Research Article

Elucidating the Pollution Sources and Groundwater Evolution in Typical Seawater Intrusion Areas Using Hydrochemical and Environmental Stable Isotope Technique: A Case Study for Shandong Province, China

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Seawater intrusion has a serious impact on industry, agriculture, and people’s daily life. Thus, the present study was designed to elucidate the pollution sources and groundwater evolution in typical intrusion areas of Shandong Province by hydrochemistry and environmental isotope techniques. The water samples were collected to analyze the groundwater evolution under different intrusion, and groundwater evolution in the south of Laizhou Bay from 2005 to 2019. The findings indicated that the groundwater level dropping funnel caused by overexploitation was the direct causation of seawater intrusion in the three typical intruded areas. The groundwater evolution paths demonstrated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin. The groundwater evolution extent and fitting of mixing lines indicated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin. The groundwater evolution extent and fitting of mixing lines indicated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin. The groundwater evolution extent and fitting of mixing lines indicated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin. The groundwater evolution extent and fitting of mixing lines indicated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin. The groundwater evolution extent and fitting of mixing lines indicated that the groundwater in the south of Laizhou Bay had the fastest evolution rate and the highest degree of evolution, followed by the Dagu River Basin.
1. Introduction

About 40% of the world’s population lives within 100 km of coastal zones [1], and freshwater stored in coastal aquifers has become a vital resource for sustaining the economy of coastal communities around the world [2]. However, with the increase in water demands, groundwater pollution caused by seawater intrusion [3–7], waste disposal of urban residents, and industrial and agricultural production [8–10] have caused severe threats to freshwater resources. Seawater intrusion is widely regarded as a common environmental problem affecting groundwater in coastal areas [11–13]. With 1% mixing of seawater, the groundwater would render the groundwater nonpotable, and further induce soil salinization, ecological degradation, and decline in the quality of agricultural and industrial products [13, 14]. In addition, seawater intrusion changes the pore medium by changing the cohesion between particles and the microbial community in the aquifer, which affects the flow of groundwater in different natural conditions [15–18]. Consequently, it is important to identify the types and evolution of seawater intrusion for proper management actions.

Normally, generalized seawater intrusion includes modern seawater intrusion and palaeosaltwater intrusion [3, 19]. Modern seawater intrusion is mainly caused by the reversal of the hydrodynamic direction between seawater and freshwater in the coastal aquifer due to the changes of natural or human factors. Naturally, seawater intrudes into the freshwater aquifer under the effect of hydraulic gradient and density difference. This type of intrusion mainly occurs in the groundwater system where the seawater is coexisting [13], while palaeosaltwater originates ancient seawater intrusion, which is stored in aquifer after evaporation. In contrast, saltwater intrusion is mainly due to groundwater overexploitation and more susceptible to ecological degradation [20, 21].

Laizhou Bay, Longkou, and Dagu River Basin are the typical areas prone to seawater intrusion in Shandong Province [7, 22, 23]. The types of intrusion include modern seawater, palaeosaltwater, and sea-saltwater mixed intrusions. The environmental problems in the study areas are mainly groundwater problems and a series of problems that it induced. The groundwater in the coastal area was salinized under the influence of the saltwater intrusion, thereby resulting in the deterioration of groundwater quality and the reduction of fresh groundwater resources. This phenomenon has led to environmental problems (such as soil salinization, vegetation degradation, and ecological deterioration) and social problems (such as the disposal of wells, the decline in the quality of industrial and agricultural products, and poor health of residents) [7, 24–27].

Previous studies on seawater/saltwater intrusion in Shandong Province mainly focused on the hydrochemical characteristics of groundwater, influencing factors of seawater intrusion, and characteristics and distribution of seawater intrusion [5, 7, 19, 28–30]. However, comprehensive approaches to type determination of seawater intrusion and comparative analysis to its influence on the ecological environment such as fluorine enrichment are few in coastal aquifer research. Based on previous studies, this work comprehensively studied the current status of seawater intrusion in typical intruded areas in Shandong. The research objectives mainly focus on the following aspects: (1) identification of types of seawater/saltwater intrusion on the south of Laizhou Bay, Longkou, and Dagu River Basins based on the physicochemical indicators and isotopic composition of groundwater; (2) carry out a comparative analysis of characteristics of groundwater evolution under different intrusion conditions and its implication on the environment. For these purposes, data from 1,031 groundwater observation wells were collected from 2005 to 2019 to establish the evolution of groundwater in the seawater/saltwater intrusion, construct a determination system for different intrusion types, and comprehensively analyze saltwater intrusion and its assessment on the ecological environment in Shandong in recent years. The results are expected to provide deep insights into the invasion mechanism under different types and have significant implications for the management of groundwater exploitation in coastal areas.

2. Materials and Methods

2.1. Location and Climatic Conditions. Shandong Province is located on the coast of eastern China, with a land area of approximately 150,000 km² and a coastline of length 3,024 km (Figure 1). The south of Laizhou Bay is located on the northern coastal area of the Shandong Peninsula, with a land area of 2,600 km² and a coastline of 43 km. The study area is bounded between 36°38′–37°20′ N and 118°40′–119°50′ E. The slope of the terrain is gentle and gradually flattens from the south (land) to the north (sea). Longkou is located in the northeast of Shandong Province and the northwest of the Jiaodong Peninsula. The topography of the region is high in the southeast and low in the northwest, thereby showing a stepwise decline. The study area is bounded between 37°31′–37°47′ N and 120°17′–120°40′ E. The Dagu River Basin is located on the west of Jiaodong Peninsula in Shandong Province, which is bounded between 36°10′–37°12′ N and 120°03′–120°25′ E, with a drainage area of 4,631.3 km² and a total river length of 179.9 km. The northern part of the basin is mountainous, and the southern portion is plain. The terrain is high in the north and low in the south, and the slope of the terrain gradually decreases from north to south. The study area ranges from 36°12′ N to 36°26′ N and 120°05′ E to 120°18′ E. These areas belong to warm monsoon climate with the average annual temperature of 11.9–12.5°C. The average temperature is the highest in July with 25.3–40.4°C, and the minimum temperature is −19.5–−4°C in January. The average annual precipitation is 600–656 mm, which is concentrated from June to September [7, 31].

2.2. Hydrogeological Conditions. The south of Laizhou Bay gradually changes from alluvial–diluvial deposits to marine sediments from south to north in the coastal plain. The bedrock is distributed in the mountainous area in the south of the study area. The aquifer is composed of Quaternary sediments [19, 32]. The upper alluvial fan in the south is mainly
composed of gravel and coarse sandstone and gradually evolved into fine sand, silty sand, sandy clay, and silty clay toward the northern seashore.

The aquifers in Longkou are alluvial and diluvial layers formed in Quaternary, which is composed of medium-fine sand-coarse sand and pebbles. The marine deposits near the coastline overlying alluvial deposits and lagoon sediments are composed of fine-coarse sand and fine gravel with good permeability. The marine surface sediments are also mainly silty sand and fine-coarse sand. Accordingly, a good hydraulic connection exists between the seawater and the groundwater in the coastal zone. Ancient river channels exist on land, and they are constructed by coarse constituent materials. Therefore, high permeability makes the ancient river channels a favorable way for seawater intrusion, and it also extends the distance of seawater intrusion [33].

