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Unraveling hydrogeochemical dynamics and mixing mechanisms in North Shandong coastal aquifers: insights from isotopic and geochemical tracers

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The muddy coastal region of North Shandong, China, including Laizhou Bay and the Huanghe River (Yellow River) Delta, is a complex depositional environment where land and sea intersect, creating diverse water types and intricate coastal groundwater formation and evolution. This study focuses on the shallow Holocene aquifer (SHA) and the deep Pleistocene aquifer (DPA) groundwater, using hydrogeochemical, isotope analysis and numerical simulation methods to infer the source of water and salt and hydrogeological chemical processes. The results reveal that the groundwater is a mix of seawater, freshwater, and brine, with significant differences in hydrochemical types and isotopic signatures between the SHA and DPA aquifers. The SHA groundwater is dominated by low salinity (TDS ≈ 8 g/L), with the freshwater dominated by Cl-Na and Cl-Na·Mg hydrochemical types. In contrast, the DPA groundwater is characterised primarily by high salinity (TDS \approx 72 g/L) and the Cl-Na type. δ^{18} O- δ^{2} H deviates from the precipitation line and is close to the seawater evaporation line, indicating stronger seawater intrusion and salt accumulation processes. Interestingly, δ^{18} O and δ^{2} H stable isotopes' relative abundance in the DPA brine samples from the Huanghe River Delta (at a burial depth of ~260 m) and Huanghe River water samples bear a resemblance, suggesting a strong correlation between the river water and the subsurface brine water source in the EPA. The Hydrochemical Facies Evolution Diagram (HFE-Diagram) analysis shows 63.77% of SHA samples underwent desalination, while 79.31% of DPA samples experienced seawater intrusion, this was restricted by structural constraints and rock salt dissolution. This study provides new insights into the hydrogeochemical evolution of coastal aquifers.

KEYWORDS

groundwater chemistry, hydrological mixing phenomena, geological aquifer dynamics, HFE-Diagram, hydrochemical evolution

Highlights

- 1. Groundwater in the south coast of Laizhou Bay and the Huanghe River delta area exhibits considerable variability across different layers.
- 2. There is a strong correlation between the water of the Huanghe River and the underground brine sources in the Early Pleistocene strata.
- The rates of seawater intrusion of the SHA and Na–Cl were 36.23% and 55.07%, respectively, whereas the rates of seawater intrusion of the DPA were significantly higher than those of the SHA, at 79.31% and 89.66%.

1 Introduction

Coastal groundwater environments, characterized by their fragility and sensitivity, possess limited resistance and self-repair ability against external environmental disturbances, a challenge faced globally (Michael et al., 2013; Jiao and Post, 2019). They also stand as zones of significant interaction between sea and land, under the dual impact of intense human activities and global climate change (He and Silliman, 2019). Similar issues are observed in coastal regions worldwide, such as North Shandong of China, highlighting the global relevance of understanding these environments. Fresh groundwater within China's eastern coastal, a critical water resource, is affected by sedimentary environments, geological historical incidents, and human activities, instigating constraints on economic development (Foster and Chilton, 2003). This has led to continental groundwater salinization, a major global change event. Its resultant freshwater salinization and brine desalination have emerged as unified concerns within the international community (Cary et al., 2015; Jayathunga et al., 2020; Han and Currell, 2022).

Groundwater's chemical elements derive from long-term hydrogeochemical interactions between groundwater and geological bodies. The complex muddy coastal contains diverse groundwater types as per total dissolved solids (TDS) contents classifiable into freshwater (<1 g/L), brackish water (1~3 g/L), saline water (3~50 g/L), and brine (\geq 50 g/L) (China Geological Survey, 2012; Gao et al., 2015). It has been found that the seawater mixture ratio in coastal aquifers spatially and temporally varies, stimulating various hydrogeochemical responses (Kwon et al., 2020). The chemical components and isotopic characteristics within groundwater environments provide an ideal framework for examining water quality's spatio-temporal evolution. Prior studies typically focused on natural state groundwater environments, identifying their controlling factors before anthropogenic action significantly impacted them (Lambrakis, 2006; Mastrocicco et al., 2021). Recent global attention has been given to seawater intrusion due to sea-level rise triggered by global warming, causing considerable changes to coastal groundwater quality (Werner, 2010; Van Pham et al., 2019; Befus et al., 2020). Groundwater cycling processes are shaped by natural influences like climate change and hydrogeochemistry (Michael et al., 2005; Gonneea et al., 2013; Han et al., 2014; Han and Currell, 2022), along with human activities (Chen et al., 2016; Sun et al., 2023a). Such interplays lead to the evolution or even mutation of groundwater quality. Groundwater exploitation critically impacts the hydrodynamic and hydrochemical properties of groundwater systems (Liu et al., 2015; MacDonald et al., 2016) and introduces considerable uncertainty into groundwater environment evolution (Flaux et al., 2013; Liu et al., 2022). Hence, coastal face common challenges, including aquifer depletion, groundwater quality degradation, and seawater intrusion, regardless of whether they arise from irrational groundwater resource exploitation or natural causes.

The salinization of coastal groundwater by seawater intrusion has been of great interest. And with the application of disciplines such as marine sedimentation, hydrogeochemistry, isotope hydrology and numerical modelling in the study of coastal zone groundwater (Clark and Fritz, 2013; Han et al., 2014; Eissa et al., 2016; Cao et al., 2020). In recent years, coastal subsurface brine research has flourished in many countries (Van Engelen et al., 2018; Hussain et al., 2020; Saeed et al., 2021), and there are conflicting views on its sources and evolutionary processes. On the Mediterranean coast, for instance, brine salinity results predominantly from the evaporative concentration of seawater, influenced by hydrogeochemistry (Sola et al., 2014). Meanwhile, a considerable amount of brine at a depth of 400-600 m in the Nile Delta is attributed to the uplift of deep brine and the evaporative concentration of seawater and surface water (Nofal et al., 2015; Van Engelen et al., 2018; Van Engelen et al., 2019). Frank and Gui (2010) theory of freezing into brine provides an explanation for subsurface brine in Antarctica's high-latitude cold region of McMurdo Sound. In addition, high-salt wastewater from desalination plants has emerged as a new salinity source for coastal subsurface brine (Jahnke et al., 2019). Groundwater salinization along China's densely populated Bohai Sea coast necessitates clarification of salinity origin in subsurface saline and brine, invoking a genesis mechanism. This will inform effective prevention and management of groundwater salinization and address related environmental and geological issues in the region.

