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Study of shallow groundwater quality evolution under saline intrusion with environmental isotopes and geochemistry

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Abstract Evolution of the shallow groundwater quality under saline intrusion in porous aquifer system has been studied with environmental isotopes and geochemistry in the Laizhou Bay area, China. Two campaigns of water sampling from various sources were carried out in spring and winter for environmental isotopic and chemical analyses. The origin of groundwater salinity from intrusion of both modern seawater and deep brine water was identified by analysing the correlations between ^{18}O , D, T, Cl^- , SO_4^{2-} and electrical conductivity. The results indicate that the brine is originated from evaporating and concentrating of intruded seawater and its δD and

$\delta^{18}\text{O}$ are different from modern seawater but similar to those of mixture of seawater with fresh groundwater. It is hard to distinguish the salinity origin in this area by the δD – $\delta^{18}\text{O}$ relationship alone. The relations between $\delta^{18}\text{O}$ and conductivity, Cl^- and SO_4^{2-} have been used to identify the salinity origin due to the distinct difference in salinity between the brine and seawater, conjunctively with use of T. A threshold of $T = 12$ TU was adopted to identify the origin of saline groundwater.

Keywords Shallow groundwater · Salinity origin · Environmental isotope · Geochemistry · Saline intrusion · Eastern China

Introduction

It is important to understand the groundwater quality evolution and seawater intrusion mechanism for groundwater resource management in coastal regions. Various techniques have been used in characterisation of the spatial and temporal characteristics of saline water in coastal aquifers and its interaction with fresh groundwater and recharge from precipitation with particularly interdisciplinary effort. Environmental isotopes and geochemical evidence, conjunctively with ecology, hydrology and hydrogeology, have been widely used in the study of groundwater quality in coastal aquifers. Extensive literatures can be found in IAEA and other publications on isotopic applications in hydrology, for example researches reported by Ortega (2003), Kendall and McDonnell (1998), Clark and Fritz (1997), Turner and Macpherson (1990) and Fritz and Fontes (1980).

In general, isotopic compositions are very different for seawater, fresh water and their mixtures. Therefore, the distribution, origin and age of different water can be determined by analysing their isotopic compositions and variation. It's useful to study the mixing and origin of saline water by analysing stable isotopes such as ^2H (deuterium, D), ^{18}O and ^{34}S based on geochemical support. Some successful applications were well reported. The hydrogeochemical method was used to evaluate the groundwater chemistry patterns and main mineralisation processes in Pico Island (Cruz and Silva 2000) and it was suggested that the changes in groundwater composition were caused by two main processes, silicate mineral dissolution and water salinisation in the coastal area. Multiple isotopes have been used to identify groundwater salinisation in the coast aquifers, study the interaction between groundwater quality and head variation and analyse the evolution of saline evaporitic

brines in coastal environment (Bendavid et al. 2004; Kim et al. 2003; Lee et al. 2003). More works using geochemistry and isotopes have been carried out on origin assessment of saline groundwater with effect of seawater intrusion and fresh–saline interactions (Bath et al. 2006; Farber et al. 2004; Carreon-Diazconti et al. 2003; Jørgensen 2002; Grobe et al. 2000; Louvat et al. 1999).

Unstable isotopes such as ^{14}C , ^3H (tritium, T) and ^{36}Cl are also very efficient tracers to study saline intrusion problems. In coastal regions with mixing of seawater and modern organic matters, isotopes (e.g. ^{14}C , T) can be used for groundwater time-scale evolution and mechanism identification as long as the geochemical condition can represent the hydro-geochemical characteristics of water system (Starkel et al. 2006; Bennetts et al. 2006; Sivan et al. 2005; Yang et al. 2004). Current researches show that saline intrusion problem can be solved efficiently by analysing unstable isotopes (e.g. ^{36}Cl , U and its decayed elements), stable isotopes (e.g. Sr, N) or noble gases (e.g. He, Ar). Louvat et al. (1999) studied origin of salinity within a groundwater system by combined interpretations of conservative dissolved ions, D and radioactive ^{36}Cl of dissolved Cl in water. The study concluded that groundwater salinity resulted from a mixing between the intruded Baltic Seawater and deep marine originated groundwater. Through investigation of the hydrochemistry and stable isotope (O, H, Sr) composition of present saline groundwater, Grobe et al. (2000) studied the origin and evolution of saline groundwater (TDS up to 250,000 mg/kg) in the evaporite-free Cretaceous Basin in Germany. The data showed that the saline groundwater was a combined result of water–rock interaction, migration, and mixing of fluids with different origins. Stable isotopes ^2H and ^{18}O were used to study the origin of patchy shallow saline groundwater in superficial postglacial marine sediments on the southern shores of an Island in Denmark (Jørgensen 2002); the stable isotopic compositions indicated a mixing of seawater and fresh meteoric groundwater in the proportion 0–50%.

Geochemistry and isotopic data have been widely used recently to study interactive relationship between waters from different origins (e.g. saline, fresh water). Research showed that concentration of cations and anions has a large difference between rainy and dry seasons and $\delta^{18}\text{O}$ –Cl relationship can be used to identify seawater and halite-dissolved solution (Lee et al. 2003). Kim et al. (2003) also identified the origin of saline groundwater in the eastern part of Jeju volcanic island, Korea by carrying out a hydrogeochemical and isotopic study for 18 observation wells. O, H, S and Sr isotopic data clearly showed the mixing of groundwater and seawater; Sr isotopic compositions and Br/Cl and I/Cl ratios strongly suggested the modern seawater intrusion as the source of salinity. Farber et al. (2004) revealed the origin of the salinity of the Jordan River by determining

the chemical and isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$, ^{11}B , $^{34}\text{S}_{\text{sulfate}}$, $^{18}\text{O}_{\text{water}}$, $^{15}\text{N}_{\text{nitrate}}$) of water from the Lower Jordan River and its major tributaries between the Galilee and Dead seas. Hydro-geochemical data and isotopes (^{18}O , D, ^{34}S) were used by González et al. (2005) to study the hydrothermal alteration at the Los Azufres geothermal field; the evolution of deep liquid water boiling, its connection to surface via fractures and the rock–water interaction were investigated.