In Dagu River Basin, the Quaternary sediments are dominated by late Pleistocene and Holocene alluvial–alluvial deposits, with a little of marine or continental alternating silt deposits on the southeast edge of the study area. The ancient valley of the Dagu River is an alluvial–diluvial double-layer structure. The upper layer is mainly composed of silty sand, mixed with silty clay and clay. The lower layer is composed of sand and gravel with a large thickness. The grain size of sand and gravel gradually becomes thinner from north to south and becomes thicker from shallow to deep. And the sand layer in the Quaternary is the main aquifer in the study area.

2.3. Sample Collection. The data of water samples are shown in Table 1. All groundwater samples were taken from local domestic supply and monitoring wells. The brine of Laizhou Bay was taken from wells of chemical and aquaculture plants. These wells were continuously pumped. The surface water was from a local river and reservoir, and seawater was local coastal seawater or estuarine seawater. The detailed data are shown in Figure 1 and Table S1 to S8 in Supplementary Data.

2.4. Analytical Methods. The collected samples were placed into precleaned polyethylene plastic bottles immediately after being filtered through a 0.45 μm membrane. The bottle
was sealed with tape to avoid air contact. Thereafter, the collected samples were stored in refrigerators with a temperature below 4°C until analyzed.

The total dissolved solids (TDS) were analyzed on-site with a portable multiparameter water quality analyzer (YSI ProPlus, American YSI). $\text{HCO}_3$ was tested by titration method with phenolphthalein and standard HCl solutions. The major anion concentrations ($\text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\text{SO}_4^{2-}$, and $\text{NO}_3^-$) were analyzed with an ion chromatograph (ICS-3000, American Dionex). The cation concentrations ($\text{K}^+$, $\text{Ca}^{2+}$, $\text{Na}^+$, and $\text{Mg}^{2+}$) were measured with an inductively coupled plasma-atomic emission spectrometer (ICP-MS, American Thermo Fisher). Before the cation was tested, the samples were acidified to $\text{pH} \approx 2$ with $\text{HNO}_3$. The charge balance error in all sample analyses was less than 8%.

The stable isotopic compositions ($\delta^{18}$O and $\delta^2$H) were analyzed with an LGR liquid water isotope laser spectroscope in Nanjing Hydraulic Research Institute. The values of $\delta^{18}$O and $\delta^2$H were calculated based on the Vienna Standard Mean Ocean Water (V-SMOW). The analytical precision values of the long-term standard measurement of $\delta^{18}$O and $\delta^2$H were $\pm 0.2\%$ and $\pm 0.6\%$, respectively.

$$\delta^{18}\text{O}(\delta^2\text{H}) = \frac{R_{\text{Sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \times 1000\%,$$

where $\delta^{18}\text{O}/\delta^{16}\text{O}$ and $\delta^2\text{H}/\delta\text{H}$ represent the isotope ratios of oxygen and hydrogen, respectively; $R_{\text{Sample}}$ represents the $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/\text{H}$ ratio of the samples; and $R_{\text{VSMOW}}$ represents the $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/\text{H}$ ratio of the Vienna Standard Mean Ocean Water.

All groundwater samples were classified into four types based on $\text{Cl}^-$ concentration: freshwater ($<250$ mg/L), brackish water (250–1,000 mg/L), saline water (1,000–19,400 mg/L), and brine (>19,400 mg/L).

### 3. Results and Discussions

#### 3.1. Determination of Intrusion Types

##### 3.1.1. Evolutionary I: Occurrence of Water and Salt

(1) Hydrochemical Compositions. The dominant hydrochemical type of groundwater in the study area can be found in Table 2. The water samples are linearly scattered on both sides of the mixing line (Figures 2 and 3). And the mixing lines are distributed closely parallel to the seawater $\text{Br}^-/\text{Cl}^-$ ratio line (Figure 3). The properties of $\text{Br}^-$ are stable, and most $\text{Br}^-$ in nature is stored in the ocean; thus, $\text{Br}^-$ can be used to infer the source of salt in coastal groundwater [23].

The Gibbs diagram usually is used to indicate the dominant geochemical effects in groundwater evolution [14]. The TDS in water samples gradually increases with an increase of evaporation degree (Figure 4). The degree of evaporation of the brackish water in the study areas is as follows: Laizhou Bay > Dagu River Basin > Longkou. The evaporation level of brine in Laizhou Bay is higher than that of seawater. The mixing line of fresh groundwater and brine coincides with that of fresh groundwater and seawater. The results indicated that brine originated from seawater. The comparison between Figures 4(a) and 4(b) indicated that the increase of $\text{Ca}^{2+}$ concentration in brackish water in Longkou is greater than that of $\text{Na}^+$ with increasing salinity, while the increase of $\text{Ca}^{2+}$ concentration in brackish water is more suppressed compared with that of $\text{Na}^+$ with increasing salinity in the Laizhou Bay and Dagu River Basin, especially for Laizhou Bay. This phenomenon in Longkou is caused by cation exchange, while these phenomena in Laizhou Bay and Dagu River Basin were caused by the palaeosaltwater intrusion. $\text{Ca}^{2+}$ gradually precipitates out of the water with the evaporation and concentration, and the $\text{Ca}^{2+}/\text{Na}^+$ ratio continuously decreases.

| Location          | Year | Groundwater | Brine | Surface water | Seawater | Total | Source           |
|-------------------|------|-------------|-------|--------------|----------|-------|-----------------|
| Shandong          | 2017 | 401         | 0     | 0            | 0        | 401   | This study       |
| Longkou           | 2017 | 50          | 0     | 2            | 52       | 115   | This study       |
| Dagu River Basin  | 2017 | 110         | 4     | 1            | 115      | 2017  | This study       |
|                   | 2009 | 125         | 7     |              |          | 132   | This study       |
|                   | 2018 | 31          | 5     | 2            | 2        | 40    | This study       |
|                   | 2019 | 24          | 10    | 3            | 2        | 39    | This study       |
|                   | 2020 | 86          | 1     |              | 1        | 86    | This study       |
|                   | 2005 | 39          | 1     |              | 1        | 41    | Han et al. [28]  |
|                   | 2006 | 24          | 1     |              |          | 25    | Han et al. [28]  |
|                   | 2007 | 27          | 2     |              |          | 29    | Han et al. [28]  |
|                   | 2008 | 18          | 2     |              |          | 18    | Han et al. [28]  |
|                   | 2009 | 33          | 1     |              |          | 34    | Han et al. [3]   |
|                   | 2010 | 31          | 6     | 1            |          | 38    | Hu [34]          |
|                   | 2013 | 58          | 5     |              |          | 63    | Zhang et al. [7] |
|                   | 2014 | 20          | 2     |              |          | 22    | Zhang et al. [7] |
δ²H and δ¹⁸O Compositions. The stable isotopic compositions of coastal groundwater can be used to infer the recharge sources of groundwater, mixing, and degree of non-equilibrium evaporation. The δ²H and δ¹⁸O values of water samples collected from Laizhou Bay, Longkou, and Dagu River Basin have been shown in Table 3 after statistical analysis.