The Bohai Sea is a semi-enclosed marginal sea located in the north of China (Zhang et al., 2024), and the shallow and deep groundwater in the coastal zone have significant differences in chemical characteristics (Cao et al., 2022). Both geographically and socio-economically, the Shandong Peninsula is an important part of the Bohai Economic Circle, and there are obvious spatial and temporal variations in the distribution of its water resources (Gao et al., 2021). The Bohai Sea coast of China has been severely affected by seawater intrusion, leading to groundwater salinization, water quality degradation and resource depletion (Xue et al., 1997; Han et al., 2014). Since the Pleistocene, these areas have experienced multiple climate fluctuations and sea-level changes. Most of the environmental problems in the coastal areas of northern Shandong originate from groundwater issues and the complex problems they cause (Chen et al., 2021). This paper aims to address two main scientific questions: 1) to investigate how evaporation, mixing, dissolution, filtration and metamorphism control groundwater

Stratigraphy	Deposit	Thickness (m)	Buried depth of floor (m)	Color	Remark
Holocene	Clayey silt	5	5	Yellow	_
	Fine sand/ Clayey silt	13	18	Yellow	_
	Silty clay	2	20	Yellow	Containing shell fragments
Late Pleistocene	Fine sandy silt	2	22	Yellow	_
	Clayey silt	18	40	Yellow	_
	Silty clay	5	45	Yellow	Shell fragments seen on the bottom
Middle Pleistocene	Fine sandy silt/ Clayey silt	34	79	greyish brown	Shell fragments seen on the bottom
	Fine sand/ Clayey silt	65	144	greyish brown	Shell fragments seen in the upper part
	Clayey silt	28	172	yellowish brown	Shell fragments seen in the upper part
Early Pleistocene	Silty clay/clayey silt	66	238	yellowish brown	_
	Silty clay/ Fine sandy silt	34	272	yellowish brown	Large amount of shell fragments seen at 260m
	Silty clay/ Fine sand	37	309	yellowish brown/ reddish brown	_

TABLE 1 Stratigraphic and lithological characteristics of offshore drill cores (Sample BH1 in Figure 1a) in the Huanghe River Delta (cited in Xin and Yin, 1999).

chemistry under different depositional environments in these coastal regions, using SHA and DPA groundwater in the muddy coastal zone of northern Shandong; and 2) to elucidate the hydrochemical evolution of the Huanghe River delta and the south coast of Laizhou Bay along different groundwater pathways and their aqueous geochemical process similarities and differences.

2 Background of the study area and sample analysis methods

2.1 Sample point collection and distribution

The muddy coastal zone in northern Shandong is a typical chalky-gravelly coastal plain with a unique geographic location and geologic-historical background (Chen et al., 2019; Sun et al., 2023a), and its multilayered groundwater aquifer structure and endowed with a variety of hydrochemical types indicate an ideal location for studying the groundwater environment of the coastal zone. The study area, located in the coastal plain of northern Shandong, China, bordering the Bohai Sea, represents a typical coastal region. Coastal environments in the coastal aquifer of Israel and Spain (Sivan et al., 2005; Martínez-Pérez et al., 2022) use similar groundwater sampling methods (Sheng et al., 2023). The study area encompasses the alluvial plain of the Huanghe River Delta and the

coastal alluvial seafloor in Laizhou Bay, characterized by a semihumid monsoon climate with an annual average temperature of 12.1°C, 599 mm of precipitation, and 1,400 mm of evaporation. Major rivers, including the Weihe, Yuhe, Bailang, Mihe, Xiaoqing, and Huanghe Rivers, traverse the study area, providing freshwater and coarse-grained sediment to the coastal groundwater (Sun et al., 2006).

The Xiaoqing River delineates the hydrogeological unit, separating the region into the southern coast of Laizhou Bay and the Yellow River Delta. The coastal zones on either side of the Xiaoqing River show different topography, geomorphology, depositional environments and erosion levels due to riverine and oceanic influences (Chen et al., 2002; Ren et al., 2023). The southern coast of Laizhou Bay, bordered by the Bohai Sea and the Shandong Peninsula, features a multi-source, short-river deltaic depositional system with Quaternary subsurface brines predominantly concentrated in the Mahe-Weichang River basin, exhibiting a distinctive 'dumbbell-shaped' distribution (Gao et al., 2015). The Huanghe River, originating from the Tibetan Plateau, has formed a fan-shaped delta with an area of about 6,000 km² (Zheng et al., 2005), with sediment accumulation in the estuary creating favorable conditions for groundwater storage (Xue, 1993).

The study area's stratigraphy consists of four layers: Early Pleistocene (burial depth: $309 \sim 172$ m), Middle Pleistocene ($172 \sim 45$ m), Pleistocene ($45 \sim 20$ m), and Holocene (< 20 m) (Xin



and He, 1991; Guo et al., 2016) (Table 1). Since the Late Pleistocene, three sea-invasion-recession events have occurred, forming three marine stratigraphic layers: Middle Holocene Huanghua (Qh^2 , 7–2.5 ka B.P.), Late Pleistocene Xianxian (Qp_3^3 , 40–21 ka B.P.), and early Late Pleistocene Cangzhou (Qp31, 110–70 ka B.P.) (Gao et al., 2015; Gao et al., 2016). The Quaternary stratigraphy, influenced by sea-land interactions, comprises numerous weakly permeable layers and aquifers with varying hydraulic properties (Xue et al., 2000). The brine aquifer, with a multi-layered structure (Figure 1b), is

primarily developed in three marine strata within Quaternary loose sediments (Zheng et al., 2014; Liu et al., 2017).