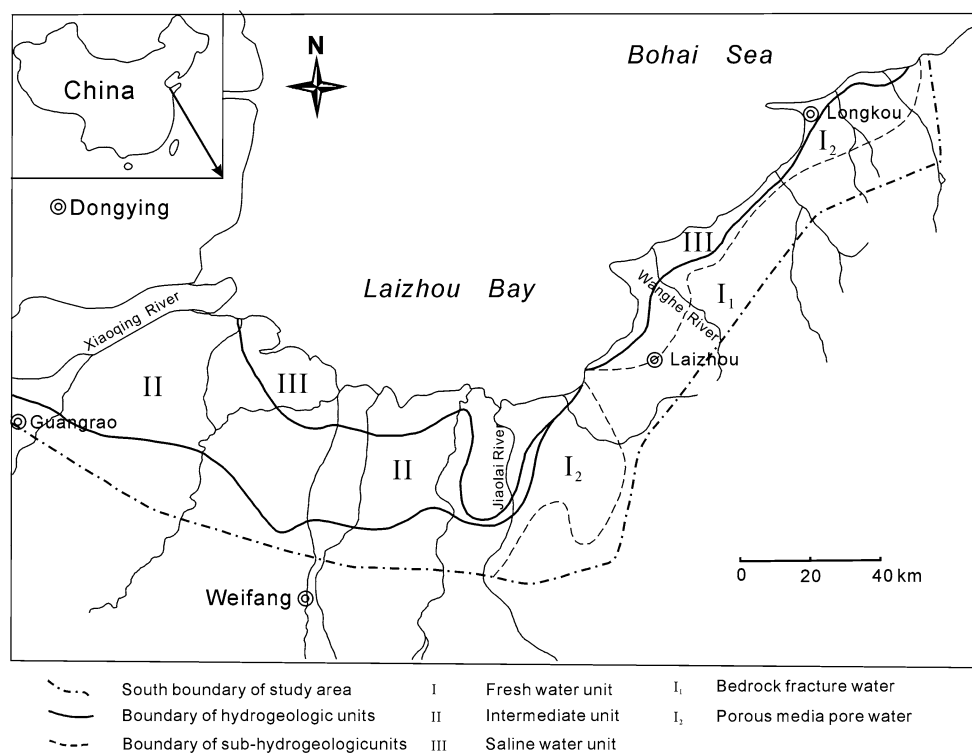
Geochemical and isotopic approach was used in our investigation for the origin of saline water in the Laizhou Bay, China. The coastal groundwater quality was investigated through sampling and analyses of groundwater, precipitation, seawater and brine water for ^{18}O , D, T and conventional geochemical analyses.

Background setting and the scientific problem

The study area is situated at the Laizhou Bay, eastern China (Fig. 1). Due to variation of the geological structures, the topography is completely different in the either sides of the Jiaolai River. It is broad and flat with low elevation in the western side of Jiaolai. The coastal plain consists of inter-layered alluvium and marine deposits near the coastal bay area. The Quaternary sediment is about 300 m thick and contacts directly to the Tertiary clay, sandstone and mudstone. However, it is hilly coast with some small-scale diluvial and alluvial pediments in the east of Jiaolai. The Quaternary sediment varies in thickness with bedrock fluctuation, from decameters to hectometers. In the study area, the formation, movement and distribution of groundwater are controlled by many geological factors such as faults, strata, geomorphology, paleogeography, climate and hydrology. Groundwater is characterised as complex and apparent variation at both horizontal and vertical directions. This area is generally groundwater discharge zone and has interactions with seawater and other saline/brine water under influence of groundwater abstractions. There are longer flowpaths from the recharge zones and thus greater travel times for the solute transport in the area. The study area is divided into three hydrogeologic units according to the objectives of this saline intrusion study and previous investigations (Fig. 1).

In the Quaternary porous media, a close hydraulic connection between fresh and saline groundwater exists. Shallow saline groundwater was found in the mid 1970s in this area (Chen and Ma 2002; Ma et al. 2005). Saline intrusion became aggravation with salinisation of groundwater in the pumping wells in 1980s. According to the preliminary analysis, it is inferred that the salinity of groundwater results from mixing of fresh groundwater, modern seawater intrusion and deep brine groundwater. Previous research demonstrated that brine

Fig. 1 Map of the regional study area and the hydrogeologic units from the previous investigations



can be syngenetic marine water formed by seawater percolating persistently into the coastal deposit and then being evaporated, concentrated and enclosed in the strata during the geologic history (Bendavid et al. 2004; Conti et al. 2000). Alternatively, it can be formed from evaporated modern seawater. The question like this was hoped to be answered by this isotopic study. It is very important to understand the origin and mechanisms of the groundwater salinity so as to propose a proper plan of prevention and management of saline intrusion.

Therefore, the origin of groundwater salinity in the Laizhou Bay area was determined by analysing the environmental isotopes (^{18}O , D and T) and some typical chemical constituents, Cl^- , SO_4^{2-} and electric conductivity (EC), in this study. This was proved very useful to understand the scale and distribution of saline intrusion in this area of China.