The δ²H and δ¹⁸O of the groundwater and surface water indicated that the δ²H and δ¹⁸O gradually enrich with increasing salinity. The δ²H and δ¹⁸O of surface water are more abundant than those of groundwater. The δ²H and δ¹⁸O values in fresh groundwater, brackish groundwater, and saline water of the study areas are as follows: Dagu River Basin > Laizhou Bay (2018–2019) > Laizhou Bay (2005) > Longkou. The δ²H and δ¹⁸O values of brine in Laizhou Bay in 2018–2019 are greater than those in 2005.

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(3) Origin of Groundwater and Salt. Most of the water samples are linearly distributed on the right side of the global meteoric water line (GMWL: δ²H = 8δ¹⁸O + 10) proposed by Craig [35] and both sides of the local meteoric water line (LMWL: δ²H = 7.4δ¹⁸O + 1.1) based on the monthly precipitation data of Changyi weather station in Laizhou Bay in 2006 [3] (Figure 5(a)). Some groundwater samples are distributed near the mixing line of groundwater and the local river (Figure 5(b)). Therefore, it can be concluded that modern precipitation promotes the renewal of groundwater, and rivers are the source of the lateral recharge of groundwater. The mixing lines are distributed closely parallel to the seawater Br⁻/Cl⁻ ratio line, and the water samples are linearly scattered on both sides of the mixing line (Figure 3), which indicates that the salt in groundwater comes from the saltwater intrusion. However, the deviation of the water sample from the mixing line in Laizhou Bay, Longkou, and Dagu River Basin is different (the deviation of Longkou > that of Dagu River Basin > that of Laizhou Bay), which indicated that the groundwater mixing sources (brine, seawater, or saltwater), the mixing level, and geochemical evolution were different. The Gibbs diagram indicates that rock dissolution contributed to the salt in fresh groundwater, and saline water and brine in Laizhou Bay are dominated by evaporation [36], which is different from that of Longkou and Dagu River Basin.

3.1.2. Evolutionary II: Mixing Process

(1) δ¹⁸O and Cl⁻. These water samples are not strictly distributed along the mixing line of two different water bodies due to the diversity of mixed water and geochemical effects. The properties of δ¹⁸O and Cl⁻ are stable, and δ¹⁸O in ground-water is closely related to the mixing line of originated waters. Therefore, the deviation of water samples from the
mixing lines can be used to determine the dominant source in the mixing process.

Most groundwater samples are scattered on the freshwater member (Figure 5(b)). The brackish water samples in 2005 and 2018–2019 are closely scattered to the mixing line of freshwater and seawater, with the seawater mixing proportion ranges of 0%–20% and 0%–5%, respectively. The saline water samples in 2005 and 2018–2019 are distributed near the mixing line of freshwater and brine, with the brine mixing proportion ranges of 5%–15% and 10%–40%, respectively. Brine (palaeosaltwater) mixing produces a more severe salinization effect compared with seawater mixing; thus, it can be used to determine the type of intrusion. Most brackish water fits a freshwater–seawater mixing trajectory, thereby suggesting classic seawater intrusion. The saline water fits a freshwater–brine mixing trajectory, thereby suggesting brine (palaeosaltwater) intrusion. The $\delta^2$H and $\delta^{18}$O values of brine in Laizhou Bay (2018–2019) are greater than those of Laizhou Bay (2005). In combination with long-term fresh groundwater and brine mining history, the results indicated that brine was diluted with seawater intrusion.

The brackish water samples are close to the mixing line of freshwater–local seawater, and the mixed level is less than 5%. The results indicate that the brackish water in Longkou is salinized by modern seawater intrusion. Some water samples in Dagu River Basin are scattered near the mixing line of freshwater–local saltwater, which is shown in the red hollow circle. These samples are collected from the east bank of the Dagu River Basin and the north side of the cutoff wall, where residual saltwater exists [23]. The results indicate that the brackish water in these two areas is salinized by residual saltwater intrusion. The other groundwater collected from the south of the Dagu River Basin is closely distributed to the mixing line of freshwater–seawater, which is affected by seawater intrusion [23]. The mixed level of brackish water is in the range of 0%–15%, and that of saline water is 30%–50%. The results further verified that groundwater in the south of the Dagu River Basin is salinized by seawater intrusion. The river samples are distributed between two mixed lines (freshwater–local saltwater and freshwater–seawater), thereby indicating that rivers play an important role in groundwater salinization.

(2) Hydrochemical Facies Evolution. It can be found from Table 2 that the hydrochemical type of freshwater is Ca-Na-HCO$_3$-Cl or Na-HCO$_3$-Cl in Laizhou Bay in 2005. The brackish is Na-Cl-HCO$_3$. The saline water and brine are Na-Cl. The complete groundwater evolution path is Ca-
HCO₃ → Ca-HCO₃-Cl → Ca-Na-HCO₃-Cl → Na-HCO₃-Cl → Na-Cl-HCO₃ → Na-Cl. The hydrochemical type of freshwater in Laizhou Bay in 2018–2019 is Ca(Na)-HCO₃ or Na-Mg-HCO₃-Cl. The brackish is Mg-Na-Cl-HCO₃ or Na-Cl-SO₄. The saline water and brine are Na-Cl. The complete groundwater evolution path is Ca-HCO₃ → Na(Mg)-HCO₃-Cl → Na(Mg)-Cl-HCO₃ → Na-Cl-SO₄ → Na-Cl. The evolution path in 2018–2019 is shorter, and the evolution speed is faster than that in 2005. The Na⁺ enrichment rate is higher compared with Cl⁻.

The hydrochemical type of fresh groundwater in Longkou is Ca-HCO₃-Cl, and that of brackish is Ca-Cl-HCO₃ or Ca-Na-Cl-HCO₃. The complete groundwater evolution path is Ca-HCO₃ → Ca-Cl-HCO₃-Cl → Ca-Cl-HCO₃ → Ca-Na-Cl-HCO₃-Cl → (Ca-Na-Cl) → (Na-Cl). The current terminal evolution stage is Ca-Na-Cl-HCO₃, and the Cl⁻ enrichment rate is higher compared with that of Na⁺.