2.2 Sample point collection and distribution

This study, supported by the 2023 Joint Fund 'Mechanism of Underground Brine Resources Formation and Evolution in

Shandong's Coastal', collected water samples from various water bodies in the study area. Our collection totaled 152 samples, compiled from 138 groundwater samples, 12 surface river samples, a single Bohai Sea sample, and a local rainfall sample, with the sea encroachment line encompassing most sample locations (Figure 1a). Primarily, the groundwater sampling was accomplished by utilizing local civil wells, machine wells, and monitoring wells to gather shallow (from SHA) and deep groundwater samples (from DPA). For detailed analysis of brine variances, deep brines in Laizhou Bay were categorized into Deepupper brine (Late Pleistocene) and Deep-lower brine (Early Pleistocene). All samples were immediately filtered on-site using a 0.22 µm membrane. Analytic cation samples were acidified to a pH below 2 with 6 mmol/L nitric acid and stored in 500 mL plastic sampling bottles for water chemistry analysis. Additionally, hydrogen and oxygen isotope testing was conducted on 141 samples using 10 mL brown glass sampling bottles.

2.3 Sample testing

In situ measurements of groundwater's redox potential, pH, conductivity, and temperature were performed using a Manta+ water quality multi-parameter analyzer produced by Eureka, U.S.A. The concentrations of various ions namely K⁺, Na⁺, Ca²⁺, Mg²⁺, and Br- were tested using an Inductively Coupled Plasma analyzer (ICAP-7400). The evaluation of SO_4^{2-} and Cl^- ions was done using Chromatographic Analysis (ICS-600), while the HCO₃⁻ ion concentration were established via titration. The Marine Geological Testing Centre of China's Ministry of Natural Resources employed High Temperature Pyrolysis-Isotope Ratio Mass Spectrometry (HTP-IRMS) to measure the water samples' stable isotope contents (δ^2 H, δ^{18} O), using the Vienna Standard Marine Water (V–SMOW) as the calculating index. The isotopic uncertainties of $\delta^2 H$ and $\delta^{18} O$ were ±1.0‰ and ±0.2‰, respectively. Additionally, Beta Laboratory performed tests and analysis on the stable isotopes (δ^2 H, δ^{18} O) of the groundwater samples.

2.4 Methods of analysis

2.4.1 Saturation index analysis

The Saturation Index (SI) serves as an indicator, reflecting whether a solution is in equilibrium, unsaturated, or supersaturated vis–à–vis the solid phase (Aghazadeh et al., 2017). Expressed as the logarithm of the ratio between the Ionic Activity Product (IAP) and the Solubility Product (LP), it utilizes a base–10 logarithmic scale (Equation 1). Realistically, SI values ranging from –0.5 to +0.5 convey quasi–equilibrium, values less than –0.5 signify unsaturation and therefore a dissolved state in relation to given minerals. Meanwhile, values surpassing +0.5 indicate supersaturation, with the relevant minerals in the solution manifesting in a precipitated state (Han et al., 2014). PHREEQC software was implemented in the execution of hydrogeochemical modelling for this study.

$$SI = \log \frac{IAP}{LP} \tag{1}$$

Where IAP signifies the ions' activity product participating in the mineral dissolution reaction. LP denotes the temperature– dependent maximum solubility of the mineral.

2.4.2 Mass balance model

In the section of our mass balance model, Cl^- in groundwater forms an ideal sensitivity indicator, owing to its wide distribution, difficulty in adsorption, and significantly minor participation in geochemical reactions, thereby reflecting seawater mixing and serving as an extensively utilized environmental tracer in hydrogeology. Utilizing ion vs. Cl^- molar ratios and the correlational ion distribution, insights into the water-rock interactions during weakly permeable layers' pore water formation are divulged.

Assuming that groundwater evolution solely incorporates seawater salts with no other water chemistry involvement, the contribution of seawater ions to groundwater salinity can be calculated using the conservation of mass theorem, i.e., the major seawater ion mixing ratio (Giambastiani et al., 2013; Han et al., 2014). Given the chloride ions' chemical stability and the observed unsaturation of salt rock minerals in groundwater samples' saturation index, this study calculated seawater's mixing ratio using Cl⁻ as a tracer via the following formula:

$$f_{SW} = \frac{Cl_{sample} - Cl_f}{Cl_{SW} - Cl_f} \times 100\%$$
⁽²⁾

Where f_{SW} is the mixing ratio of seawater. Cl_{sample} is the concentration of chloride ions in the groundwater sample (mg/L). Cl_{SW} is the concentration of chloride ions in seawater (mg/L). Cl_f is the concentration of chloride ions in the freshwater end element (mg/L).

Based on the computed f for the chloride ion, the theoretical concentration for each of the major ions present in groundwater can be calculated further (Equation 3).

$$C_{i,mix} = f_{sw} \times C_{i,SW} + (1 - f_{SW}) \times C_{i,f}$$
(3)

where $C_{i,mix}$ is the theoretical concentration of *i* ions in groundwater. $C_{i,SW}$ and $C_{i,f}$ are the concentrations of *i* ions in seawater and freshwater end elements, respectively.

The difference between the actual measured sample ion concentration $C_{i,sample}$ and the theoretical ion concentration $C_{i,mix}$ is the aqueous chemical reaction value of the ion ΔC_i (Equation 4). Thus, we can express it as follows:

$$\Delta C_i = C_{i,sample} - C_{i,mix} \tag{4}$$

This result reflects the occurrence of certain hydrogeochemical processes within groundwater that induce variations in the concentration of i ions, as asserted by De Montety et al. (2008). Such alterations underscore the dynamic nature of groundwater composition and its susceptibility to environmental and geochemical changes.



