

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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(Received 19 July 2018, Accepted 26 February 2019)

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सार – पानी में फ्लोरीन का स्तर जीवों के जीवन की गुणवत्ता को काफी प्रभावित करता है, और समुद्री जल के नदी के जल के साथ मिलने से पानी विशेषताओं में परिवर्तन आ जाता है और यह क्लोरीन स्तर को प्रभावित करता है। हालांकि, यह शोध पत्र मुख्य रूप से भू-जल पर केंद्रित है, यहाँ नदी मुख मुहाने के पानी के बारे में अधिक जानकारी नहीं है। जब मीठा पानी और समुद्री जल मिलते हैं तो भू-रासायनिक प्रक्रियाएँ होती हैं। यहाँ जियाहे ज्वारनदमुखी क्षेत्र में फ्लोरीन के स्तर पर प्रभाव की पड़ताल की गई है। समुद्री जल के मिश्रित होने के कारण नदीमुख जल में फ्लोरीन (F⁻), क्लोरीन (Cl⁻), ब्रोमीन (Br⁻), नाइट्रेट (NO₃⁻), सल्फेट (SO₄²⁻), सोडियम (Na⁺), पोटेशियम (K⁺), मैग्नेशियम (Mg²⁺), कैल्शियम (Ca²⁺) के आयन काफी उच्च स्तर में हैं। $\gamma\text{Na}^+ / C \gamma\text{Na}^+ + C\gamma\text{Na}^+ + \gamma\text{Cl}^-$ का अनुपात मानक समुद्री जल की तुलना में कम होते हैं जबकि $\gamma\text{Mg}^{2+} / \gamma\text{Cl}^-$ और $\gamma\text{Ca}^{2+} / \gamma\text{Cl}^-$ के अनुपात मानक समुद्री जल अधिक होते हैं। सोडियम आयन (Na⁺) और सल्फेट आयन (SO₄²⁻) मजबूत ऋणात्मक विचलन दर्शाता है, परंतु मैग्नेशियम आयन (Mg²⁺) और कैल्शियम आयन (Ca²⁺) मजबूत धनात्मक विचलन दर्शाता है। ये तथ्य व्युत्क्रम धनायन विनिमय को दर्शाते हैं। संतृप्त सूचकांक (SI) दर्शाते हैं कि कैल्साइट, मैग्नेसाइट और एफसोमाइट कम संतृप्त हैं जबकि जिप्सम 1 से 8 नमूनों में अधिक संतृप्त है। सेलाइट और फ्लोराइट अवक्षेपित होता है। इस तरह की प्रक्रियाएँ जिप्सम अवक्षेपण और पानी में फ्लोरीन की सांद्रता में कमी को दर्शाती हैं। इसके अलावा Ca²⁺ से Mg²⁺ का सांद्रण स्तर अधिक होने और जिप्सम अवक्षेपण के कारण तथा धनायन विनिमय के कारण जलीय फ्लोरीन में Mg²⁺ अधिक होता है। इस प्रकार की प्रक्रियाएँ भू-जल में प्रवेश करने से भिन्न होती है और जब ज्वारनदमुखी क्षेत्रों में जल में फ्लोरीन भिन्नता गतिशीलता की जाँच की जा रही हो तो इसका ध्यान रखा जाना चाहिए।

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 F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺ due to the seawater mixing. The $\gamma\text{Na}^+ / (\gamma\text{Na}^+ + \gamma\text{Cl}^-)$ ratios are less than those of the standard seawater, while $\gamma\text{Mg}^{2+} / \gamma\text{Cl}^-$ and $\gamma\text{Ca}^{2+} / \gamma\text{Cl}^-$ 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. Sellaite 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 geo-chemical 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 km². 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.