The hydrochemical type of fresh groundwater in the Dagu River Basin is Ca(Na)-HCO₃ or Na-Ca-HCO₃-Cl. The brackish and saline water types are Na-Cl-HCO₃(SO₄) and Na-Cl, respectively. The groundwater evolution path is Ca-Na-HCO₃ → Na-Ca-HCO₃-Cl → Na-HCO₃-Cl → Na-Cl-HCO₃-Cl → Na-Cl. During salinization, the increased rate of Na⁺ and Cl⁻ in groundwater determines the evolution speed and path, while the type of mixed water and the degree of mixing determine the enrichment rate of Na⁺ and Cl⁻. The salinization efficiency of brine (paleosalternate) mixing in Laizhou Bay is greater than that of sea-saltwater mixing in the Dagu River Basin, and the salinization efficiency of seawater intrusion in Longkou is the lowest one according to the δ¹⁸O and Cl⁻ mixing process and Piper diagram (Figure 6). Accordingly, the groundwater in Laizhou Bay had a higher degree of mixing and faster speed of evolution in 2018–2019 compared with those in 2005. The groundwater evolution in the Dagu River had a high starting level, and the evolution speed is second only to the groundwater in Laizhou Bay. The saltwater in Longkou had the lowest degree of mixing.

3.1.3. Evolutionary III: Water-Rock Interaction

(1) Ion Exchange. In a conservative mixing process of different water, the hydrochemical compositions of mixed water will increase strictly along the mixing line in a fixed ratio with the increase of the mixing degree. However, most mixed water in nature would deviate from the mixing line to varying degrees. The dominant effect contributing to
this phenomenon is ion exchange, namely, CaX⁺₂Na⁺₊→Ca²⁺₂NaX and MgX⁺₂Na⁺₊→Mg²⁺₂NaX. Most groundwater samples are distributed on the upper side of the mixing line (Figure 7(a)). The groundwater in Longkou deviates the most from the mixing line, followed by Laizhou Bay (2005), Laizhou Bay (2018–2019), and Dagu River Basin. This finding indicates that the Ca²⁺–Na⁺ exchange rate in groundwater in Longkou is the highest, followed by Laizhou Bay in 2005, Laizhou Bay in 2018–2019, and Dagu River Basin. The degree of the Mg²⁺–

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**Table 3: Stable isotopic compositions of water samples.**

| Type of samples | Range of δ²H (‰) | Mean value of δ²H (‰) | Range of δ¹⁸O (‰) | Mean value of δ¹⁸O (‰) |
|-----------------|-------------------|-----------------------|-------------------|-----------------------|
| **Laizhou Bay (2005)** | | | | |
| Fresh | −70 to −40 | −50.44 | −9.7 to −4.6 | −6.76 |
| Brackish | −73 to −51 | −57.94 | −9.7 to −5.4 | −7.34 |
| Saline | −68 to −41 | −56.38 | −8.9 to −4.2 | −6.55 |
| Brine | −43 to −21 | −36.31 | −6.2 to −1.3 | −3.65 |
| **Laizhou Bay (2018–2019)** | | | | |
| Fresh | −60.99 to −36.55 | −51.81 | −8.52 to −4.86 | −7.25 |
| Brackish | −57.12 to −40.28 | −49.96 | −7.62 to −6.05 | −6.89 |
| Saline | −56.98 to −38.85 | −50.14 | −7.78 to −2.98 | −6.52 |
| Brine | −50.3 to −15.64 | −33.49 | −6.22 to −2.31 | −4.36 |
| Surface | −52.12 to −23.55 | −34.08 | −6.69 to −2.9 | −4.09 |
| **Longkou** | | | | |
| Fresh | −60.31 to −27.99 | −55.39 | −8.57 to −2.44 | −7.65 |
| Brackish | −61.45 to −52.29 | −56.8 | −8.47 to −7.24 | −7.89 |
| **Dagu River Basin** | | | | |
| Fresh | −55.09 to −37.58 | −49.49 | −7.74 to −4.48 | −6.94 |
| Brackish | −55.58 to −42.52 | −50.03 | −7.88 to −5.09 | −6.8 |
| Saline | −44.5 to −33.6 | −39.28 | −5.89 to −3.48 | −4.78 |
| Surface | −25.72 to −19.77 | −22.25 | −2.49 to −1.22 | −1.71 |
Na⁺ exchange in the groundwater samples of Laizhou Bay (2005) is low (Figure 7(b)). No significant difference exists in the degree of Mg²⁺–Na⁺ exchange in the remaining groundwater samples. Compared with the ion exchange between Ca²⁺–Na⁺ and Mg²⁺–Na⁺, the degree of Ca²⁺–Na⁺ exchange in groundwater is significantly higher than that of Mg²⁺–Na⁺. The degree of ion exchange in the freshwater and brackish water is greater than that of saline water, which indicates that salinity has no significant positive correlation with the ion exchange in groundwater.

(2) Enrichment Effect. Ion enrichment is also one of the dominant effects that cause the water samples to deviate from the mixing line, for example, F⁻ enrichment in groundwater.

The fluoride-rich groundwater [37] can be caused by anthropogenic activities. However, the fluoride-rich of groundwater in most areas is due to natural conditions, for example, the dissolution of fluoride-rich minerals [38]. CaF₂ is considered to be the dominant source of fluoride in groundwater. The main mechanism of fluorine enrichment in groundwater is as follow:

\[
\text{CaF}_2 + 2\text{NaHCO}_3 = \text{CaCO}_3 + 2\text{Na}^+ + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2 \\
\text{CaF}_2 + 2\text{HCO}_3^- = \text{CaCO}_3 + 2\text{F}^- + \text{H}_2\text{O} + \text{CO}_2
\]

The solubility of NaF (41,700 mg/L) is much greater than that of CaF₂ (15 mg/L), and F⁻ is easier to bind with Na⁺ compared with Ca²⁺ and Mg²⁺. The increase of (Na⁺ + K⁺)/Ca²⁺ in groundwater will promote the release and enrichment of F⁻ in the surrounding rocks [39]. Meanwhile, the increase of HCO₃⁻ content in groundwater will also play the same role as (Na⁺ + K⁺)/Ca²⁺ [14]. Saltwater intrusion has a positive effect on the release of F⁻ in groundwater in coastal areas by increasing the (Na⁺ + K⁺)/Ca²⁺ value in groundwater [40].

![Figure 5: Stable isotopic compositions and the relationship between Cl⁻ and δ¹⁸O. The samples of LZB were collected in 2018–2019.](http://pubs.geoscienceworld.org/gsa/lithosphere/article-pdf/doi/10.2113/2021/4227303/5398230/4227303.pdf)
The $F^{-}$ in groundwater increases with the increase of $\text{HCO}_3^-$ and $(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$ (Figure 8). The linear relationship of $F^{-}-\text{HCO}_3^-$ and $F^{-}-(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$ are $F^{-} = 0.0016\text{HCO}_3^- + 0.6592$ ($R^2 = 0.0687$, $N = 142$) and $F^{-} = 0.0398(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+} + 0.9576$ ($R^2 = 0.2219$, $N = 142$), respectively, while the value of $\text{HCO}_3^-$ concentration is much larger than $(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$ value, which indicates that the enrichment efficiency of $\text{HCO}_3^-$ for $F^{-}$ is significantly higher than that of $(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$. There is no significant difference in groundwater $\text{HCO}_3^-$ content in the three study areas, while values of $(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$ increase with the increase of salinity, and the values of $(\text{Na}^+ + \text{K}^+)/\text{Ca}^{2+}$ in groundwater are as follows: Laizhou Bay $>$ Dagu River Basin $>$ Longkou. It can be concluded that the high fluorine in groundwater originates from the dissolution of fluorine-containing minerals caused by saltwater intrusion. And the palaesoaltsaltwater intrusion in Laizhou Bay has the most significant promotion effect on fluorine enrichment, followed by the sea-saltwater mixed intrusion in the Dagu River, and the last is the seawater intrusion in Longkou.