Piper's trilinear plot of multiple water samples (black curve indicates the evolutionary path from freshwater to brine; black dotted circles indicate the main distributions of SHA freshwater, DPA freshwater, brackish water, saline water and brine, respectively).

2.4.3 HFE-diagram

The HFE–Diagram as proposed by (Giménez–Forcada, 2010, Giménez–Forcada, 2014), serves as a tool for recognizing and comprehending the temporal and spatial intrusion of seawater into coastal aquifers. It provides crucial insights into the hydrochemical variability within these areas. Primarily, the HFE–Diagram is employed to evaluate the mixing processes occurring between fresh and saline waters. It is considered particularly efficacious for assessing the intrusion processes of fresh and sea (saline) water within the groundwater of coastal, and identify by the distribution of positive and negative ion percentages (Giménez–Forcada, 2014). This method largely centers around the distribution and behavior of anions and cations.

3 Results

3.1 Groundwater chemical characteristics

In the study region, TDS contents in SHA and DPA groundwater ranged from 0.38–34.20 g/L and 0.46–156.96 g/L, respectively, with average values of 8.06 g/L and 72.07 g/L. The

dominant hydrochemical compositions were Cl–Na and Cl–Na·Mg (Figure 2). Major ions indicated a transition from freshwater to brine, with cations evolving from Ca²⁺ and Mg²⁺ to Na⁺, and anions from Bicarbonate and Sulfate to Chloride. The hydrochemistry of freshwater in SHA is mainly HCO₃–Ca and Cl·SO₄–Ca·Mg, while in DPA, it's predominantly HCO₃–Ca, HCO₃–Ca·Na. The brackish water mainly comprises of Cl·SO₄–Na and Cl·SO₄–Ca·Mg, while Cl–Na characterizes both saline and brine waters. DPA groundwater exhibited a larger range of TDS contents and more complex hydrochemical types. Most brines were similar to local seawater, suggesting a seawater origin.

From a regional perspective, Cl–Na type groundwater in the offshore DPA of the Huanghe River Delta is more homogeneous, likely due to the extensive marine layer. In contrast, groundwater along the southern coast of Laizhou Bay shows more diverse hydrochemical types, indicating potential mixing with other aquifers.

TDS contents of groundwater samples generally decreased with increasing distance from the coastline (Figure 3). Within the coastal (<20 km) area, DPA groundwater had higher TDS contents, often exceeding local seawater (24.1 g/L). Beyond 20 km, SHA groundwater TDS significantly lowered to freshwater levels. Near



the sea, SHA groundwater was mainly saline, with some brine levels within 10 km. In the 20~30 km range, only DPA groundwater had relatively higher TDS, similar to seawater, suggesting past seawater intrusion influence. The fitted curve showed DPA groundwater had higher TDS than SHA groundwater, with greater change near the coastline. SHA groundwater near the coast had TDS equivalent to local seawater, indicating significant seawater mixing and intrusion influence in near-coastal Holocene strata.

3.2 Major ion trends

The relationship between ions and Cl⁻ can indicate the source of groundwater salinity (e.g. Edmunds et al., 2006). In ion vs. Cl⁻ plots (Figure 4), most water samples, particularly saline and brine waters, align closely with the seawater ratio line, as seen in Na⁺ vs. Cl⁻ (Figure 4a), Mg²⁺ vs. Cl⁻ (Figure 4b), SO₄²⁻ vs. Cl⁻ (Figure 4c), and Br vs. Cl relationships (Figure 5a). Fresh and brackish water samples, however, are scattered and shifted upward. Lower salinity groundwater is likely influenced by mineral weathering, which dissolves certain ions and increases total solutes. In highsalinity conditions, re-dissolving mineral ions is difficult. Using the mass balance model (Equation 2), the mixing line between endelement samples was calculated and plotted across water chemistry indicators (Figure 7). Most ions align with seawater and brine endmembers, but Ca2+ vs. Cl shows a scattered distribution for groundwater samples (Figure 4d), with significant blending of SHA and DPA freshwater end-members.

Saline water with TDS contents exceeding seawater and brine is closely distributed near the seawater evaporation line, indicating groundwater salinity may be linked to seawater or concentrated saline water. Na⁺, Mg²⁺, and SO₄²⁻ contents in Northern Shandong's coastal groundwater generally correlate positively with Cl⁻ concentration. Cl⁻, Na⁺, and Mg²⁺ are key seawater components. Groundwater salts could originate from seawater intrusion, marine aerosols, or dissolution of salt rocks by precipitation (see Figures 4a–c). Most fresh, brackish, and saline water lies below the mixing line (Figure 4a), showing Na⁺ depletion and possible cation exchange. Brackish and saline waters deviating from the mixing line may exhibit SO₄²⁻ enrichment (Figure 4c), suggesting sulfate mineral dissolution. Further hydrogeochemical analyses are needed to confirm these observations and the groundwater formation evolution due to aquifer sediment contact.

3.3 $\delta^{18}O - \delta^2H$ stable isotopes

Located in a temperate semi-humid monsoon climate zone, the study area is a transitional region between land and sea with high evaporation rates. Using the global atmospheric precipitation line equation ($\delta^2 H = 8\delta^{18}O + 10$, Craig, 1961), the local meteorological water line (LMWL) was determined as $\delta^2 H = 7.8\delta^{18}O + 6.3$, based on monthly average rainfall data in Yantai from 1986–1990. The $\delta^{18}O$ and $\delta^2 H$ values for average monthly rainfall were obtained from the IAEA Global Network of Isotopes in Precipitation (GNIP) (IAEA/WMO, 2006). The regression equation for water samples had a slope of 5.8 (R² = 0.91) (Figure 7), lower than global and local atmospheric precipitation lines. The Bohai Coastal Plain, affected by past climatic conditions and sea intrusion-recession events, shows distinct shifts in $\delta^{18}O$ and $\delta^2 H$ values in groundwater (–78.07 ‰ to –19.17 ‰ for $\delta^2 H$, –11.26 ‰ to –2.09 ‰ for $\delta^{18}O$). Most groundwater samples are isotopically below global and local