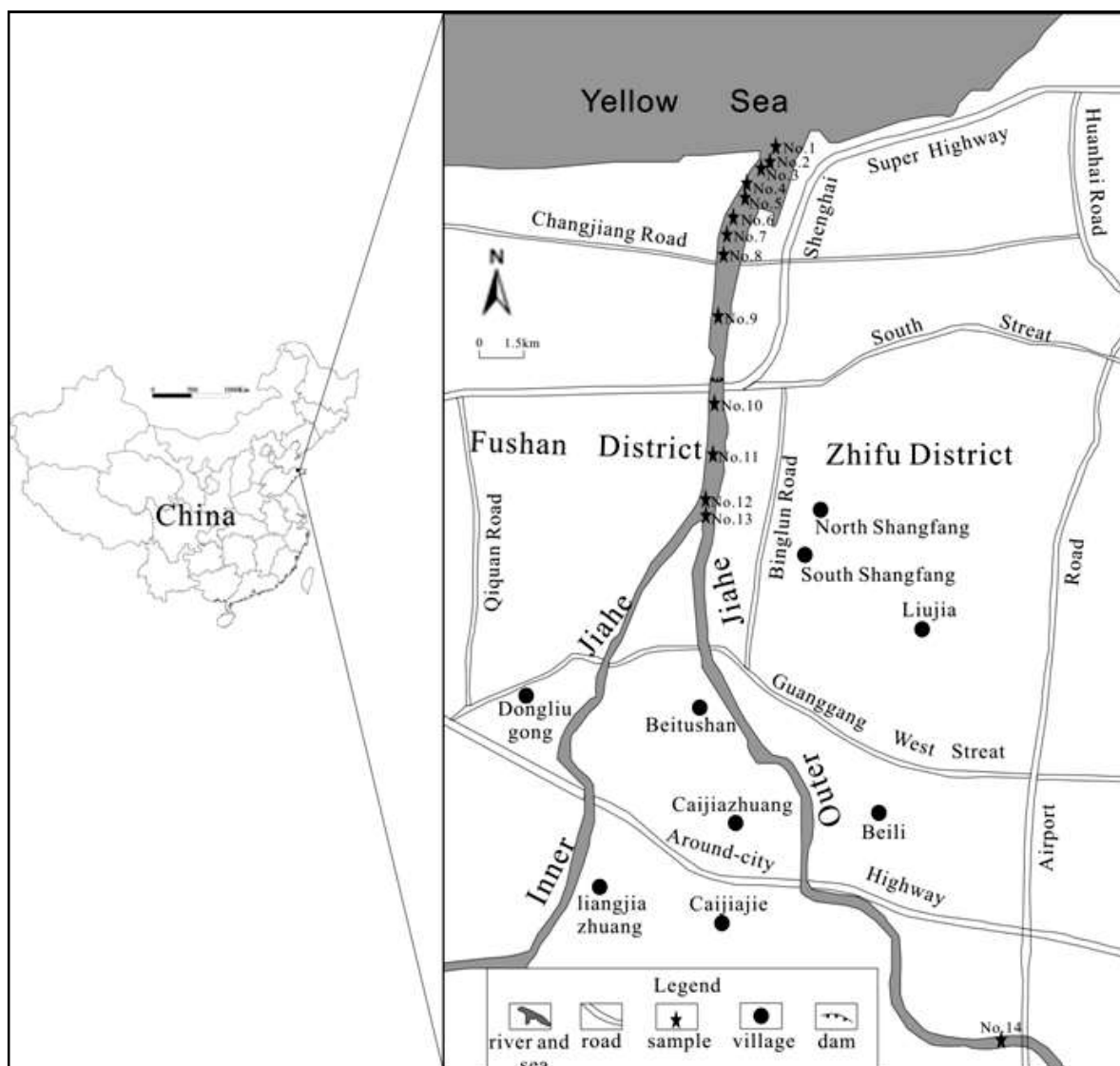


Fig. 1. The geographical sketch and sampling sites in Jiahe estuary

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

TABLE 1
Geo-chemical composition of water in the Jiahe River estuary and its comparison with other water analyses

		F ⁻	HCO ₃ ⁻	Cl ⁻ (×10 ⁴)	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺ (×10 ⁴)	K ⁺	Mg ²⁺	Ca ²⁺
Jiahe River samples	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
	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	313.5	1121	387.1
	No.7	0.97	147.3	1.455	49.97	5.08	1796	0.795	293.7	1078	374
	No.8	0.88	116.3	1.421	48.65	6.52	1753	0.780	287.5	1057	350.5
	No.10	0.60	117.6	0.0043	0.85	13.12	68.60	-	4.79	21.24	1.14
	No.11	0.40	190.6	0.0033	0.54	17.40	66.37	-	4.33	19.15	4.25
	No.12	0.45	133.7	0.0082	1.65	12.12	74.65	0.0031	12.96	27.79	16.15
	No.13	0.35	151	0.0031	-	16.42	62.08	-	4.60	19.49	12.87
	No.14	0.36	151	0.0026	-	19.28	56.03	-	4.47	17.61	18.04
	Ground water*	PZ town	2.33	7.75	0.0454	0.86	42.78	338.4	0.039	31.12	58.25
TS town		0.91	4.18	0.0301	0.51	291.66	107.9	0.0111	2.0	42.24	199.35
	seawater	1.3	142	1.935	-	-	2712	1.076	387	1294	413