3.2. Types of Intrusion in the Study Areas. Most groundwater in coastal areas of Shandong has been intruded to varying degrees (Figure 8). The main intrusion types include modern seawater, palaesoaltsaltwater, and sea-saltwater mixed intrusion. The groundwater in Laizhou Bay has the fastest evolution speed and the highest extent of evolution in the three study areas. The saline water samples of Laizhou Bay in 2018–2019 are scattered near the mixing line of freshwater and brine, with the mixing proportion ranges from 10% to 40%, which indicated that the groundwater in Laizhou Bay is affected by the palaesoaltsaltwater intrusion. The groundwater samples in Longkou are close to the mixing line of freshwater and seawater, and the mixed level is less than 5%. This finding indicated that the brackish water in Longkou is salinized by modern seawater intrusion. The speed and extent of groundwater evolution in the Dagu River Basin are between Laizhou Bay and Longkou. And some water samples are scattered near the mixing line of freshwater and saltwater, and the others are closely distributed to the mixing line of freshwater and seawater. This finding verified that
groundwater in the Dagu River Basin is dominated by sea-saltwater mixed intrusion.

According to the regional survey of Shandong in 2017, the distribution of salt groundwater is approximate 23,000 km² (Figure 9). Palaeosaltwater intrusion is mainly distributed in the south and west of Laizhou Bay, accounting for about 22,000 km². Seawater intrusion is distributed along the coastline of Shandong accounting for 700 km². And sea-saltwater mixed intrusion distributed in the east of Laizhou Bay and Dagu River Basin accounts for 300 km².
With regarding the scope of the intrusion, the area of palaeo-saltwater intrusion in the Laizhou Bay area is the largest; the intrusion distance to inland is the longest. The distance of sea-saltwater mixed intrusion to inland in the Dagu River Basin is larger than that of Longkou.

Three large groundwater level dropping funnels are in Changyi City, Shouguang City, and the coastal area on the south of Laizhou Bay, respectively (Figure 9(a)). The dropping funnels in Changyi and Shouguang are fresh groundwater level dropping funnels, while those in the coastal area are brine dropping funnels, which are distributed in a stripe shape along the east-west direction. From the sea to the land, brine, saline water, brackish water, and freshwater are distributed in sequence. Saline water and brackish water are evolution products of brine intruding into fresh groundwater. The width of the saline groundwater zone near the groundwater level dropping funnel in Changyi City is larger. This finding indicates that the decline of the groundwater level is the main factor of palaeosaltwater intrusion. The scope of intrusion increases from 2009 to 2013 and then decreases in the south of Laizhou Bay.

Two large groundwater level dropping funnels are in the northern coastal area of Longkou city (Figure 9(b)). The scope of seawater intrusion is near the dropping funnel, thereby indicating that the main factor of seawater intrusion in this area is the overexploitation of groundwater. From 2005 to 2018, the scope of intrusion has increased, and the increased area is mainly distributed between the two dropping funnels. However, the cutoff wall has decreased the seawater intrusion distance in the north-south direction but increased in the east-west direction.

The scope of intrusion in the Dagu River Basin has decreased from 2009 to 2018 (Figure 9(c)). The intrusion in 2009 and 2018 shows that the intrusion distance on the north of Jiaozhou Bay is greater than that on the east and west of Jiaozhou Bay. However, the cutoff wall has hindered sea-saltwater mixed intrusion towards the north, but the intrusion scope on the east side of the cutoff wall gradually
increases. It can be concluded that the cutoff wall hinders the longitudinal intrusion and causes the horizontal expansion of intrusion along the cutoff wall. Moreover, dense villages and farming areas are distributed on the north side; thus, the long-term overexploitation of groundwater causes the sea-saltwater mixed intrusion.

3.3. Evolution of Groundwater in Laizhou Bay. Three large-scale groundwater level dropping funnels (one palaeosaltsaltwater level dropping funnel and two freshwater level dropping funnels) are distributed in a stripe shape along the east-west direction on the south of Laizhou Bay. The coastal palaeosaltsaltwater has intruded the fresh groundwater due to the groundwater level dropping funnel, and the degree of intrusion gradually decreases from sea to inland. Therefore, brine, saline, brackish groundwater, and fresh groundwater are distributed in a stripe from the sea to the inland. The width of the brine gradually decreased from west to east, while the width of the saline and brackish water gradually increased from west to east. In the Changyi area, the boundary between saline water and brackish water is blurred, and the width of the saline water is large. The intrusion line is consistent with the east-west centerline of the dropping funnel. The palaeosaltsaltwater intrusion cannot cross the center of the groundwater level dropping funnel. Thus, the groundwater level dropping funnel hinders the further development of the intrusion even though it induces palaeosaltsaltwater intrusion.

We have selected a typical section I–I’ to study the evolution of palaeosaltsaltwater intrusion on the south of Laizhou Bay from 2005 to 2019 (Figure 10). The scope and extent of palaeosaltsaltwater intrusion were the smallest in 2005, gradually increased from 2006 to 2009, reached the largest in 2010, and then gradually decreased until 2019.

The saltwater of Laizhou Bay maintained the mixing between brine and freshwater from 2005 to 2006 (Figure 11; red dashed circle). The oxygen isotopic composition did not significantly change with the increase of Cl\(^{-}\) concentration. In 2010 (green dashed circle), the distance of palaeosaltsaltwater intrusion was large. The oxygen isotope in saline water gradually enriched with the increase of intrusion. In 2013–2014 (black dashed circle), palaeosaltsaltwater intrusion gradually weakened. However, the hydrochemical characteristics of saline water were similar to that in 2010, showing a trend of continued enrichment. In 2018–2019 (blue dashed circle), the oxygen isotopic composition remained stable with the
increase of the intrusion, its mixing degree was between 2010 and 2013–2014, and the groundwater samples in 2018–2019 are scattered near to the average mixing line of freshwater and brine compared with that of 2013–2014. According to Figure 12(a), the major ion in brackish and saline water in Laizhou Bay remains stable, while Figure 12(b) shows that the ratio of Br/Cl increases from 2006 to 2010 and then decreases, which is consistent with the intrusion characteristics in Laizhou Bay. It can be concluded that the hydrogen and oxygen isotopes in the mixed water enrich gradually when the proportion of brine mixed into freshwater increases, while the decrease of the stable isotopes in the mixed water is delayed compared with the regression of palaeosaltwater intrusion.