Sampling and measurements

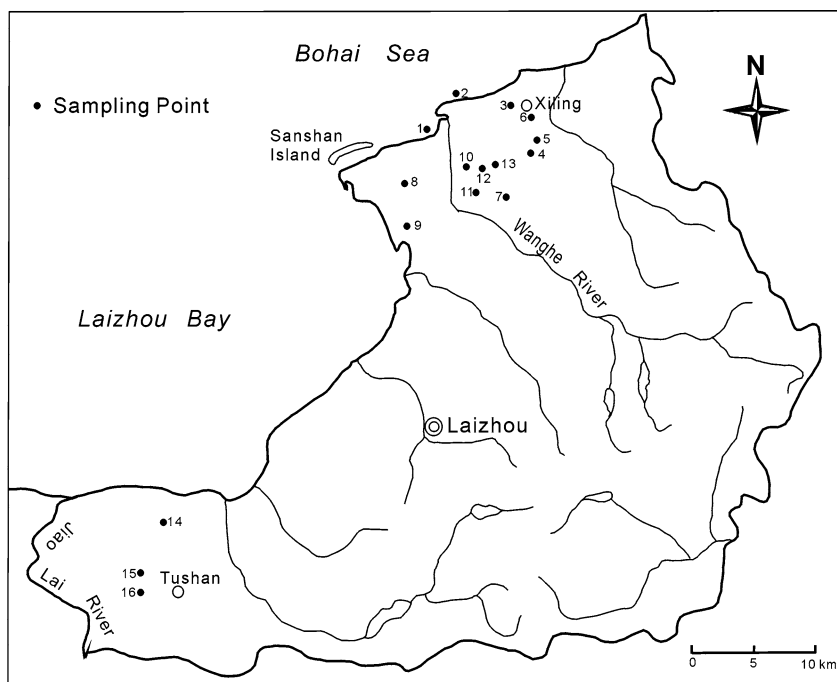
According the research plan, two rounds of groundwater samples were collected in April–May 1996 and January 1997. These data discussed here are relatively old; however, they are still useful to interpret the origin of saline groundwater. Nevertheless, groundwater utilisation, landuse and climate, hence regional flow and solute transport, have not changed too much since then as problem with seawater intrusion. To study the origin of

the groundwater salinity in the wells at the lower reaches of the Wanghe River, 16 water samples were collected in this area in the first round (Fig. 2). These include 11 saline groundwater samples from wells at the lower Wanghe reaches and the Tushan salterns, 1 rainfall water sample in the area, 2 brine groundwater samples at the Xiling and Tushan salterns and 2 seawater samples at the Sanshan Island (Fig. 2). The sampling wells have penetrated the Quaternary deposits of sandy clay and clayed silts at depths of about 20–75 m as reported previously by Ma et al. (2005). As we focused on salinity source of groundwater in the porous media in this study, there was no groundwater sampling from the fractured bedrocks (I₁ in Fig. 1) in the area.

T, D and ^{18}O were analysed for all samples and the T content was analysed with the low background measurement. Samples were concentrated by electrolysation and then formulated into scintillator liquid. The radioactivity level of T was analysed by the liquid scintilloscope with ± 0.2 TU analytical errors. D and ^{18}O were analysed by the mass spectrometry and the results were expressed as SMOW per mill (δ). The isotopic composition of hydrogen was analysed by the Zn reduction reagent method; oxygen was by the $\text{H}_2\text{O}-\text{CO}_2$ equilibration method. The analytical precision was within $\pm 2\text{‰}$ for δD and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$. The results are presented in Table 1.

To further study the origin of saline intrusion in the Laizhou Bay, 21 samples were taken in January 1997.

Fig. 2 Locations of sampling points and rivers in Laizhou City



These include 1 brine groundwater sample, 4 saline groundwater samples from wells and 4 fresh groundwater samples from the Guangrao County; 1 brine groundwater sample, 1 seawater sample, 3 fresh groundwater samples and 2 fresh groundwater samples from Laizhou City; and 1 seawater sample, 3 saline groundwater samples from wells and 2 fresh groundwater samples from Longkou City (Fig. 3). T, D, ^{18}O , Cl^- , SO_4^{2-} and EC were measured or analysed for these water samples. There was no rainfall water sample collected due to the winter dry season. The analysing and testing techniques for isotopes were the same as the first round. All data from this sampling campaign were listed in Table 2.

Results and interpretation

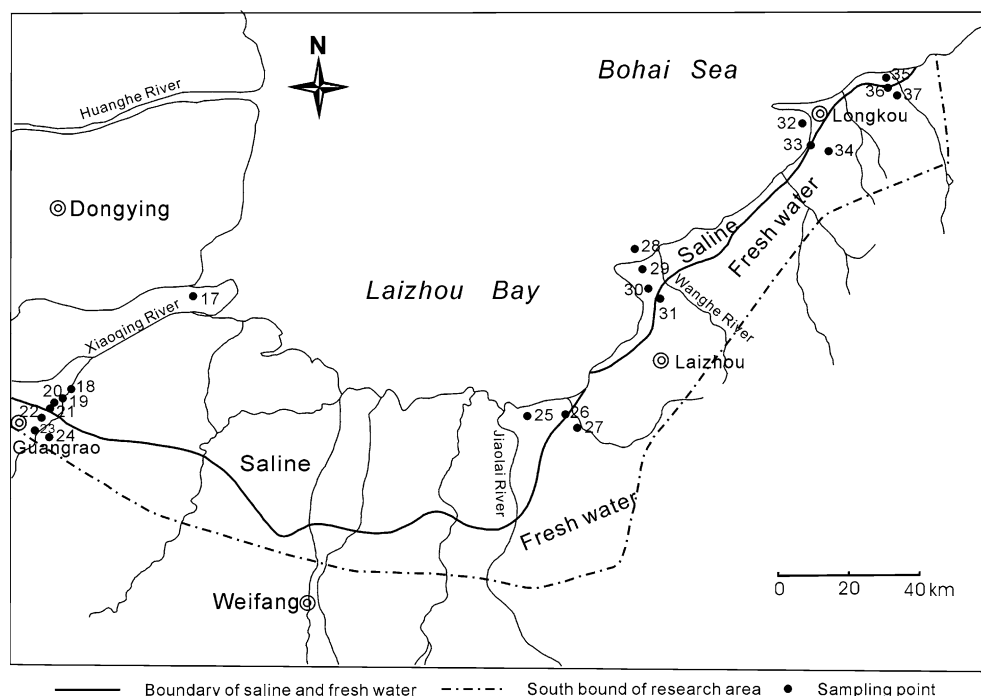
Local groundwater quality of Laizhou City