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

with seawater. The NO₃⁻ in No. 1-8 shows lower levels than that in No. 10-14. This may be due to the fact that NO₃⁻ 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 HCO₃⁻ 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⁻, HCO₃⁻ are obviously higher. The concentrations of Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻ in estuary water are appropriately 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):

$$\text{for mixture ratio with seawater: } f_{sea} = \frac{(C_{Cl, sample} - C_{Cl, f})}{(C_{Cl, sea} - C_{Cl, f})}$$

$$\text{for the theoretical levels of each ion: } C_{mix} = f_{sea} \cdot C_{i, sea} + (1 - f_{sea}) \cdot C_{i, f}$$

$$\text{for the deviation of ion concentration: } \Delta C_i = C_{i, sample} - C_{mix}$$

where, $C_{Cl, sample}$ is the Cl⁻ levels, $C_{Cl, sea}$ is the seawater Cl⁻ level, $C_{Cl, f}$ is the Cl⁻ level of fresh water, f_{sea} is the mixing ratio, $C_{i, sample}$ is the ion level of samples, $C_{i, sea}$ is the ion level of standard seawater, $C_{i, f}$ is the ion level in fresh water and is referenced to No. 14 sample, C_{mix} is the theoretical level of each ion and ΔC_i is the deviation of ion concentration.

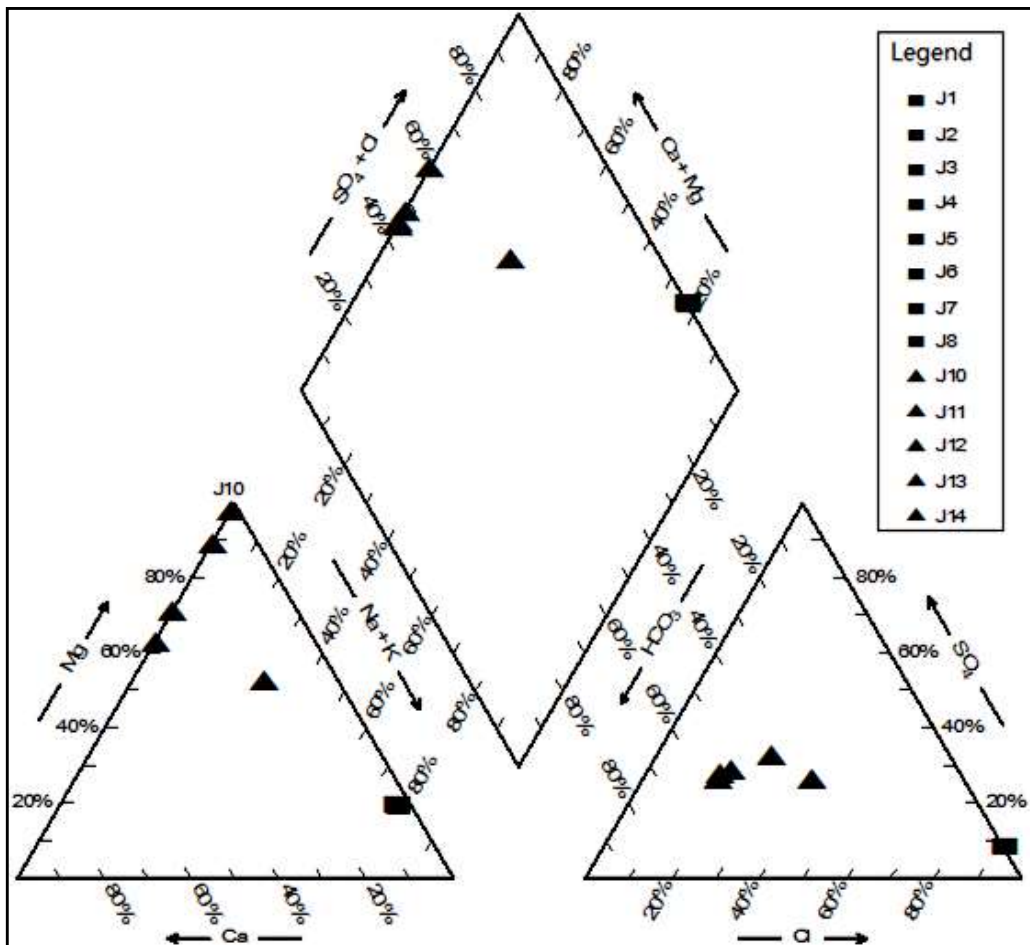


Fig. 2. Piper graph of water in the Jiahe estuary

TABLE 2

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

Sample No.	Mixing ratio	ΔNa^+	ΔK^+	ΔMg^{2+}	ΔCa^{2+}	ΔBr^-	ΔHCO_3^-	ΔSO_4^{2-}	ΔF^-
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	-	-0.0002	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	0.00