The borehole data from Laizhou Bay in 2020 (Table S8 and Figure S9) shows that there is a porewater hydrochemical mutation interface at 40 m depth; the value of the stable isotopes and Br⁻ in the groundwater buried within 40 m is higher than that of the groundwater buried between 40 and 80 m. These results indicate that palaeosaltwater intrusion mainly occurs in aquifers buried within 40 m, while aquifers deeper than 40 m are slightly affected by palaeosaltwater intrusion and anthropogenic activities. In the groundwater system where palaeosaltwater intrusion occurs, the stable isotopes in the aquiclude are more enriched compared with the aquifer, and the salinity ratio of aquiclude to the aquifer is lower than the stable isotopes. Combined with the attenuation hysteresis of the stable isotopes in mixed water, it can be proved that the chemical osmosis [41–43] and the electric double layer of clay film allow the stable isotope exchange and enrichment in the aquiclude compared to salinity during the seawater intrusion. The stable isotopes in the aquiclude are released and attenuate after salinity in the aquifer attenuates during the saltwater retreat.

3.4. Anthropogenic Influences on the Local Environment

3.4.1. Fluorine Pollution. Fluoride is highly toxic to living organisms. When the concentration exceeds 25 ppm, fluoride irritates the eyes and respiratory system and harms the liver and kidneys. When the concentration of fluorine reaches 100 ppm, the eyes and nose will be seriously damaged. If the concentration reaches 1000 ppm, then breathing for a few minutes can be fatal. Organic fluorine is biopersistent and can stay in nature for a long time and enrich in the organism.

F⁻ pollution in Laizhou Bay is more serious than that in the Dagu River Basin (Figure 8). The F⁻ concentration in almost all groundwater samples of Longkou is far below safety standards. Approximately 5.13% of the total groundwater samples in the Dagu River Basin exceeded the safety standard (C_F < 1 mg/L) set by the National Sanitary Standard for drinking water in China [44]. 28 of the 63 groundwater samples in Laizhou Bay in 2013 exceeded the safety standard, accounting for 44.44% of the total water samples. The proportion of groundwater samples exceeding the safety standard in 2014, 2018, and 2019 is 35%, 70%, and 54.84%, respectively. The F⁻ pollution in 2018 is most serious, followed by that of 2019. And the pollution degree in saline water and brine is higher than that of freshwater and brackish water.

3.4.2. Nitrate Pollution. Nitrate is a common pollutant in groundwater. The nitrate sources are mainly industrial, agricultural, and domestic waste, which is closely related to anthropogenic activities. Nitrate will be reduced to toxic nitrite under certain conditions, and nitrite reacts with the human blood to form methemoglobin. Accordingly, the blood loses its oxygen-carrying capacity, thereby causing health problems.

The safety standard for nitrate in drinking water is less than 20 mg/L, which is set by the Standardization Administration of China (GB/T 14848-2017) [45]. 46 of the 89 groundwater samples in Laizhou Bay in 2005 exceed the safety standard, accounting for 51.69% of the total water samples. The proportion of groundwater samples exceeding the safety standard in Laizhou Bay in 2018–2019 is 41.79%, Longkou is 95.92%, and Dagu River Basin is 56.25%. The nitrate content of groundwater in Laizhou Bay (2005) has a range of 0.2 mg/L–309.2 mg/L, with an average value of 56.30 mg/L. Meanwhile, the nitrate content of groundwater in Laizhou Bay (2018–2019) is 0.09 mg/L–881.78 mg/L, with an average value of 57.78 mg/L. The nitrate concentration of groundwater in Longkou is 14.11 mg/L–672.48 mg/L, and the average value is 225.14 mg/L. Meanwhile, the nitrate concentration of groundwater in the Dagu River Basin is 1.68 mg/L–366.76 mg/L, and the average value is 67.7 mg/L.
Therefore, the nitrate pollution in groundwater in the Longkou area is the most serious, followed by the Dagu River Basin. Nitrate pollution in groundwater in the Laizhou Bay is severe though it has been decreasing from 2005 to 2019. Groundwater nitrate pollution is serious in freshwater and brackish water distribution areas (Table 4). The aforementioned areas are agricultural farming or population gathering areas. Accordingly, the chemical fertilizers and pesticides, industrial waste, and domestic waste are the main causes of nitrate pollution in coastal groundwater of Shandong. In the south of Laizhou Bay, nitrate pollution in saline water and brine samples were serious in 2005.
However, pollution in 2018–2019 has been alleviated. Many saltworks and chemical plants are distributed in the brine area in the south of Laizhou Bay. The sampling wells are generally close to the human activity area. Domestic waste enters the saline groundwater or brine through the leaching infiltration or poor water stop wells, thereby causing nitrate pollution.

4. Conclusions

The palaeosaltsaltwater mixing would produce a more severe salinization impact compared with seawater mixing; thus it can be used to determine the type of intrusion. The groundwater evolution speed and extent in Laizhou Bay are the highest in the three study areas, the groundwater samples are scattered close to the mixing line of brine and freshwater, and the brine as the initial groundwater distributed in a stripe shape on the south of Laizhou Bay. These findings confirm that the groundwater in Laizhou Bay is dominated by palaeosaltsaltwater intrusion. The groundwater evolution speed and extent in Longkou are the lowest, and the groundwater samples are close to the mixing line of freshwater and local seawater. These findings show that the brackish water in Longkou is salinized by modern seawater intrusion. Meanwhile, the brackish water in Dagu River Basin is between Laizhou Bay and Longkou. Some groundwater samples are scattered near the mixing line of freshwater and local saltwater. And the others are closely distributed to the mixing line of freshwater and local seawater, thereby verifying that the groundwater in Dagu River Basin is dominated by the sea-saltwater mixed intrusion.

The groundwater samples of the three typical intrusion areas are in different stages of evolution and present varying evolutionary trends due to diverse intrusion. The groundwater evolution path of Laizhou Bay in 2005 is Ca-HCO$_3$ $\rightarrow$ Ca-HCO$_3$+Cl $\rightarrow$ Ca-Na-HCO$_3$+Cl $\rightarrow$ Na-HCO$_3$+Cl $\rightarrow$ Na-Cl-HCO$_3$ $\rightarrow$ Na-Cl. The groundwater evolution path is Ca-HCO$_3$ $\rightarrow$ Na(Mg)-HCO$_3$+Cl $\rightarrow$ Na(Mg)-Cl-HCO$_3$ $\rightarrow$ Na-Cl-SO$_4$ $\rightarrow$ Na-Cl in 2019. The evolution path of groundwater in the Longkou area is Ca-HCO$_3$ $\rightarrow$ Ca-HCO$_3$+Cl $\rightarrow$ Ca-Cl-HCO$_3$ $\rightarrow$ Ca-Na-Cl-HCO$_3$ $\rightarrow$ (Ca-Na-Cl) $\rightarrow$ (Na-Cl). The evolution path of groundwater in the Dagu River Basin is Ca-Na-HCO$_3$ $\rightarrow$ Ca-Na-HCO$_3$+Cl $\rightarrow$ Na-Cl-HCO$_3$ $\rightarrow$ Na-Cl-HCO$_3$ $\rightarrow$ Na-Cl. The groundwater in Laizhou Bay has the fastest evolution rate and the highest degree of evolution, followed by that of the Dagu River Basin. By contrast, the evolution starting point of groundwater in the Dagu River Basin is high. In Laizhou Bay, the extent and scope of palaeosaltsaltwater intrusion gradually increased from 2005 to 2010 and then slowly eased from 2011 to 2019. The palaeosaltsaltwater intrusion was small in 2005 and large in 2010. Correspondingly, the isotopes are gradually enriched as the intrusion increases, while the decrease of that is delayed compared with the saltwater retreat, which is caused by that the stable isotopes enriched in the aquiclude due to chemical osmosis will be released and attenuate after salinity in the aquifer attenuate during the saltwater retreat.

