zero. Obviously, the mineral phases of CaF$_2$ and MgF$_2$ precipitated during the mixing. In brief, the increasing of Ca$^{2+}$ and Mg$^{2+}$ levels due to inverse cation exchange should be responsible for the fluorine deviation in the estuary. Mg$^{2+}$ contributes more to the fluorine deviation than Ca$^{2+}$ and the reason may be two facts: the higher levels of Mg$^{2+}$ and the precipitation of gypsum.

4. Discussions

Seawater mixing or intrusion is common geological process along coastal areas. These processes significantly influence the water quality and consequently have recently attracted much attention from scholars in the past few years (Savenije, 2015; Guo et al., 2015; Haddout et al., 2016; Yevences et al., 2017; Zhao et al., 2017; Liu et al., 2018). However, the influence on water fluorine levels by seawater mixing or intrusion has received little attraction. Research into the geochemical process are mainly focused on the intruded groundwater, hardly any
information about the influence on water quality in estuarine regions is available.

Cation exchange has been frequently documented from situations where seawater intruded, especially concerning the Na\((\text{K}^-)\)-Ca\(^{2+}\)(Mg\(^{2+}\)) exchange (Wu et al., 1996; Zhang et al., 1998; Xue et al., 1998; Su et al., 2012; Jia et al., 2019). The Na\(^+\) and Ca\(^{2+}\)(Mg\(^{2+}\)) levels in the water are changed by such cation exchange. Na\(^+\) is prior to Ca\(^{2+}\) and Mg\(^{2+}\) when combined with F\(^-\) and NaF has a higher solubility than CaF\(_2\) or MgF\(_2\) (Wang et al., 2015; Chen et al., 2019; Jia et al., 2019). Furthermore, Ca\(^{2+}\) and F\(^-\) commonly correlate negatively because their contents in water are restricted by CaF\(_2\). Experiments have confirmed that NaF complexes increase and HF, CaF\(^-\) complexes decrease in water when Na ions are added (Gao et al., 2007). Numerous studies and field investigations also revealed that F\(^-\) in water increases with increasing of Na\(^+\) and decreasing of Ca\(^{2+}\) or Mg\(^{2+}\) (Saxena and Ahmed 2001; Walna et al., 2007; Oszvath, 2009; Jia et al., 2019). It is evident that the cation exchange affects the fluorine concentration in water by changing the balance between Na\(^+\) and Ca\(^{2+}\)(Mg\(^{2+}\)). Series of studies concluded that cation exchange causes fluorine variations in water, such as in Laizhou Bay, Shandong of China (Wang et al., 2015; Chen et al., 2019), the Dindigul district in Tamilnadu, India (Chidambaram et al., 2013), the Vellore district in southern India (Sajil Kumar et al., 2014), Rio Grande do Sul in southern Brazil (Marimont et al., 2013) and the Weihe River in China (Li et al., 2014). Unfortunately, these conclusions are only based on groundwater and have no results about the estuarine water.

Cation exchange takes places as following:

\[
2\text{Na}^+\text{(K}^-\text{)} + \text{Ca(Mg)X} \Leftrightarrow 2\text{Na(K)X} + \text{Ca}^{2+}\text{(Mg}^{2+}\text{)}
\]

including cation exchange and inverse cation exchange. Only inverse cation exchange is observed in estuarine water. The reason may be that the residence time in estuarine water is too short. Actually, inverse cation exchange only occurs in the initial phase of the salinization stage in intruded groundwater. Thus, the mixing of seawater and river water in estuaries can result only in the decrease of fluorine levels. In contrast, both processes have been documented for the intruded groundwater. In the cation exchange process, Na\(^+\) is absorbed by clay and Ca\(^{2+}\) (Mg\(^{2+}\)) is released into groundwater. This frequently occurs resulting in high concentrations of Na\(^+\) and low concentrations of Ca\(^{2+}\) (Mg\(^{2+}\)). Consequently, numerous researches state that fluorine levels in groundwater exceed the limits due to cation exchange (Gao et al., 2007; Sajil Kumar et al., 2014; Wang et al., 2015; Chen et al., 2019).