To analyse the shallow groundwater quality in Laizhou City, diagrams were drawn from the data in Table 1 with respect to rainfall 13[#], seawater 1[#], 2[#] and the Tushan brine water 14[#]. The relationships between δD and $\delta^{18}\text{O}$, T and $\delta^{18}\text{O}$ were obtained and showed in Figs. 4 and 5. The values of all saline groundwater samples from the wells and the brine samples are closely located in between two lines fitted by rainfall 13[#] and seawater 1[#] and 2[#], the Tushan brine groundwater 14[#],

Table 1 Isotopic compositions of water samples in Laizhou City (the first sampling campaign)

Areas	Water types	No.	$\delta^{18}\text{O}$ (‰)	δD (‰)	Tritium (TU)
Lower reaches, Wanghe River	Seawater	1	-1.93	-26.1	13.1
		2	-1.77	-28.1	14.1
	Brine	3	-7.10	-56.2	9.9
		4	-7.44	-62.1	13.7
	Saline groundwater	5	-7.39	-60.5	5.6
		6	-6.41	-57.1	7.5
		7	-7.67	-61.2	19.9
		8	-7.60	-60.9	10.6
		9	-7.41	-59.9	1.8
		10	-7.66	-63.4	4.8
		11	-6.00	-55.7	18.1
		12	-7.93	-78.3	18.6
		13	-14.76	-106.5	17.2
Tushan	Rainfall	13	-14.76	-106.5	17.2
	Brine	14	-2.43	-38.1	8.9
	Saline groundwater	15	-7.54	-59.1	12.7
		16	-7.57	-63.5	10.5

Fig. 3 Locations of sampling points and major rivers in the regional Laizhou Bay area



respectively (Fig. 4). They locate fairly close along the rainfall-seawater/brine lines (except 12[#]), and thus the relationship between δD and $\delta^{18}O$ cannot show the origin of the groundwater salinity in this case. However, in the diagram of T versus $\delta^{18}O$ (Fig. 5), 15[#] and 16[#] samples known intruded by the Tushan saltern groundwater (cf. Ma et al. 2005) are situated between

the brine groundwater 14[#] in the Tushan saltern and the rainfall 13[#]; the brine groundwater 3[#] in the Xiling saltern deviates underneath the line fitted by seawater (1[#], 2[#]) and rain water (13[#]). Therefore, it is possible to determine the origin of salinity in the water by the T- $\delta^{18}O$ relationship. The tritium of seawater is 13.1–14.1 TU and brine is 8.9–9.9 TU (Fig. 5). The samples

Table 2 Chemical and isotopic compositions of water samples in the regional Laizhou Bay area (the second sampling campaign)

Areas	Water types	No.	$\delta^{18}O$ (‰)	δD (‰)	T (TU)	Conductivity ($\mu S/cm$)	Cl^- (ppm)	SO_4^{2-} (ppm)	
Guangrao County	Brine	17	-5.70	-54.30	5.4	5.60E+04	48426.0	4976.4	
	Saline ^a	18	-7.83	-61.30	13.1	1.87E+04	6716.2	1229.0	
	Saline groundwater	19	-8.80	-66.00	22.0	1.60E+03	184.5	171.7	
		20	-9.35	-73.00	3.8	2.25E+03	397.8	204.3	
		21	-9.15	-72.10	10.9	1.75E+03	229.5	139.5	
	Fresh water	22	-10.14	-78.60	10.5	7.00E+02	24.2	81.6	
		23	-9.21	-72.80	10.9	1.25E+03	148.2	61.1	
24		-9.88	-72.90	7.4	8.00E+02	42.1	66.1		
Laizhou City		Brine	25	-3.17	-42.40	14.1	8.13E+04	87051.5	9239.2
		Saline groundwater	26	-7.70	-60.00	14.3	1.97E+02	345.9	233.6
Laizhou City	Fresh water	27	-7.77	-58.50	23.0	9.50E+02	149.9	32.1	
	Seawater	28	-1.73	-23.90	16.6	3.40E+04	16142.0	1735.3	
	Saline groundwater	29	-9.00	-64.10	12.0	3.42E+03	446.8	647.5	
	30	-7.94	-62.90	11.6	3.42E+03	559.2	173.1		
	Fresh water	31	-7.73	-68.90	23.4	1.73E+03	193.7	73.9	
	Longkou City	Seawater	32	-1.68	-19.30	14.2	3.30E+04	15565.5	1961.3
		Saline groundwater	33	-7.55	-55.70	16.4	4.50E+03	1268.3	33.5
Fresh water		34	-7.96	-64.40	17.2	6.70E+02	85.3	21.3	
Saline groundwater		35	-7.43	-57.40	15.3	1.27E+03	170.1	102.9	
36		-8.11	-62.90	17.0	1.52E+03	250.8	28.5		
Fresh water		37	-7.73	-60.50	17.8	1.78E+03	292.9	161.8	