Anthropogenic activity is the main cause of saltwater intrusion and environmental pollution in the coastal area of Shandong. The F$^-$ pollution in groundwater has been attributed to saltwater intrusion. Among the three typical intruded areas, the groundwater F$^-$ pollution in the south of Laizhou Bay is the most serious due to the palaeosaltsaltwater intrusion. The F$^-$ concentration in most groundwater in the Longkou and Dagu River Basin is below the safety standard. The F$^-$ concentration in saline water and brine is higher than those of freshwater and brackish water. Under the influence of anthropogenic activities, the nitrate concentration in groundwater in the Longkou area seriously exceeded the safety standards, followed by the Dagu River Basin. Although the groundwater nitrate pollution in the Laizhou Bay area is gradually mitigating, the pollution situation is still severe.

**Data Availability**

The data are listed in the Supplementary Materials.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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**Supplementary Materials**

The supplementary file includes Tables S1~S8. These data are obtained by the sampling and analysis from 2009 to 2020, and the analysis method can be found in Section 2.4 of the manuscript. The data of Cl$^-$ concentration from Tables S1, S2, S3, S4, S5, and S7 are mainly used to indicate the seawater intrusion and determine the groundwater type (discussed in the manuscript) and draw the intrusion extent in Shandong Province (results in Figures 1, 9, and 10). These data of conventional hydrochemical indexes and stable isotope from Tables S2 to S5 are mainly used to study the determination of intrusion type and groundwater evolution in Section 3 of the manuscript. These data of F$^-$ and NO$^{-3}$-3 from Tables S2~S6 are mainly used to study the anthropogenic influences on the local environment (discussed in Section 3.4 and the results in Section 3.4 and conclusion). The data from Table S8 is used to explain the isotope hysteresis phenomenon in intruded aquifer (discussed in the Section 3.3, Figure 11).
References

[1] R. Panipilla, “Ocean conference: learning from the ocean,” Samadhu Report, vol. 77, pp. 62–65, 2017.

[2] I. E. M. de Graaf, T. Gleson, L. P. H. (Rens) van Beek, E. H. Sutanudjaja, and M. F. P. Bierkens, “Environmental flow limits to global groundwater pumping,” Nature, vol. 574, no. 7776, pp. 90–94, 2019.

[3] D. M. Han, X. F. Song, M. J. Currell, J. L. Yang, and G. Q. Xiao, “Chemical and isotopic constraints on evolution of groundwater salinization in the coastal plain aquifer of Laizhou Bay, China,” Journal of Hydrology, vol. 508, pp. 12–27, 2014.

[4] H. Ketabchi and M. S. Jahangir, “Influence of aquifer heterogeneity on sea level rise-induced seawater intrusion: a probabilistic approach,” Journal of Contaminant Hydrology, vol. 236, p. 103753, 2021.

[5] G. Q. Liu, S. Y. Zhou, X. D. Huang, T. Liu, D. Xu, and C. D. Yue, “Multiple methods to recognize sources of underground water nitrate contamination in plain area of Dagu River, Qingdao, China,” Acta Scientiarum Circumstantiarum, vol. 37, no. 1, pp. 347–356, 2017.

[6] X. Xu, G. Xiong, G. Chen et al., “Characteristics of coastal aquifer contamination by seawater intrusion and anthropogenic activities in the coastal areas of the Bohai Sea, eastern China,” Journal of Asian Earth Sciences, vol. 217, p. 104830, 2021.

[7] X. Y. Zhang, J. Miao, B. X. Hu, H. Liu, H. Zhang, and Z. Ma, “Hydrogeochemical characterization and groundwater quality assessment in intruded coastal brine aquifers (Laizhou Bay, China),” Environmental Science and Pollution Research, vol. 24, no. 26, pp. 21073–21090, 2017.

[8] F. Alshehri, S. Almadani, A. S. el-Sorogy, E. Alwaqdan, H. J. Alifaifi, and T. Alharbi, “Influence of seawater intrusion and heavy metals contamination on groundwater quality, Red Sea coast, Saudi Arabia,” Marine Pollution Bulletin, vol. 165, p. 112094, 2021.

[9] M. N. Amin, C. Kroeze, and M. Strokal, “Human waste: an underestimated source of nutrient pollution in coastal seas of Bangladesh, India and Pakistan,” Marine Pollution Bulletin, vol. 118, no. 1-2, pp. 131–140, 2017.

[10] G. van Drecht, A. F. Bouwman, J. Harrison, and J. M. Knoop, “Global nitrogen and phosphate in urban wastewater for the period 1970 to 2050,” Global Biogeochemical Cycles, vol. 23, no. 4, 2009.

[11] S. Jaseckho, D. Perrone, H. Seybold, Y. Fan, and J. W. Kirchner, “Groundwater level observations in 250,000 coastal US wells reveal scope of potential seawater intrusion,” Nature Communications, vol. 11, no. 1, p. 3229, 2020.

[12] L. Shi and J. J. Jiao, “Seawater intrusion and coastal aquifer management in China: a review,” Environmental Earth Sciences, vol. 72, no. 8, pp. 2811–2819, 2014.

[13] A. D. Werner, M. Bakker, V. E. A. Post et al., “Seawater intrusion processes, investigation and management: recent advances and future challenges,” Advances in Water Resources, vol. 51, pp. 3–26, 2013.

[14] G. Y. Xiong, G. Q. Chen, X. Y. Xu et al., “A comparative study on hydrogeochemical evolution and quality of groundwater in coastal areas of Thailand and Bangladesh,” Journal of Asian Earth Sciences, vol. 195, p. 104336, 2020.

[15] Y. Chen, Z. Zhou, J. Wang, Y. Zhao, and Z. Dou, “Quantification and division of unfrozen water content during the freezing process and the influence of soil properties by low-field nuclear magnetic resonance,” Journal of Hydrology, vol. 602, p. 126719, 2021.

[16] Z. Dou, Z. Chen, Z. Zhou, J. Wang, and Y. Huang, “Influence of eddies on conservative solute transport through a 2D self-affine fracture,” International Journal of Heat and Mass Transfer, vol. 121, pp. 597–606, 2018.