Many investigations conclude that the exchange of Na\(^-\)Ca\(^{2+}\) ions is prior to that of Na\(^-\)Mg\(^{2+}\) ions in intruded groundwater (Wu et al., 1996; Zhang et al., 1998; Wang et al., 2015) and Ca\(^{2+}\) variation in groundwater seems to be the main responsible factor for the F\(^-\) variations because of the lower solubility of CaF\(_2\) than MgF\(_2\). Mg\(^{2+}\) deviation shows high values and MgF\(_2\) is over-saturation in estuarine water. This implies that Mg\(^{2+}\) variation due to inverse cation exchange is the controlling factor for the fluorine variation. The reason may be that Mg\(^{2+}\) level in the mixed estuarine water is much higher than that in groundwater, so that sellaite becomes easily over-saturated. In addition, the distinctly higher levels of SO\(_4^{2-}\) in estuarine water than in groundwater lead to gypsum precipitation and part of the Ca\(^{2+}\) is consumed. In fact, based on the co-ions effect, the need of Ca\(^{2+}\) amounts to precipitate in the form of gypsum is much less than to precipitate as fluorite in this research. In brief, the increasing of Ca\(^{2+}\) and Mg\(^{2+}\) levels due to inverse cation exchange should be responsible for the fluorine deviation in estuarine regions. Mg\(^{2+}\) has more contribution for fluorine deviation than Ca\(^{2+}\) due to the higher levels of Mg\(^{2+}\) and the precipitation of gypsum. So the ion level difference between intruded groundwater and estuary water results in different geochemical process of fresh water and seawater mixing, causing different effects of fluorine levels.

5. Conclusions

The water in the Jiahe estuary, where the mixing of seawater with estuarine water occurs, was sampled to discuss the geo-chemical processes and their effect on water fluorine levels. The following conclusions were gained:

(i) The water in the estuary has high levels of F\(^-\), Cl\(^-\), Br, NO\(_3^-\), SO\(_4^{2-}\), Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) because of the mixing of seawater with river water. Moreover, the \(\gamma\text{Na}^+/\gamma\text{Na}^+\gamma\text{Cl}^\text{~}\) ratios are lower, while \(\gamma\text{Mg}^{2+}/\gamma\text{Cl}^\text{~}\) and \(\gamma\text{Ca}^{2+}/\gamma\text{Cl}^\text{~}\) ratios are higher than those of the standard seawater. The Na\(^+\) deviations are negative and Mg\(^{2+}\) (Ca\(^{2+}\)) deviations are positive. These facts imply another geo-chemical process, an inverse cation exchange, occurs. That is, the Na\(^+\) is absorbed by the clays of the substratum and Ca\(^{2+}\) (Mg\(^{2+}\)) is released into the water during the mixing process, which differs from what happens in the case of intruded groundwater.

(ii) The fluorine deviation has negative values, indicating the precipitation of mineral phase bearing fluorine elements. The increase of the Mg\(^{2+}\) and Ca\(^{2+}\) levels due to inverse cation exchange causes the over-saturated SI values and the precipitation of CaF\(_2\) and MgF\(_2\) in No. 1-8 samples, which is the main factor
causing the decreasing of fluoride levels in the estuarine water. Furthermore, SI indicates CaCO₃, MgCO₃ and MgSO₄ in No. 1-8 samples are under-saturated, while CaSO₄ is over-saturated due to the higher levels of SO₄²⁻. Thus, Mg²⁺ contributes more than Ca²⁺ to the precipitation of F⁻ because of the two aspects: Mg²⁺ levels are much higher than Ca²⁺ and part of Ca²⁺ is consumed when gypsum precipitates during the mixing processes. These are also different from the processes taking place in the intruded groundwater by seawater.

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