Hydrochemical relationships between some ions in groundwater and mean seawater constituents in the study area (a) Cl⁻ vs. Na⁺ relationship plot (b) Cl⁻ vs. Mg²⁺ relationship plot (c) Cl⁻ vs. SO₄²⁻ relationship plot (d) Cl⁻ vs. Ca²⁺ relationships (black dashed line is the freshwater and seawater mixing line, and red dashed line is the freshwater and brine mixing line) (SW, G, H, E, S, C, and B represent the standard seawater values, gypsum saturation point, rock salt saturation point, lagoonal salt saturation point, and the saturation points of potash rock, carnallite, and magnesium hydromagnesite, respectively (refer to Chen, 1983)) (symbols are the same as in Figure 2).

atmospheric precipitation lines, especially those with $\delta^{18}O > -8$ %. Isotopes in saline and brine water are enriched, while fresh and brackish water samples align with river water.

Most groundwater samples experience evapotranspiration, resulting in smaller regression equation slopes and intercepts, as depicted by the green dashed line in Figure 8. This is evident in saline and brine waters with significantly depleted δ^{18} O and δ^{2} H values. Fresh, brackish, and partially saline waters are near the atmospheric precipitation line, indicating minimal evapotranspiration impact. While saline/brine water from seawater evaporation typically has δ^{18} O and δ^{2} H values above standard seawater (δ^{2} H = 0 ‰, $\delta^{18}O = 0$ ‰) (Horita, 2005), study area groundwater has lower values, suggesting alternative recharge sources. Subsurface brine samples, particularly SHA brine, are depleted in δ^{18} O and δ^{2} H, indicating freshwater mixing with terrestrial isotopes during brine formation. SHA groundwater samples (HD38 and HD40) near the Xiaoqing

River's offshore zone have high δ^{18} O and δ^{2} H values, suggesting postevaporation seawater origin within SHA, similar to standard seawater. Climate factors cause isotopic depletion in most DPA brines. Notably, δ^{18} O and δ^2 H in the Huanghe River Delta DPA brine sample (HD46, ~260 m) closely match the Huanghe River water sample, indicating a strong link between river water and Early Pleistocene strata brine moisture sources.

4 Discussion

4.1 Mixing process

As previously discussed, groundwater in the study area results from the mixing of seawater, freshwater, and brine. A three-endmember mixing model (SHA freshwater (LB01) and DPA freshwater



(LB32) as freshwater end–members, seawater (Sea) as the seawater end–member, and DPA brine (LB44) as the brine end–member) using Cl⁻ concentration and δ^{18} O values was applied to trace mixing trajectories and quantify variations in water types (Figure 7). The model shows a correlation between Cl⁻ concentration and δ^{18} O values, with δ^{18} O increasing as Cl⁻ concentration rises, indicating the model's validity. Most samples are above the DPA fresh-brine mixing line, with freshwater samples between the two mixing lines, having δ^{18} O values from –9.5 to –8.2 ‰. The mass balance model (Equation 2) can estimate the contributions of freshwater, seawater, and brine to the mixed samples.



Saturation index of calcite, dolomite, gypsum and rock salt plotted against $\mbox{Cl}^-.$

River water from the Bailang River (BLH) and Weihe River (WH) has high δ^{18} O values due to upstream reservoir mixing and evaporation. SHA groundwater, recharged by these rivers, shows enriched δ^{18} O values near the river basins. Post-sea recession interaction between rivers and groundwater is a key process for flushing saline water and reducing groundwater salinity (Kwong and Jiao, 2016). Atmospheric precipitation also contributes to high δ^{18} O in SHA water. Most Huanghe River Delta groundwater is in the mixing zone. SHA brines (HD38, HD40) near the Xiaoqing River have high $Cl^- - \delta^{18}O$ values, suggesting a blend of evaporated seawater or modern precipitation. This differs from the Laizhou Bay south coast groundwater origin, hypothesizing brine from Holocene seawater via strong evaporation. DPA brine (HD46) at 260m depth has δ^{18} O values similar to the Huanghe River, indicating Early Pleistocene brine recharge by river water. Other DPA brines at 100m depth mix with desalinated groundwater and seawater, clustering within the mixing line.

4.2 Water-rock action

4.2.1 Dissolution-filtration action

Saturation indices (Figure 6) indicate Rock Salt is mainly dissolved, Gypsum is mostly dissolved or in equilibrium in SHA groundwater, only supersaturated in high-salinity DPA groundwater. Calcite and Dolomite precipitate significantly when Cl^- exceed 10,000 mg/L.

As salinity increases, ion vs. Cl⁻ relationships tighten towards the mixing line (Figure 9). Na⁺ experiences cation exchange, resulting in ratios below the mixing line (Figure 10). Most saline and brine samples have Na⁺ vs. Cl⁻ ratios similar to seawater (Figure 9a). Mg²⁺ vs. Cl⁻ ratios are minimal (Figure 9b) due to dolomite saturation (Figure 8), which induces saturation and precipitation even at lower salinities. Fresh and brackish waters show a wider range of SO₄²⁻ vs. Cl⁻ ratios, indicating sulphate



FIGURE 7

Plot of stable isotope δ^{18} O versus Cl⁻ in groundwater and surface water in the study area, with the black dashed circle showing the underground brine subject to strong evaporation. (The water types represented by each serial number in the figure are 0-Shallow freshwater; 0-Shallow brackish water; 0-Shallow saline water; 0-Shallow brine; 0-Deep freshwater; 0-Deep brackish water; 0-Deep brackish water; 0-Deep brackish water; 0-River).