Notes: the units are in meq/L except the mixing ratio in %

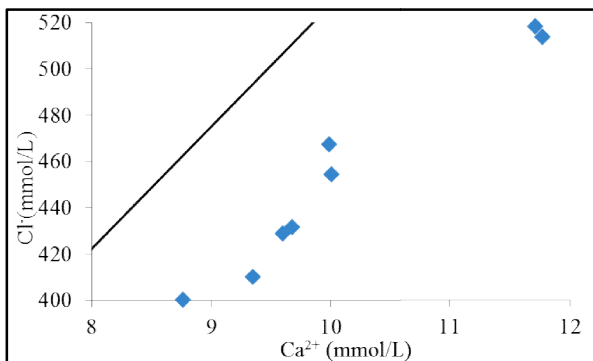
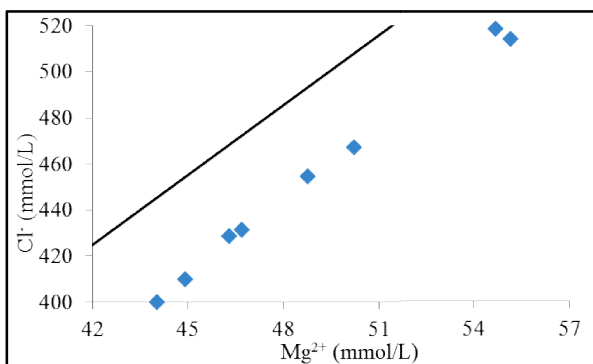
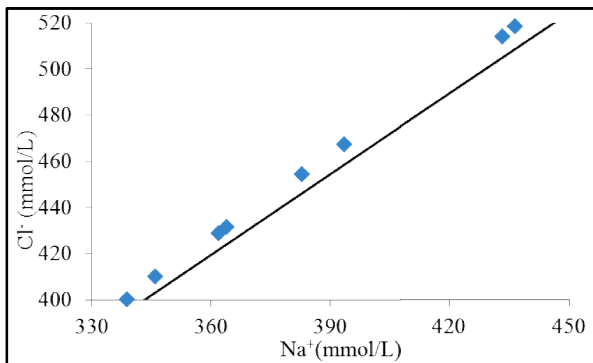


Fig. 3. Na⁺, Mg²⁺, Ca²⁺ plotted against Cl⁻ (mmol/L) during mixing of river water with seawater in the estuarine region of No. 1-8 samples (the drawn line represents the standard seawater)

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 SO₄²⁻ show a strong negative deviation, whereas Mg²⁺ and Ca²⁺ show a strong positive deviation and other ions show only slight deviations. This indicates a deficit of Na⁺ and an excess of Ca²⁺, Mg²⁺ compared to Cl⁻. Thus, an inverse cation exchange is confirmed to occur during the mixing process. Na⁺ is captured by the exchanger (clay of the substratum), while Mg²⁺ or Ca²⁺ is released into estuarine water (Yu *et al.*, 2014). Their $\gamma_{Na^+}/(\gamma_{Na^+} + \gamma_{Cl^-})$ ratios are less than the standard seawater (0.5), while $\gamma_{Mg^{2+}}/\gamma_{Cl^-}$ and $\gamma_{Ca^{2+}}/\gamma_{Cl^-}$

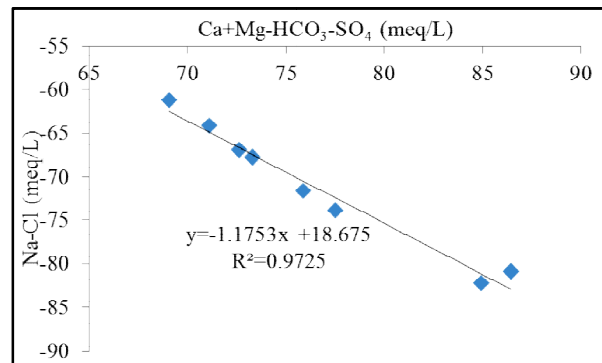


Fig. 4. The diagram of Ca⁺Mg⁺SO₄HCO₃ versus Na⁻Cl of No.1-8 samples

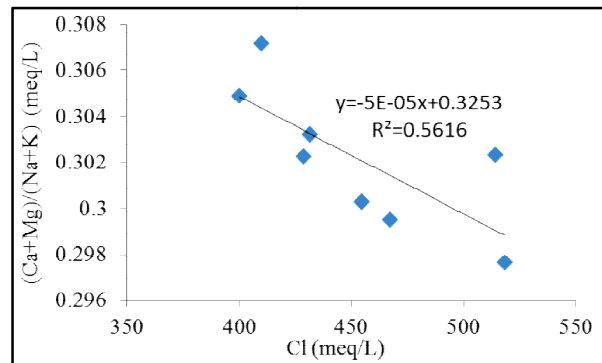


Fig. 5. The diagram of (Ca⁺Mg⁺)/(Na⁺K) versus Cl of No. 1-8 samples

are higher than the standard seawater (0.099 and 0.019 respectively) in No. 1-8 samples (Fig. 3). The Ca⁺Mg⁺SO₄⁻HCO₃ versus Na⁻Cl diagram is seen in Fig. 4, these samples plot along a line with a slope of -0.9725, which indicates that ion exchange is indeed taking place (Jankowski *et al.*, 1998).

