Hydrochemical characteristics and salinization processes of groundwater in the shallow aquifer of Eastern Laizhou Bay, China

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Abstract:

Groundwater salinization has become a crucial environmental problem worldwide and is considered the most widespread form of groundwater contamination in the coastal zone. In this study, a hydrochemical investigation was conducted in the eastern coastal shallow aquifer of Laizhou Bay to identify the hydrochemical characteristics and the salinity of groundwater using ionic ratios, deficit or excess of each ions, saturation indices and factor analysis. The results indicate that groundwater in the study area showed wide ranges and high standard deviations for most of hydrochemical parameters and can be classified into two hydrochemical facies, Ca^{2+}-Mg^{2+}-Cl^- facies and Na^+-Cl^- facies. The ionic ratio, deficit or excess of each ions and SI were applied to evaluate hydrochemical processes. The results obtained indicate that the salinization processes in the coastal zones were inverse cation exchange, dissolution of calcite and dolomite, and intensive agricultural practices. Factor analysis shows that three factors were determined (Factor 1: TDS, EC, Cl^-, Mg^{2+}, Na^+, K^+, Ca^{2+} and SO_4^{2-}; Factor 2: HCO_3^- and pH; Factor 3: NO_3^- and pH), representing the signature of seawater intrusion in the coastal zone, weathering of water–soil/rock interaction, and nitrate contamination, respectively. Copyright © 2011 John Wiley & Sons, Ltd.

KEY WORDS   hydrochemical characteristics; groundwater salinization; ionic ration; factor analysis; shallow coastal aquifer; Laizhou Bay

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INTRODUCTION

Groundwater is a vital resource for communities and ecosystems of the coastal zone, groundwater withdrawals for public supplies, agriculture, industry, and other uses in coastal areas (Barlow 2003). During the past decades, groundwater in the coastal area has been intensively studied in terms of both scientific interest and social relevance. Salinization is the most widespread form of the groundwater containment, especially in the coastal areas, and is represented by the increase of total dissolved solid (TDS) and some special chemical constituents (Park *et al*., 2005). Groundwater in coastal areas is vulnerable to salinization by seawater, which can make it unfit for drinking or agricultural use; moreover, groundwater salinization, which can be enhanced by natural processes and anthropogenic factors, seems to have become a worldwide concern (Pulidoleboeuf, 2004; Sivan *et al*., 2005; Abou Zakhem and Hafez, 2006; Lee and Song, 2006; Papatheodorou *et al*., 2007; Trabelsi *et al*., 2007; Carol *et al*., 2009; Elyaouti *et al*., 2009; Kouzana *et al*., 2009; Mondal *et al*., 2010).

The salinization of groundwater has been investigated using variety of methods such as geophysical surveys (Elyaouti *et al*., 2009), numerical modelling (Giambastiani *et al*., 2007; He *et al*., 2008; Padilla *et al*., 2008), isotopic methods (Abou Zakhem and Hafez, 2006; Carol *et al*., 2009), hydrochemical surveys (Kim *et al*. 2005; Mondal *et al*., 2010) and multivariate statistical techniques (Liu *et al*., 2003; Kim *et al*. 2005; Papatheodorou *et al*., 2007). Hydrochemical surveys, as the most important and successful tool for investigating the salinization processes of groundwater to elucidate the source of salinity and to understand the hydrochemical conditions, have been performed in many coastal areas. (Park *et al*., 2005). The multivariate analysis, such as factor analysis, has been widely used as unbiased methods in analysis of hydrochemical data, and it is useful for evidencing the hydrochemical variations caused by natural and anthropogenic processes (Morell *et al*., 1996; Liu *et al*., 2003; Kim *et al*. 2005; Papatheodorou *et al*., 2007).

The Laizhou Bay is located in the south of the Bohai Sea, east of China (Figure 1). For the last few decades, with the rapid population increase and remarkable economic development, water demands in this area have become greater, and groundwater has been over-abstracted. In the eastern Laizhou Bay, the annual exploitation of groundwater was $1.54 \times 10^8 \, m^3$ (Li 2005). Because of over-abstraction of groundwater, the groundwater levels were significantly lowered, and seawater intrusion throughout the area is one of the most serious areas of seawater intrusion in China (Yin 1992).