^aExtremely saline groundwater, identified by EC and Cl^- values

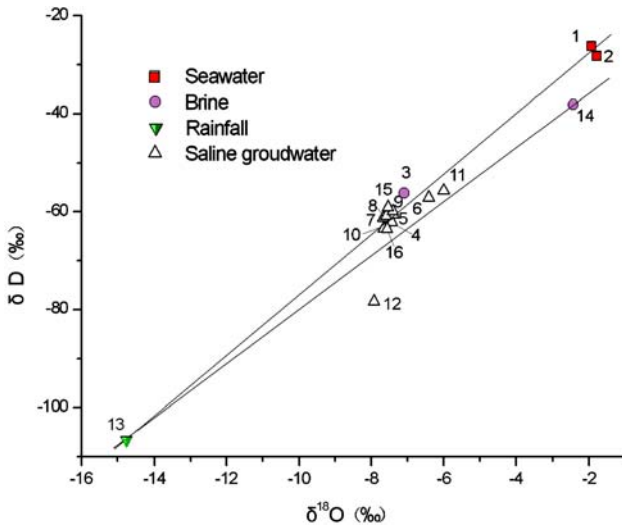


Fig. 4 Relationship between $\delta^{18}\text{O}$ and δD of the water samples from different sources in Laizhou City

4[#], 7[#], 11[#] and 12[#] near the line fitted by seawater and the rainfall samples are 13.7–19.9 TU, which indicates a modern seawater origin. The T content of samples 15[#], 16[#] is 12.7 and 10.5 TU respectively, located around the line fitted by the brine water in the Tuashan saltern and the rainwater and being close to the T level of the Tushan saltern brine water. The tritium of samples 5[#], 6[#], 8[#], 9[#], 10[#] are in 1.8–10.6 TU, resulting from the Xiling saltern brine intrusion (sample 3[#] 9.9 TU) mixing with freshwater of possibly much longer travel time from the upper gradient recharge area. Bearing in mind that T in water can vary greatly during the recharge, movement and

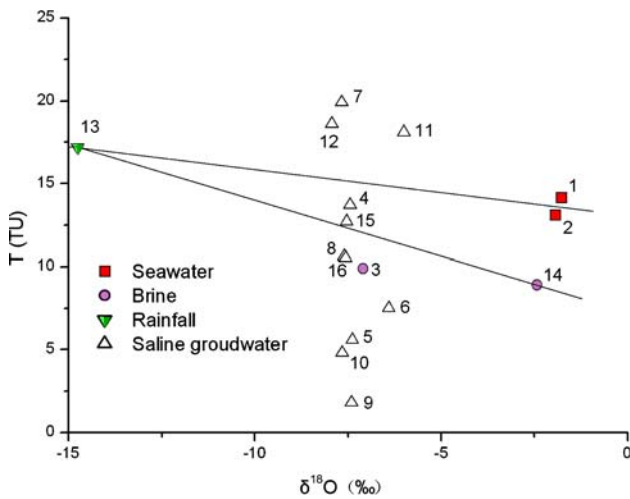


Fig. 5 Relationship between $\delta^{18}\text{O}$ and T of the water samples from different sources in Laizhou City

interaction with seawater or abstractions, as T is radioactive and decays in groundwater system. This hence may also indicate the decay of T during groundwater transport through the fractured matrix aquifer system.

Groundwater quality of the regional Laizhou Bay

For interpretation of the groundwater quality in the regional Laizhou Bay area, more diagrams were plotted for correlation analysis using the data of $\delta^{18}\text{O}$, D, EC, Cl^- and SO_4^{2-} in Table 2. Figures 6, 7 and 8 are the relationships between $\delta^{18}\text{O}$ and EC, Cl^- and SO_4^{2-} , respectively. These diagrams show similar trend with some variation, demonstrating geochemical support to isotope data (^{18}O). Two apparent curves are showed in these figures; the upper curve with two ends of seawater (e.g. 28[#], 32[#]) and fresh water (e.g. 34[#]) respectively indicating mixing of seawater and fresh whilst the lower one with ends of brine (e.g. 17[#], 25[#]) and fresh waters (e.g. 22–24[#]), respectively. The saline groundwater samples 35[#], 26[#], 36[#], 30[#] and 33[#] are distributed closely on to this “fresh–sea curve” with the origin of seawater intrusion; whilst the saline groundwater samples 19[#], 20[#], 21[#] and 29[#] are distributed on the “fresh–brine curve” with the origin of brine intrusion. Sample 18[#] is closer to the brine showing more influence from the brine intrusion.

Figure 9 shows the δD – $\delta^{18}\text{O}$ relationship. All samples in this figure are located in the right flank of the global meteoric water line (GMWL) defined by Craig (Kendall and McDonnell 1998). The $\delta^{18}\text{O}$ value of seawater samples ranges between -1.68 and -1.173‰ , δD between -19.3 and -29.90‰ due to the intense evapo-

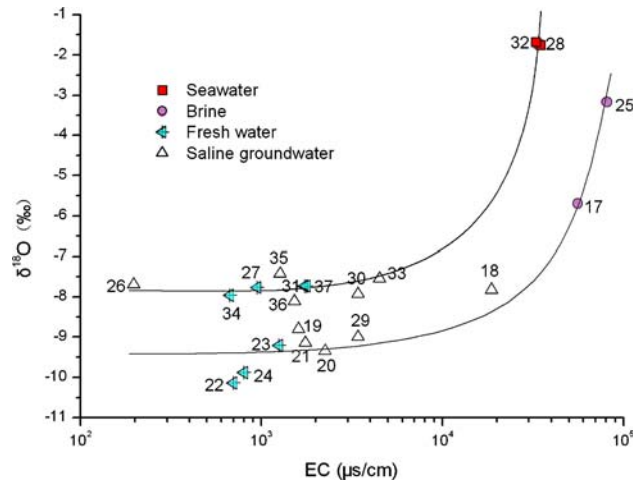


Fig. 6 Relationship between $\delta^{18}\text{O}$ and conductivity of the water samples in the regional Laizhou Bay area