Stable isotopes in groundwater and surface water (symbols are the same as in Figure 2), black solid line is LWML, black dashed line is GWML, green dashed line indicates the fitted curve of groundwater samples, and the green dashed line is the Huanghe River water sample.

enrichment and depletion processes (Figure 8c). Decreasing SO_4^{2-} vs. Cl⁻ ratios with increasing mineralization suggest brine saturation with gypsum (Andersen et al., 2005). Some Ca²⁺ vs. SO_4^{2-} ratios are minimal (Figure 9d), especially in DPA groundwater, suggesting influence from gypsum dissolution or another SO_4^{2-} source. SPA groundwater samples with high Ca² +/SO₄²⁻ ratios suggest Ca²⁺ originates from cation exchange at lower salinities. As salinity rises, dolomite and calcite precipitation (Figure 8) results in decreasing Ca²⁺ vs. SO_4^{2-} ratios.

4.2.2 Cation exchange

Water–rock interactions involve more than just dissolution and precipitation. Δ values of Na⁺, Ca²⁺, and Mg²⁺ were calculated using the mass balance model.

$$\Delta Na^{+} < 0 \ \Delta Ca^{2+} > 0 :$$

$$2Na + Ca \cdot X_{2} \rightarrow Ca + 2Na \cdot X$$

$$\Delta Na^{+} < 0 \ \Delta Mg^{2+} > 0 :$$

$$2Na + Mg \cdot X_{2} \rightarrow Mg + 2Na \cdot X$$

$$\Delta Ca^{2+} < 0 \ \Delta Mg^{2+} > 0 :$$
(6)

$$Ca + Mg \cdot X_2 \to Mg + Ca \cdot X_2 \tag{7}$$

From Figure 10a, Ca^{2+} is replaced by Na⁺ in SHA groundwaters (Equation 5), while DPA groundwaters show the reverse (the reverse of Equation 5). $\Delta Ca < 0$ in most brines and DPA saline waters is due to calcite and dolomite precipitation (Figure 8). The fitted curve for the saline water samples was y = -0.19x+166.96 (R² = 0.51), showing a good correlation between Na⁺ and Ca²⁺ ion exchange in saline water. The correlation between Na⁺ and Ca²⁺ ion exchange is evident, but Mg²⁺ also participates (Figure 10b).Most groundwater samples show Mg²⁺ enrichment (Figure 10b), with Na⁺ displacing Mg²⁺ in SHA groundwater (Equation 6). In both SHA and DPA brines, Ca²⁺ displacing Mg²⁺ (Equation 7), explaining the low ΔCa in Figure 10a. One sample (LB70) shows Mg²⁺ is swapped for Na⁺ (the reverse of Equation 6), leading to elevated Na⁺ concentrations (Figure 10b).

4.2.3 Sulphate reduction reactions

SHA freshwater and most brackish water show positive ΔSO_4 values, indicating sulphate enrichment, while saline and brine water show both enrichment and depletion (Figure 11a). Gypsum dissolution contributes to SO_4^{2-} enrichment in fresh and brackish water, while gypsum saturation and CaSO₄ precipitation lead to SO_4^{2-} reduction in brines. Most samples diverge from the 1:1 line, suggesting additional processes result in SO_4^{2-} depletion. The reductive environment due to limited permeability and organic matter in marine sediments favors sulphate reduction reactions



Variation of ion/Cl⁻ with increasing salinity and correspondence with seawater and brine composition. (a) Na⁺/Cl⁻ vs. Cl⁻ relationship. (b) Mg²⁺/Cl⁻ vs. Mg²⁺ relationship. (c) SO_4^{2-}/Cl^- vs. SO_4^{2-} relationship. (d) Ca^{2+}/SO_4^{2-} vs. Ca^{2+} relationship. (same symbols as in Figure 2).

(Dang, 2022). The reaction could be represented by the forthcoming (Equation 8):

$$SO_4^{2-} + 2\frac{1}{n}(CH_2O)_4^{Sulphate-reducing bacteria}H_2S + 2HCO_3^{-}$$
 (8)

Positive Δ HCO₃ values in nearly all samples indicate an excess of HCO₃⁻ (Figure 11a). Calcite and dolomite dissolution at lower salinities (Figure 8) explains elevated Δ HCO₃ in fresh and brackish waters. High Δ HCO₃ in saline and brine waters, especially in DPA brines, supports sulphate reduction reactions. Δ SO₄ shows pronounced depletion when superimposed on gypsum precipitation. Moreover, owing to the copious presence of HCO₃⁻ in the groundwater, further depletion transpires through precipitation with Ca²⁺ in the groundwater. This phenomenon sheds light on why most brines in Figure 10a display Δ Ca<0. The deviation of samples from the 1:2 line results from the interplay of these processes.

4.3 Hydrogeochemical modelling

In Section 4.2, we discussed the water-rock interactions of groundwater. To further understand these interactions, we conducted inversion simulations to identify hydrochemical reactions and changes in ion concentrations.

We selected three paths along the groundwater flow direction to simulate the south bank of Laizhou Bay and the Huanghe River Delta. The paths in the Laizhou Bay area are Path I (LB30 \rightarrow LB35), Path II (LB35 \rightarrow LB73), and Path III (LB73 \rightarrow LB46). In the Huanghe River Delta, we considered Path IV (HD23 \rightarrow HD59) and Path V (HD59 \rightarrow HD62) (Table 2). Given the selected pathways and the hydrogeological background of the study area, we finally selected dolomite, calcite, gypsum, rock salt, quartz, sodium feldspar, potassium feldspar, and cation exchange as the 'probable mineral phases' in the Huanghe River delta (Tian et al., 2021), with



the additional presence of hematite and pyrite in the Laizhou Bay area (Wang et al., 2023; Li et al., 2021) (Table 3). Dolomite was set to only precipitate, while gypsum and calcite were set to only dissolve. Simulations accounted for cation exchange between Ca² ⁺, Mg²⁺, and Na⁺ under seawater intrusion or aquifer renewal conditions. The outcomes were used to analyze CO₂ dissolution and release, identifying inorganic carbon sources and sinks. The analysis focused on seven elements: Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻, and SO₄²⁻.