K⁺ deviation values are no more than 15 mg/L, which shows that K⁺-Ca²⁺(Mg²⁺) 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⁺(K⁺)-Ca²⁺ exchange has priority to Na⁺(K⁺)-Mg²⁺ exchange (Xue *et al.*, 1998). However, Mg²⁺ shows larger deviation values than Ca²⁺ in estuarine water. This may be because Mg²⁺ 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 Ca²⁺/Mg²⁺ in estuarine water is higher than that of the standard seawater (0.33) also indicates the priority of Ca²⁺ 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).

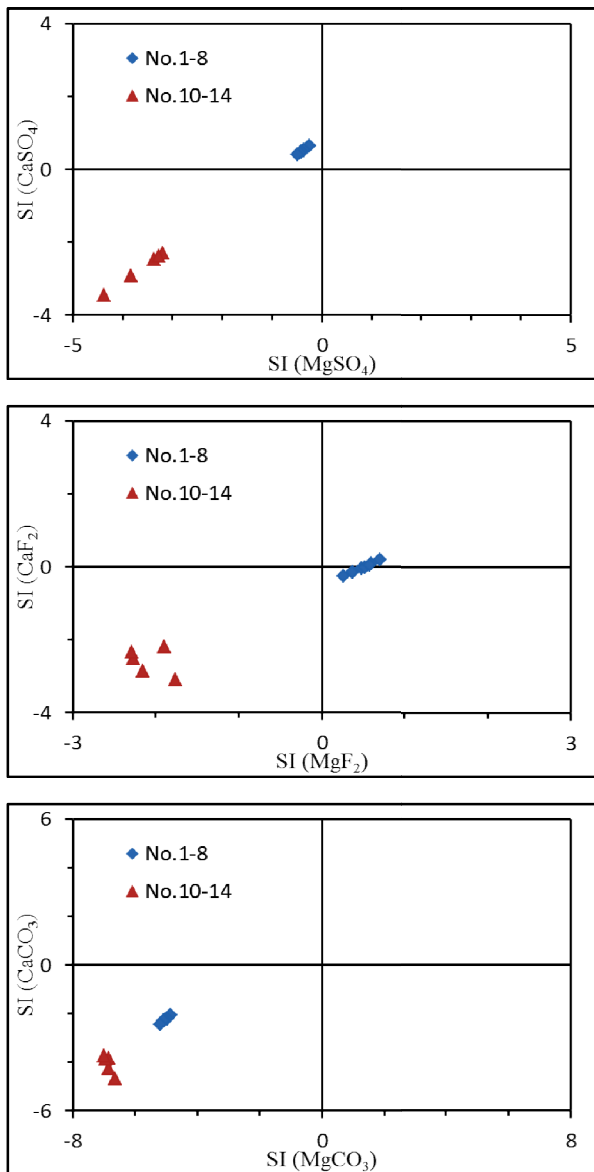


Fig. 6. Saturation indices of different mineral phases in the water of the Jiahe estuary

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:

$$SI = \text{Log} (IAP/Ksp)$$

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, Mg²⁺ and Ca²⁺.

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 (CaCO₃), magnesite (MgCO₃) and epsomite (MgSO₄) in No. 1-8 is under-saturated, indicating these mineral phases did not precipitate. The SI values of gypsum (CaSO₄) indicate that gypsum precipitation when seawater mixes with river water. Thus, the negative SO₄²⁻ deviation can be logically explained by this process. Besides, it implies more Ca²⁺ is consumed by precipitation of gypsum, which may result in the less Ca²⁺ deviation than Mg²⁺ deviation. The SI values of fluorite (CaF₂) are near zero and within the central band of 0.4 units; those of sellaite (MgF₂) are more than zero. Obviously, the mineral phases of CaF₂ and MgF₂ precipitated during the mixing. In brief, the increasing of Ca²⁺ and Mg²⁺ levels due to inverse cation exchange should be responsible for the fluorine deviation in the estuary. Mg²⁺ contributes more to the fluorine deviation than Ca²⁺ and the reason may be two facts: the higher levels of Mg²⁺ and the precipitation of gypsum.