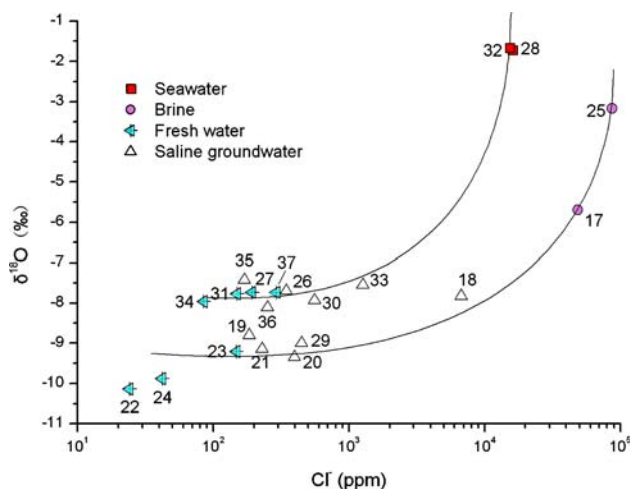


Fig. 7 Relationship between $\delta^{18}\text{O}$ and Cl^- of the water samples in the regional Laizhou Bay area

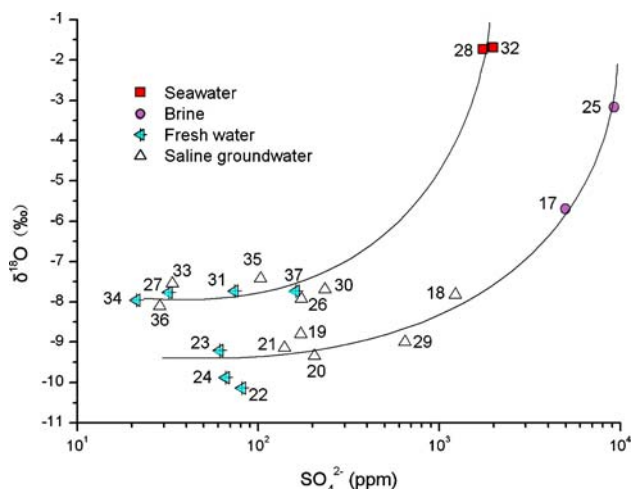


Fig. 8 Relationship between $\delta^{18}\text{O}$ and SO_4^{2-} of the water samples in the regional Laizhou Bay area

ration on the surface of the sea. The $\delta^{18}\text{O}$ value of the brine groundwater samples is within a range of -5.70 to -3.17‰ and δD -54.30 to 42.40‰ , deviating the GMWL far to the right and originating from modern seawater with evaporation. This is a good evidence to answer the question of ‘what is the origin of brine in groundwater’. For the fresh groundwater samples, the $\delta^{18}\text{O}$ ranging between -10.14 and -7.73‰ , and δD between 72.90 and 58.50‰ , are distributed to the lower-right of the GMWL, indicating that fresh groundwater is from precipitation and undergoes evaporation for a long time because of the shallow ground water level. For the saline groundwater samples from wells, the $\delta^{18}\text{O}$ value ranging between -9.35 and -7.55‰ , and δD between -73.00 and -55.70‰ , are distributed between the

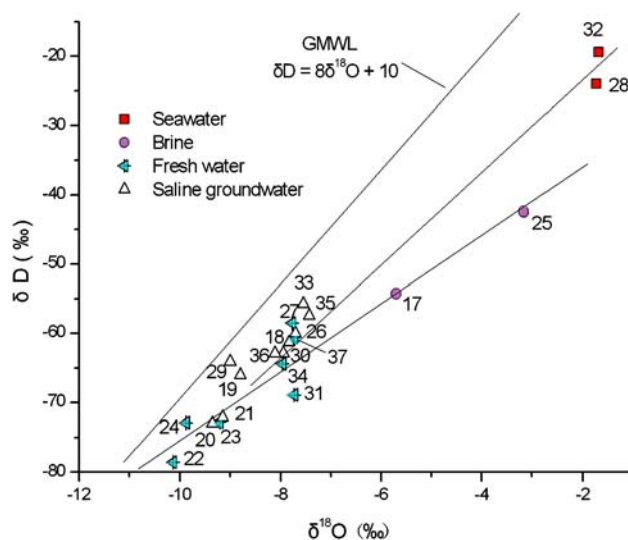


Fig. 9 $\delta^{18}\text{O}$ versus δD for the various water samples in the regional Laizhou Bay area

shallow groundwater and seawater/brine, resulting from mixing of fresh water and seawater or/and brine. Because the saline groundwater samples from the wells are crowded around mixing line, it is not easy to distinguish their origin of salinity by the δD – $\delta^{18}\text{O}$ relation alone in this study. However, the δD and $\delta^{18}\text{O}$ values of the saline groundwater with brine intrusion, as suggested by Figs. 6, 7 and 8, are relatively small, e.g. δD of $19^\#$, $20^\#$, $21^\#$, $29^\#$ is -72.1 to -61.3‰ and the $\delta^{18}\text{O}$ -9.35 to -7.83‰ ; the saline water with seawater intrusion has higher $\delta\text{D}/\delta^{18}\text{O}$ value, e.g. δD of $26^\#$, $30^\#$, $33^\#$, $35^\#$, $36^\#$ samples is within a range of -62.90 to -55.70‰ and $\delta^{18}\text{O}$ -8.11 to -7.55‰ .