The cation exchange involving Na^+ replacing Ca^{2+} or Mg^{2+} , and Ca^{2+} replacing Mg^{2+} in all pathways along the south coast of

Laizhou Bay aligns with the findings in Section 4.2.2, suggesting active seawater intrusion. In Path I, the transition from freshwater to saltwater involves the dissolution of gypsum, rock salt, and potassium salt, leading to increased ion content, dolomite precipitation, and CO_2 release. Despite Ca^{2+} consumption by dolomite precipitation, Ca^{2+} concentration in groundwater slightly rises due to gypsum dissolution and Na⁺ exchange. Path II (from saltwater to brine) and Path III (from brine to brine) exhibit similar patterns, with calcite, gypsum, rock salt, and potassium salt dissolution and CO_2 absorption. High Na⁺ concentration in coastal groundwater triggers Na⁺ replacement





reactions with Ca^{2+} and Mg^{2+} in the aquifer. Extensive gypsum dissolution increases calcium ions, enhancing calcite solubility and leading to calcite dissolution.

The Huanghe River Delta includes Path IV (from brackish water to brine) and Path V (from high concentration (TDS content: 121 g/L) brine to low concentration (TDS content: 92 g/L) brine). Path IV involves gypsum dissolution and potassium salt precipitation. Path V involves the dissolution of albite and the precipitation of potassium feldspar, with CO_2 absorption. Seawater intrusion at the HD62 sample site leads to albite dissolution and potassium feldspar precipitation, indicating significant interaction between seawater and subsurface brine. Both paths show equal cation exchange between Ca^{2+} and Mg^{2+} , due to the ionic radius and adsorption energy of Ca^{2+} in the coastal aquifer, facilitating exchange with clay minerals (Capuano and Jones, 2020). In the

saline environment, Na^+ and Mg^{2+} concentrations are elevated, with Na^+ being predominant (Qin et al., 2023).

4.4 Cl⁻ vs. Br⁻ relationship

Significant fluctuations in the Br⁻ vs. Cl⁻ ratio in freshwater and brackish water with lower Cl⁻ concentration are noted, influenced by atmospheric precipitation or anthropogenic factors (Figure 5b). Offshore groundwater samples are close to the seawater ratio line, indicating predominant seawater mixing as the source of salinity. The Br⁻/Cl⁻ ratio is unreliable for identifying salinity sources when TDS is less than 2 g/L (Han et al., 2011). SHA brine and certain brackish waters show lower Br⁻/Cl⁻ values compared to seawater, enclosed within the black dashed line of the study region, which is

 TABLE 2 Inverse modelling scenarios for mineral assemblage and molar transfer.

Simulation pathway	Minimal phases										
	Calcite	Dolomite	Gypsum	Halite	MgX ₂	CaX ₂	NaX	CO ₂ (g)	Sylvite	Albite	Potash feldspar
Path I (LB30 → LB35)		-5.4e-4	2.4e-2	5.3e-1	8.4e-2		-1.68e-1	-2.5e-3	2.0e-3		
Path II (LB35 \rightarrow LB73)	1.3e-2		4.9e-2	1.0e+0	1.2e-1	-6.5e-2	-1.08e-1	1.4e-2	1.1e-2		
Path III (LB73 → LB46)	-8.9e-3		5.1e-2	1.8e-1	6.8e-2	-3.9e-2	-5.77e-2	-9.9e-3	6.3e-3		
Path IV (HD23 → HD59)			4.8e-2	7.4e-1	5.6e-2	-5.6e-2			-1.9e-4		
Path V (HD59 \rightarrow HD62)			-2.5e-3		5.7e-3	-5.7e-3		3.3e-3		8.8e-3	-8.8e-3

A positive number of phase transfer moles indicates dissolution of the mineral, a negative number is precipitation. Concentrations in mol/L. CaX2, MgX2 and NaX represent exchange species including stoichiometry of exchange ion and exchanger.

Minimal phases	Chemical formula	Reaction equation
Calcite	CaCO ₃	$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$
Dolomite	$CaMg(CO_3)_2$	$CaMg(CO_3)_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 2HCO_3^- + 2OH^-$
Gypsum	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$
Halite	NaCl	$NaCl = Na^+ + Cl^-$
Sylvite	KCl	$KCl = K^+ + Cl^-$
Pyrite	FeS ₂	$2FeS_2 + 2H^+ = 2Fe^{2+} + 2HS^-$
Hematite	Fe ₂ O ₃	$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$
Albite	NaAlSi ₃ O ₈	$NaAlSi_{3}O_{8} + 8H_{2}O = Na^{+} + Al(OH)_{4}^{-} + 3H_{4}SiO_{4}$
Anorthite	$CaAl_2Si_2O_8$	$CaAl_2Si_2O_8 + 8H_2O = Ca^{2+} + 2Al(OH)_4^- + 2H_4SiO_4$
Potash feldspar	KAlSi ₃ O ₈	$KAlSi_3O_8 + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4$
Quartz	SiO ₂	$SiO_2 + 2H_2O = H_4SiO_4$
Cation exchange	NaX, CaX_2, MgX_2	$\begin{aligned} 2Na + Ca \cdot X_2 &\rightarrow Ca + 2Na \cdot X2Na + Mg \cdot X_2 \rightarrow Mg + 2Na \cdot \\ XCa + Mg \cdot X_2 &\rightarrow Mg + Ca \cdot X_2 \end{aligned}$

TABLE 3 Chemical formulae and reaction equations for mineral phases.

due to the significant increase in Cl^- concentration from the dissolution of rock salt. Highly mineralized SHA brine and Deep-upper brine (LZ) show a linear decrease in Br^-/Cl^- with increasing Cl^- .