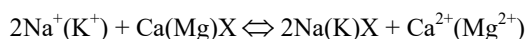
4. Discussions

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 $\text{Na}^+(\text{K}^+)-\text{Ca}^{2+}(\text{Mg}^{2+})$ exchange (Wu *et al.*, 1994; Zhang *et al.*, 1998; Xue *et al.*, 1998; Su *et al.*, 2012; Jia *et al.*, 2019). The Na^+ and $\text{Ca}^{2+}(\text{Mg}^{2+})$ 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; Ozsvath, 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 $\text{Ca}^{2+}(\text{Mg}^{2+})$. 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 (Marimon *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:



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 $\text{Ca}^{2+}(\text{Mg}^{2+})$ is released into groundwater. This frequently occurs resulting in high concentrations of Na^+ and low concentrations of $\text{Ca}^{2+}(\text{Mg}^{2+})$. 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 $\text{Na}^+-\text{Ca}^{2+}$ ions is prior to that of $\text{Na}^+-\text{Mg}^{2+}$ 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 $\gamma\text{Na}^+(\gamma\text{Na}^++\gamma\text{Cl}^-)$ ratios are lower, while $\gamma\text{Mg}^{2+}/\gamma\text{Cl}^-$ and $\gamma\text{Ca}^{2+}/\gamma\text{Cl}^-$ 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 fluorine levels in the estuarine water. Furthermore, SI indicates CaCO_3 , MgCO_3 and MgSO_4 in No. 1-8 samples are under-saturated, while CaSO_4 is over-saturated due to the higher levels of SO_4^{2-} . Thus, Mg^{2+} contributes more than Ca^{2+} to the precipitation of F⁻ because of the two aspects: Mg^{2+} levels are much higher than Ca^{2+} and part of Ca^{2+} is consumed when gypsum precipitates during the mixing processes. These are also different from the processes taking place in the intruded groundwater by seawater.

Acknowledgement

This work is supported by the Natural Science Fund of Shandong Province (ZR2018MD012, ZR2011DQ006), the Natural Science Fund of China (No. 40901027, 41572244), 2017 Special Fund for Scientific Research of Shandong Coalfield Geologic Bureau [2017(10)], Ministry of Education Research Fund for the Doctoral Program (20133718110004) and Taishan Scholars Construction Projects Funded by Special Funds.

The contents and views expressed in this research paper are the views of the authors and do not necessarily reflect the views of their organizations.