The tritium versus $\delta^{18}\text{O}$ relationship is showed in Fig. 10 based on the data of the second sampling

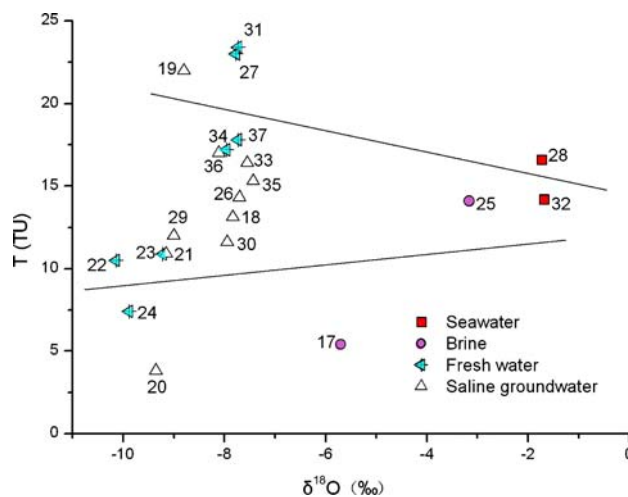


Fig. 10 $\delta^{18}\text{O}$ versus T for the various water samples in the regional Laizhou Bay area

campaign in Table 2. Tritium of the seawater samples is 14.2–16.6 TU and the brine samples 5.4–14.1 TU. The fresh groundwater samples are between 7.4 and 23.4 TU with the greatest variation due to different flow and transport patterns in the study area. As the groundwater recharge in the eastern area (Longkou and Laizhou) is from the offshore mountains lateral flow and precipitation infiltration, its T content is higher, 17.2–23.4 TU. As the sampling locations are far away from the recharge area in the west part (Guanrao) with much greater residence time, the T level of groundwater samples over there is lower, 7.4–10.9 TU. From the above origin analyses (Figs. 6, 7, 8, 9), the saline groundwater samples from the wells resulted from brine intrusion has T values of 3.8–13.1 TU and the saline water samples from seawater intrusion has T of 11.6–17.8 TU. Therefore, the tritium content can help interpret the water sources along with other isotopes. In this study, a threshold value of tritium 12 TU was used to identify the water sources; water with T of greater than 12 TU indicates salinity from seawater intrusion and the smaller values than 12 TU shows groundwater origin from brine, which was also shown similarly in Fig. 5.

Discussion

It is a popular hydrogeological topic to study the origin of groundwater salinity, which has practical significance for preventing and controlling of salty water intrusion in the coastal areas. The environmental isotopes and hydrochemical methods are effective for solving such a problem.

The salinity origin of ground water can generally be distinguished by using δD – $\delta^{18}O$ relationship, because the stable isotope fractionation is mainly related to temperature (Kendall and McDonnell 1998; Huddart et al. 1999). If the brine and modern seawater in the coastal aquifers were formed under different temperature, their δD and $\delta^{18}O$ values can be different. If the ancient temperature was similar to the modern one, there can be little difference. Therefore, the case-specific situations must be carefully considered in studying the salinity origin of the saline groundwater using δD and $\delta^{18}O$ (Clark and Fritz 1997; Jørgensen 2002; Carreon-Diazconti et al. 2003; Wilcox et al. 2004). Our research indicated that the brine in the Laizhou Bay area originated from the modern existing or invading seawater by evaporating and concentrating. The δD and $\delta^{18}O$ of such brine are different from the modern seawater; however the saline waters formed by mixing of fresh water with these two types of water share much similar values of δD and $\delta^{18}O$. These analyses were similar to those used by Huddart et al. (1999) and Carreon-Diazconti et al. (2003). Therefore, it is difficult to

distinguish the origin of such waters using δD and $\delta^{18}O$ approach alone in our case study.

Because of the distinct difference in salinity between the brine and seawater, the relations between $\delta^{18}O$ and EC, Cl^- and SO_4^{2-} can be used to distinguish the salinity origin of groundwater in the study area (cf. Bath et al. 2006). During the mixing and concentrating processes of fresh groundwater and the highly-mineralised brine or seawater, the water quality and $\delta^{18}O$ value increases with the quantity of the mixing waters. They change proportionally along the mixing curves with ends of fresh groundwater and brine or seawater. Therefore, the mixed water falls on the mixing-curves or nearby in the mixing-water diagrams between $\delta^{18}O$ and Cl^- , SO_4^{2-} and EC, respectively. In other words, $\delta^{18}O$ and groundwater salinity increases proportionally along the mixing-curves with mixing of the highly mineralised salty water into fresh groundwater; $\delta^{18}O$ increases at a linear logarithm relationship with SO_4^{2-} , Cl^- and EC in the mixing process (Dutkiewicz et al. 2000; Wilcox et al. 2004).

The salinity origin from water intrusion can also be distinguished by using tritium (T) analysis. The T level of brine is generally lower than that of seawater. In some localities of the study area, such as the lower reaches of Wanghe in Laizhou City, the salinity origin of the saline groundwater can be distinguished clearly by using the T and $\delta^{18}O$ relations from whether the mixture of fresh water and seawater, or fresh water and brine. However, it is not clear from the T versus $\delta^{18}O$ relational curves in the larger region, e.g. the Laizhou Bay region, due to the variation of tritium content in fresh groundwater in different areas, which may reflect the complexity of groundwater flowpaths and variation of travel time in the regional system. The T = 12 TU can be regarded as the threshold of identifying salinity origin of salinised groundwater; i.e., it is salinised by the modern seawater if T > 12 TU and by the brine intrusion if T < 12 TU.

The comprehensive analyses of environmental isotopes and hydrochemistry in the study indicate that Guanrao in the west is the brine intruded area, where groundwater over-exploitation caused groundwater level drawdown and the brine intrusion in the stratum. Longkou in the east is the area where groundwater salinised by the modern seawater intrusion; the salinity origin in this area is completely from the modern seawater. Laizhou in the middle of study area is originated from both the seawater and brine intrusion (mixing), where the problem of the salt water intrusion is the most serious part of the area and further thorough study is needed. The dynamic groundwater system was dominantly controlled by over-abstraction in the past decades which let to change of groundwater quality and overall regime. The detailed salinisation, conceptualisation and numerical modelling have been

reported previously by Chen and Ma (2002) and Ma et al. (2005).