[17] Z. Dou, B. Sleep, H. Zhan, Z. Zhou, and J. Wang, “Multiscale roughness influence on conservative solute transport in self-affine fractures,” International Journal of Heat and Mass Transfer, vol. 133, pp. 606–618, 2019.

[18] Z. Dou, Z. Zhou, J. Wang, and Y. Huang, “Roughness scale dependence of the relationship between tracer longitudinal dispersion and Peclét number in variable-aperture fractures,” Hydrological Processes, vol. 32, no. 10, pp. 1461–1475, 2018.

[19] Y. Xue, J. Wu, S. Ye, and Y. Zhang, “Hydrogeological and hydrogeochemical studies for salt water intrusion on the south coast of Laizhou Bay, China,” Ground Water, vol. 38, no. 1, pp. 38–45, 2000.

[20] S. Liu, Z. Tang, M. Gao, and G. Hou, “Evolutionary process of saline-water intrusion in Holocene and Late Pleistocene groundwater in southern Laizhou Bay,” Science of The Total Environment, vol. 607-608, pp. 586–599, 2017.

[21] D. S. Vinson, T. Tagma, L. Bouchaou, G. S. Dwyer, N. R. Warner, and A. Vengosh, “Occurrence and mobilization of radium in fresh to saline coastal groundwater inferred from geochemical and isotopic tracers (Sr, S, O, H, Ra, Rn),” Applied Geochemistry, vol. 38, pp. 161–175, 2013.

[22] J. C. Wu, F. Meng, X. Wang, and D. Wang, “The development and control of the seawater intrusion in the eastern coastal of Laizhou Bay, China,” Environmental Geology, vol. 54, no. 8, pp. 1763–1770, 2008.

[23] G. Xiong, Q. An, T. Fu, G. Chen, and X. Xu, “Evolution analysis and environmental management of intruded aquifers of the Dagu River Basin of China,” Science of The Total Environment, vol. 719, p. 137260, 2020.

[24] T. Li, Q. Y. Wu, L. Yao, J. F. Cao, Y. H. Liu, and R. C. Song, “Effects of different land use types on pollution distance of heavy metals in north plain of Longkou city,” Research of Environmental sciences, vol. 32, no. 7, pp. 1224–1230, 2019.

[25] K. Li, C. Liu, Y. Ma, and X. Wang, “Land-based dissolved organic nitrogen dynamics and bioavailability in Jiaozhou Bay, China,” Estuarine, Coastal and Shelf Science, vol. 220, pp. 13–24, 2019.

[26] W. Qu, H. Li, H. Huang et al., “Seawater-groundwater exchange and nutrients carried by submarine groundwater discharge in different types of wetlands at Jiaozhou Bay, China,” Journal of Hydrology, vol. 555, pp. 185–197, 2017.

[27] X. Zhou, Source, Spatial Distribution and Ecological Risk Assessment of Heavy Metals in Soil of Longkou City, Shandong Normal University, Jinan, 2019.

[28] D. M. Han, C. Kohfahl, X. Song, G. Xiao, and J. Yang, “Geochemical and isotopic evidence for palaeo-seawater intrusion into the south coast aquifer of Laizhou Bay, China,” Applied Geochemistry, vol. 26, no. 5, pp. 863–883, 2011.

[29] J. C. Wu, P. M. Liu, Q. B. Jiang, and J. J. Wang, “Seawater intrusion in Laizhou Bay district of Shandong Province,” Jiangsu Geology, vol. 17, no. 1, pp. 27–31, 1993.

[30] Y. X. Zhang, Y. Q. Xue, and H. H. Chen, “Salt-brine water intrusion and its chemical characteristics in Weifang area of
southern coast of Laizhou Bay,” *Earth Science-Journal of China University of Geosciences*, vol. 22, no. 1, pp. 94–98, 1997.

[31] Q. F. Yang, R. J. Wang, S. N. Xu et al., "Hydrogeochemical and stable isotopic characteristics of brine in Laizhou Bay," *Geological Review*, vol. 62, no. 3, pp. 343–352, 2016.

[32] Z. C. Peng, Y. Han, X. Zhang et al., "The study of the changes of sedimental environments in the Laizhou Bay area," *Geological Review*, vol. 38, no. 4, pp. 360–367, 1992.

[33] J. C. Wu, Y. Q. Xue, P. M. Liu et al., "Development and hydrochemical characteristic of sea water intrusion in Longkou-Laizhou district," *Journal of Nanjing University (Natural Sciences Edition)*, vol. 30, no. 1, pp. 98–110, 1994.

[34] Y. Z. Hu, *Hydrogeochemical Reactions in Sea Water Intrusion Process at Changyi-Liutuan in Laizhou Bay*, China University of Geosciences (Beijing), Beijing, 2014.

[35] H. Craig, "Standard for reporting Concentrations of deuterium and oxygen-18 in natural Waters," *Science*, vol. 133, no. 3467, pp. 1833-1834, 1961.

[36] M. S. Gao, Y. M. Zheng, S. Liu et al., "Palaeogeographic condition for origin of underground brine in southern coast of Laizhou Bay, Bohai Sea," *Geological Review*, vol. 61, no. 2, pp. 393–400, 2015.

[37] S. V. Ramanaiah, S. Venkata Mohan, B. Rajkumar, and P. N. Sarma, "Monitoring of fluoride concentration in ground water of Prakasham district in India: correlation with physicochemical parameters," *Journal of Environmental science and Engineering*, vol. 48, no. 2, pp. 129–134, 2006.

[38] P. Lahermo, H. Sandström, and E. Malisa, "The occurrence and geochemistry of fluorides in natural waters in Finland and East Africa with reference to their geomedical implications," *Journal of Geochemical Exploration*, vol. 41, no. 1-2, pp. 65–79, 1991.

[39] X. Gao, Y. Wang, Y. Li, and Q. Guo, "Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China," *Environmental Geology*, vol. 53, no. 4, pp. 795–803, 2007.

[40] Q. Chen, W. Shi, Q. Lu, Z. Song, and B. Di, "Potential effect of seawater intrusion on fluorine-releasing in groundwater in the region surrounding the Laizhou Bay," *Advances in Marine Science*, vol. 30, pp. 219–228, 2012.

[41] S. Bader and H. Kooi, "Modelling of solute and water transport in semi-permeable clay membranes: comparison with experiments," *Advances in Water Resources*, vol. 28, no. 3, pp. 203–214, 2005.

[42] C. E. Neuzil, "Osmotic generation of 'anomalous' fluid pressures in geological environments," *Nature*, vol. 403, no. 6766, pp. 182–184, 2000.

[43] H. W. Olsen, "Simultaneous fluxes of liquid and charge in saturated kaolinite," *Soil Science Society of America Journal*, vol. 33, no. 3, pp. 338–344, 1969.

[44] GB5749-2006, *Standards for drinking water quality*, National standard of People’s Republic of China, 2006.

[45] GB/T14848-2017, *Standards for groundwater quality*, National Standard of People’s Republic of China, 2017.