References

- Abdullah, A. D., Gisen Jacqueline, I. A., Pieter, V. D. Z., Hubert, H. G. Savenije, Usama, F. A. Karim, Masih, Ilyas and Popescu, Ioana, 2016, "Predicting the salt water intrusion in the Shatt al-Arab estuary using an analytical approach", *Hydrology and Earth System Sciences*, **20**, 4031-4042.
- Appelo, C. A. J. and Postma, D., 1993, "Geochemistry, Groundwater and Pollution", Balkema, Rotterdam.
- Barletta, M., Lima, A. R. A. and Costa, M. F., 2019, "Distribution, Sources and consequences of nutrients, persistent organic, metals and micro-plastics in South American estuaries", *Science of the Total Environment*, **651**, 1199-1218.
- Chen, Q., Wei, J., Wang, H., Shi, L., Gao, Z., Liu, S., Ning, F., Jia, C., Ji, Y., Dong, F. and Jia, Z., 2019, "Discussion on the fluorosis in seawater-intrusion areas along coastal zones in Laizhou Bay and other parts of China", *International Journal of Environmental Research*, **13**, 435-442.
- Chidambaram, S., Krishna Prasad, M. B. and Manivannan, R., 2013, "Environmental hydrogeochemistry and genesis of fluoride in groundwaters of Dindigul district, Tamilnadu (India)", *Environmental Earth Sciences*, **68**, 333-342.
- Gao, X. B., Wang, Y. X., Li, Y. L. and Guo, Q. H., 2007, "Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China", *Environmental Geology*, **53**, 795-803.
- Gopal, V., Shanmugasundaram, A., Nithya, B., Magessh, N. S. and Jayaprakash, M., 2018, "Water quality of the Uppanar estuary, Southern India: implications on the level of dissolved nutrients and trace elements", *Marine Pollution Bulletin*, **130**, 279-286.
- Guo, J. Y., Wang, J. B., Hu, Z. B., Hwang, C. and Chen, C. F., 2015, "Temporal-spatial variations of sea level over China seas derived from altimeter data of TOPEX/Poseidon, Jason-1 and Jason-2 from 1993 to 2012", *Chinese Journal of Geophysics-Chinese Edition*, **58**, 3103-3120.
- Haddout, S., Igouzal, M. and Maslouhi, A., 2016, "Analytical and numerical study of the salinity intrusion in the Sebou River estuary (Morocco)-effect of the "Super Blood Moon" (total lunar eclipse) of 2015", *Hydrology and Earth System Sciences*, **20**, 3923-3945.
- Jankowski, J., Acworth, R. I. and Shekarforoush, S., 1998, "Reverse ion exchange in a deeply weathered porphyritic dacite fractured aquifer system, Yass, New South Wales, Australia", Arehart GB, Hulston JR (eds) Proceedings of the 9th International Symposium on water-rock interaction, Taupo, New Zealand, 30th March-3 April, 1998, 243-246, Balkema, Rotterdam.
- Jia, C. P., Chen, Q., Wei, J. C., Wang, H. M., Shi, L. Q., Ning, F. Z., Liu, S. L., Yang, M. Y., Xue, X., Dong, F. Y., Jia, Z. W. and Ji, Y. H., 2019, "The study on the mechanism of fluorine transformation between water and rock (soil) in seawater intrusion areas based on FTIR spectrum", *Spectrosc Spect Anal.*, **39**, 4, 1036-1040.
- Kouzana, L., Mammou, A. B. and Felfoul, M. S., 2009, "Seawater intrusion and associated processes: case of the Korba aquifer (Cap-Bon, Tunisia)", *Comptes Rendus Geoscience*, **341**, 21-35.
- Li, D. L., Liu, X. B. and Liu, Z. G., 2016, "Variations in total organic carbon and acid-volatile sulfide distribution in surface sediments from Luan River Estuary, China", *Environmental Earth Sciences*, **75**, 14, 1073.
- Li, H., Li, Z., Li, Z., Yu, J. and Liu, B., 2015, "Evaluation of ecosystem services: A case study in the middle reach of the Heihe River Basin, Northwest China", *Physics and chemistry of the Earth*, **89-90**, 40-45.
- Li, H., Lv, Y., Wang, G., Liu, Y. and Li, J., 2013, "Study on Hydro-mechanical Coupling Interaction of the Fractured Rock", *Disaster Advances*, **6**, 302-309.
- Li, P. Y., Qian, H. and Wu, J. H., 2014, "Occurrence and hydrogeochemistry of fluoride in alluvial aquifer of Weihe River, China", *Environmental Earth Sciences*, **71**, 3133-3145.
- Li, W., Wang, W., Zhang, C., Yang, Q. and Feng, W., 2018, "Monitoring groundwater storage variations in the Guanzhong area using GRACE satellite gravity data", *Chinese Journal of Geophysics-Chinese Edition*, **61**, 2237-2245.
- Liu, K., Zhao, D., Fang, J., Zhang, X. and Zhang, Q., 2017, "Estimation of Heavy-Metal Contamination in Soil Using Remote Sensing Spectroscopy and a Statistical Approach", *Journal of the Indian society of remote sensing*, **45**, 805-813.
- Ma, F. S., Wei, A. H., Deng, Q. H. and Zhao, H. J., 2014, "Hydrochemical characteristics and the suitability of groundwater in the coastal region of Tangshan, China", *Journal of Earth Sciences*, **25**, 1067-1075.
- Marimon, M. P. C., Roisenberg, A. and Viero, A. P., 2013, "Evaluation of the potential impact of fluoride-rich fertilizers on the Guarani Aquifer System, Rio Grande do Sul, Southern Brazil", *Environmental Earth Sciences*, **69**, 77-84.
- Ozsvath, D. L., 2009, "Fluoride and environmental health: A review", *Reviews in Environmental Science and Biotechnology*, **8**, 1, 59-79.
- Prusty, P., Farooq, S. H., Zimik, H. V. and Barik, S. S., 2018, "Assessment of the factors controlling groundwater quality in a coastal aquifer adjacent to the Bay of Bengal, India", *Environmental Earth Sciences*, **77**, 762.