The effective study on evolution of groundwater quality and, in particular, salinity origin of groundwater is important in the decision making to prevent and mitigate seawater intrusion. It is indeed useful to setup a monitoring network of isotopes and hydrochemistry near the salty–fresh water interface for regular sam-

plings, so that a better groundwater management plan for sustainable water use can be achieved.

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References

- Bath A, Richards H, Metcalfe R, McCartney R, Degnan P, Littleboy A (2006) Geochemical indicators of deep groundwater movements at Sellafeld, UK. *J Geochem Explor* 90:24–44
- Bendavid OK, Sass E, Katz A (2004) The evolution of marine evaporitic brines in inland basins: The Jordan–Dead Sea Rift valley. *Geochim Cosmochim Acta* 68(8):1763–1775
- Bennetts DA, Webb JA, Stone DJM, Hill DM (2006) Understanding the salinisation process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. *J Hydrol* 323:178–192
- Carreon-Diazconti C, Nelson ST, Mayo AL, Tingey DG, Smith M (2003) A mixed groundwater system at Midway, UT: discriminating superimposed local and regional discharge. *J Hydrol* 273:119–138
- Chen M, Ma F (2002) Groundwater and environment of China (in Chinese). Seismological Press, Beijing, 481p
- Clark ID, Fritz P (1997) Environmental isotopes in hydrogeology. CRC-Press LLC, Florida, p 328
- Conti A, Sacchi E, Chiarle M, Martinelli G, Zuppi GM (2000) Geochemistry of the formation waters in the Po plain (Northern Italy): an overview. *Appl Geochem* 15:51–65
- Cruz JV, Silva MO (2000) Groundwater salinization in Pico Island (Azores, Portugal): origin and mechanisms. *Environ Geol* 39(10):1181–1189
- Dutkiewicz A, Herczeg AL, Dighton JC (2000) Past changes to isotopic and solute balances in a continental playa: clues from stable isotopes of lacustrine carbonates. *Chem Geol* 165:309–329
- Farber E, Vengosh A, Gavrieli I, Marie A, Bullen TD, Mayer B, Holtzman R, Segal M, Shavit U (2004) The origin and mechanisms of salinization of the Lower Jordan River. *Geochim Cosmochim Acta* 68:1989–2006
- Fritz P, Fontes JCH (1980) Handbook of environmental isotope geochemistry, 1. The terrestrial environment. Elsevier, Amsterdam, pp 75–140
- González PE, Carrillo AC, Levresse G, Tello EH, Venegas SS, Ramirez GS, Pal-Verma M, Tritlla J, Camprubi A (2005) Hydro-geochemical and isotopic fluid evolution of the Los Azufres geothermal field. Central Mexico *Appl Geochem* 20(1):23–39
- Grobe M, Machel HG, Heuser H (2000) Origin and evolution of saline groundwater in the Munsterland Cretaceous Basin, Germany: oxygen, hydrogen, and strontium isotope evidence. *J Geochem Explor* 69–70:5–9
- Huddart PA, Longstaffe FJ, Crowe AS (1999) δD and $\delta^{18}O$ evidence for inputs to groundwater at a wetland coastal boundary in the southern Great Lakes region of Canada. *J Hydrol* 214:18–31
- Jørgensen NO (2002) Origin of shallow saline groundwater on the Island of Denmark. *Chem Geol* 184:359–370
- Kendall C, McDonnell JJ (eds) (1998) Isotope tracers in catchment hydrology. Elsevier, Amsterdam, 839p
- Kim Y, Lee K-S, Koh D-C, Lee D, Lee S, Park W, Koh G, Woo N (2003) Hydrogeochemical and isotopic evidence of groundwater salinization in a coastal aquifer: a case study in Jeju volcanic island, Korea. *J Hydrol* 270:282–294
- Lee J, Kim R, Chang H (2003) Interaction between groundwater quality and hydraulic head in an area around an underground LPG storage cavern, Korea. *Environ Geol* 43:901–912
- Louvat D, Michelot JL, Aranyosy JF (1999) Origin and residence time of salinity in the Äspö groundwater system. *Appl Geochem* 14:917–925
- Ma F, Yang Y, Cai Z, Chen M, Yuan R (2005) Dynamic process analyses of saline intrusion with over-exploitation by coupled flow and dispersive modeling. *Environ Geol* 48(6):818–828
- Ortega GA (2003) Origin and geochemical evolution of groundwater in a closed-basin clayey aquitard, Northern Mexico. *J Hydrol* 284:26–44
- Sivan O, Yechieli Y, Herut B, Lazar B (2005) Geochemical evolution and timescale of seawater intrusion into the coastal aquifer of Israel. *Geochim Cosmochim Acta* 69(3):579–592
- Starkel L, Soja R, Michczynska DJ (2006) Past hydrological events reflected in Holocene history of Polish rivers. *Catena* 66:24–33
- Turner JV, Macpherson DK (1990) Mechanisms affecting streamflow and streamwater quality: an approach via stable isotope, hydrogeochemical and time series analysis. *Water Resour Res* 26:3005–3019
- Wilcox WM, Solo-Gabriele HM, Sternberg LO (2004) Use of stable isotopes to quantify flows between the Everglades and urban areas in Miami-Dade County Florida. *J Hydrol* 293:1–19
- Yang YS, Cronin A, Elliot T, Kalin RM (2004) Characterizing heterogeneous systems through inverse groundwater flow and geochemical modelling. *J Hydraul Res* 42:147–155