Typically, the Br⁻/Cl⁻ ratio stays consistent during seawater evaporation, that is, as groundwater salinity intensifies (Bottomley et al., 1994; Vengosh and Hendry, 2001), until it reaches rock salt saturation. Underground brine samples from the Huanghe River Delta, particularly the DPA brine, exhibit larger Br⁻/Cl⁻ ratios, exceeding those of the seawater ratio line. This suggests that they may have passed the rock salt saturation stage, advancing towards the lagoonal salt saturation phase, which could have prompted Cl⁻ precipitation in water, followed by mixing with freshwater, subsequently reducing salinity. Deep–lower brine (LZ) samples within the red dotted line, located along the river–adjacent coastal, with a burial depth of 80~200m, possess higher Br⁻/Cl⁻. This could be attributed to the decomposition of organic matter within the marine layer of the DPA groundwater.

4.5 HFE-diagram analysis

The HFE–Diagram analysis confirms that groundwater salinity is high (within a 20 km radius from the coastline), with significant seawater intrusion. The mineralization of SHA and DPA groundwater decreases with desalination and increases with seawater intrusion inFigure 12. Brine samples cluster near the end stages of intrusion. The desalination endpoints in SHA align with LB01 (Figure 12a), and in DPA with LB32 (Figure 12b), consistent with previous mixing process findings in Figure 6. In SHA, 63.77% of samples undergo desalination and 36.23% intrusion, with Na–Cl as the predominant phase (55.07%). This reflects the influence of shallow water controlled by hydrologic cycle processes and surface water recharge. In DPA, 79.31% of samples experience intrusion and 20.69% desalination, with Na–Cl being most abundant (89.66%). The DPA groundwater, on the other hand, is predominantly saline, which is controlled by tectonic conditions of confinement and rock salt dissolution. Extensive groundwater extraction has impacted both quantity and quality (Currell et al., 2012), but most samples show a trend towards seawater intrusion, reflecting global coastal aquifer trends (Ri et al., 2022; Azari and Tabari, 2024).

5 Conclusions

This study uses hydrogeochemical and environmental isotope methods to examine the mixing processes of groundwater in the muddy coastal region of northern Shandong. We integrated a mass balance model with hydrogeochemical simulations to explore processes such as mineral dissolution, precipitation, ion exchange, and reduction reactions. The research enhances understanding of salinization and desalination in coastal aquifers, contributing to global coastal aquifer management.

 The study area's groundwater shows diverse quality types: freshwater, brackish water, saline water, and brine. Freshwater chemistry stems from mineral dissolution, brackish water from rock weathering and seawater mixing, and brine water from early evaporation and concentration. Both SHA and DPA aquifers are affected by seawater intrusion, with high Cl⁻ and Na⁺ concentrations, especially in DPA.

- 2. A three-component mixing model of freshwater, brine, and seawater was identified, estimating their relative contributions. This model offers a new reference for studying coastal groundwater formation. SHA groundwater mixing is complex, with recent formation and short-lived processes, making it susceptible to quality changes. Isotope analyses show that the SHA and DPA groundwater is recharged by precipitation and river infiltration. Concentrated brines originate from lowisotopic-abundance atmospheric water, which leads to δ^{18} O and δ^{2} H depletion in the brines.
- 3. There are significant differences in groundwater hydrochemistry, ion composition, isotopic characteristics and environmental impacts between Laizhou Bay's south coast and the Huanghe River Delta. Laizhou Bay's SHA aquifer shows HCO3-Ca and Cl-SO4-Ca-Mg types, while its DPA aquifer is dominated by HCO3-Ca and HCO3-Ca-Na types. The Huanghe River Delta's SHA aquifer is primarily Cl-Na, and its DPA aquifer contains Cl-Na and Cl-Na-Mg types. Laizhou Bay's SHA aquifer has higher calcium and magnesium, while the Huanghe River Delta's DPA aquifer has significant sodium. The isotopic signatures of Laizhou Bay's SHA aquifer show high variability, indicating diverse water sources and processes, while the Huanghe River Delta's DPA aquifer shows stable signatures similar to Huanghe River water, indicating riverine contribution. These differences highlight the distinct hydrogeological conditions and evolution histories of the two regions.
- 4. The study also investigated the distribution and genesis of groundwater brines. The brine layer along Laizhou Bay's south coast shows clear stratification, divided into SPA brine, DPA shallow brine, and DPA deep brine. The Br vs. Cl⁻ ratio in DPA deep-upper brine decreases linearly with Cl⁻ concentration, indicating salinity from evaporated seawater salt dissolution. The Huanghe River Delta's brines are divided into two layers: SHA brine in the Xiaoqing River estuary's north and DPA brine associated with the Huanghe River channel aquifer, strongly mixed by early river recharge. Data support that brine formation relates to seawater evaporation and sedimentation, providing a basis for understanding regional groundwater brine distribution and mechanisms. Future studies should focus on isotopic and hydrogeochemical processes to elucidate the groundwater system's evolutionary history.
- 5. Most groundwater shows a seawater intrusion trend. Mineralization decreases with desalination and increases with intrusion. The highest HFE-diagram for SHA groundwater is Na-Cl (55.07%), with 63.77% undergoing desalination and 36.23% intrusion. For DPA groundwater, the highest HFE-diagram is also Na-Cl (89.66%), with 79.31% intrusion and 20.69% desalination, which is controlled by tectonic conditions of confinement and rock salt dissolution.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

ZL: Formal Analysis, Writing – original draft, Data curation, Methodology, Writing – review & editing, Investigation, Conceptualization, Software. MG: Supervision, Writing – review & editing, Methodology, Funding acquisition, Investigation, Visualization, Validation, Resources, Project administration. LW: Writing – review & editing, Validation, Methodology, Visualization. QS: Investigation, Writing – review & editing, Software, Formal Analysis. XC: Investigation, Software, Methodology, Writing – review & editing, GH: Methodology, Investigation, Writing – review & editing, Visualization. MW: Investigation, Visualization, Writing – review & editing, Supervision.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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