- Saccon, P., Leis, A. and Marca, A., 2013, "Multi-isotope approach for the identification and characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area", *Applied Geochemistry*, **34**, 75-89.
- Sajil Kumar, P. J., Jegathambal, P. and James, F. J., 2014, "Factors influencing the high fluoride concentration in groundwater of Vellore District, South India", *Environmental Earth Sciences*, **72**, 2437-2446.
- Savenije, H. H. G., 2015, "Prediction in ungauged estuaries: An integrated theory", *Water Resources Research*, **51**, 2464-2476.
- Saxena, V. K. and Ahmed, S., 2001, "Dissolution of fluoride in groundwater: A water-reaction study", *Environmental Geology*, **40**, 1084-1090.
- Seitzinger, S. P., Kroeze, C. and Styles, R. V., 2000, "Global distribution of N₂O emission from system: natural emissions and anthropogenic effects", *Chemosphere Global Change Science*, **2**, 267-279.
- Shi, X. T., Zhuang, P. and Zhang, L. Z., 2009, "The bioaccumulation of fluoride ion (F⁻) in Siberian sturgeon (*Acipenser baerii*) under laboratory conditions", *Chemosphere*, **75**, 3, 376-380.
- Singh, G., Kumari, B., Sinam, G., Kumar, K. N. and Mallick, S., 2018, "Fluoride distribution and contamination in the water, soil and plants continuum and its remedial technologies, an Indian perspective- A review", *Environmental Pollution*, **239**, 95-108.
- Su, Q., Yu, H. J., Xu, X. Y. and Yao, J., 2012, "The groundwater hydrochemical characteristics in eastern and southern coasts of the Laizhou Bay", *Journal of Marine Sciences (in Chinese)*, **30**, 74-78.
- Tellam, J. H., 1995, "Hydrochemistry of the saline groundwaters of the lower Mersey Basin Permo-Triassic sandstone aquifer, UK", *Journal of Hydrology*, **165**, 45-84.
- Walna, B., Kurzyca, I. and Siepak, J., 2007, "Variations in fluoride level in precipitation in a region of human impact", *Water Air and Soil Pollution Focus*, **7**, 33-40.
- Wang, L. F., Chen, Q., Wu, X. B. and Sun, L., 2015, "Comparative analysis of groundwater fluorine levels and other characteristics in two areas of Laizhou Bay and its explanation on fluorine enrichment", *Water Science and Technology: Water supply*, **15**, 384-394.
- Wu, J. C., Xue, Y. Q. and Liu, P., 1994, "Development and hydrochemical characteristics of sea water intrusion in Longkou-Laizhou district", *Journal of Nanjing University (Natural Sciences Edition) (in Chinese)*, **30**, 98-110.
- Xu, F., Hu, B., Dou, Y., Song, Z. and Liu, X., 2018, "Prehistoric heavy metal pollution on the continental shelf off Hainan Island, South China Sea: From natural to anthropogenic impacts around 4.0 kyr BP", *Holocene*, **28**, 455-463.
- Xue, W. J., Li, S. J. and Jia, R. H., 2016, "Acute toxicity and safety assessment of fluoride on juveniles *Poecilia reticulata*", *Freshwater Fisheries (in Chinese)*, **46**, 99-102.
- Xue, Y. Q., Wu, J. C. and Xie, C. H., 1998, "Sea water intrusion and salt water intrusion in the coastal area of Laizhou Bay", *Chinese Science Bulletin*, **43**, 983-992.
- Yan, M. T., Nie, H. Y., Xu, K. H., He, Y. H., Hu, Y. T., Huang, Y. M. and Wang, J., 2019, "Microplastic abundance, distribution and composition in the Pearl River along Guangzhou city and Pearl River estuary, China", *Chemosphere*, **217**, 879-886.
- Yang, F., Lu, X., Li, J., Han, X., Han, Y. and Zheng, X., 2011, "Precise Positioning of Underwater Static Objects without Sound Speed Profile", *Marine Geodesy*, **34**, 138-151.
- Yevenes, M. A., Bello, E. and Sanhueza Guevara, S., 2017, "Spatial distribution of Nitrous Oxide (N₂O) in the Reloncavi estuary-sound and adjacent sea (41°-43° S), Chilean Patagonia", *Estuaries and Coasts*, **40**, 807-821.
- Yu, H., Huang, X., Ning, J. G., Zhu, B. and Cheng, Y., 2014, "Effect of cation exchange capacity of soil on stabilized soil strength", *Soils and Foundations*, **54**, 1236-1240.
- Zhang, K., Li, Y., Zhao, J. and Rizos, C., 2016, "Underwater Navigation Based on Real-Time Simultaneous Sound Speed Profile Correction", *Marine Geodesy*, **39**, 98-111.
- Zhang, Z. L. and Peng, L. M., 1998, "The underground water hydrochemical characteristics on sea water intruded in eastern and southern coasts of Laizhou Bay", *China Environmental Science (in Chinese)*, **18**, 121-125.
- Zhao, Y., Lu, Z. H., Liu, J. and Hu, S., 2017, "Flora characteristics of Chenier Wetland in Bohai Bay and biogeographic relations with adjacent wetlands", *Frontiers of Earth Science*, **11**, 620-628.