In recent years, the Chinese government and many scientists have carried out many research on the

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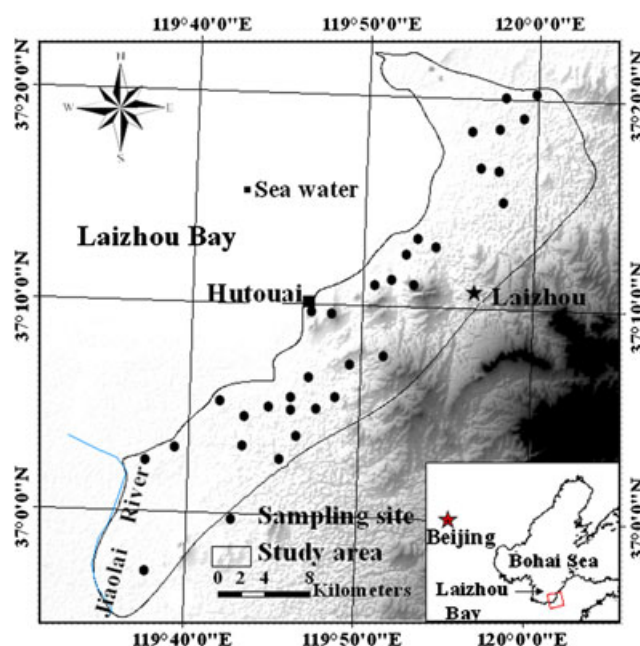E-mail: xhwen@yic.ac.cn

Figure 1. Location of the study area and the sampling sites

assessment of seawater intrusion in the Laizhou Bay. Many research focused on the quality assessment of groundwater, understanding of the relations between seawater intrusion and environmental change, and recognizing how to practice groundwater management (Yin 1992; Xue *et al*., 1998; Zhang and Dai 2001; Zhang *et al*., 2001; Han 2003; Ma *et al*., 2006). Despite the importance of groundwater in the eastern coastal Laizhou Bay, little is known about the natural processes governing the salinity of the groundwater or the anthropogenic factors currently affecting it. Increased knowledge on salinity evolution of groundwater in these coastal regions can improve the understanding of hydrochemical systems and promote sustainable development of water resources and effective management of groundwater resources.

The goal of this study was to identify the mechanisms of groundwater salinization in the eastern coastal aquifer of Laizhou Bay using hydrochemical data and factor analysis. The results of this study provided essential information for the effective design of water resource management strategies in the area.

Geographical and hydrogeological setting

The study area is located in the eastern of the Laizhou Bay, extending from 36°50' to 37°20'N latitude and 119°30' to 120°10'E longitude and including Laizhou City (Figure 1). The area has a continental climate with a mean annual temperature of 12.4 °C. The average annual precipitation is 640.3 mm, with the majority (72.4%) falling from June to September. The average annual potential evaporation is 2118.7 mm (Fu *et al*., 1994).

The research area borders on Bohai in the north. The coast is made up of sandbar, lagoon and bedrock. Five types of landforms, that is, marine deposits plain, alluvial plain, pluvial plain and bedrock hills, spread from coast to inland. The plains distribute in shape of belt in east-north direction with the width of 5–10 km and 2–3 km in some parts (Figure 2).

From Hutouai to the northern part of study area, the Quaternary deposits are generally 15–25 m thick. The sediments mainly consist of sandy clay, medium-fine grade of sand and clayey sand interbed. From Jiaolai River mouth plains to the Hutouai, the littoral plain is composed of alternating strata of land facies and marine facies sediments, which consists of alluvial or diluvial mild clay, sandy clay, fine and medium sands, coarse sands and gravels, usually 10–100 m in thickness.

There are two types of water-bearing bodies in the study area, Quaternary loose beds and bedrock-fissured aquifer. The Quaternary water-bearing media are made up of fluvial and pluvial sediments, sand layers of marine phase and talus strata. The thickness of deposits is 10–100 m in the west and 15–25 m in the east. There are two to three aquifers that mainly consist of different lithofacies, that is, gravel sand, coarse sand, medium-granular sand, small-granular sand and so on and transit to the sediments of marine phase or lagoon phase. The hydraulic connection between up and down aquifers is very close because of the existence of 'deposit windows' and a large amount of withdrawal from boreholes.

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 characterized 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 flow paths from the recharge zones and, thus, greater travel times for the solute transport in the area (Ma *et al*., 2006).
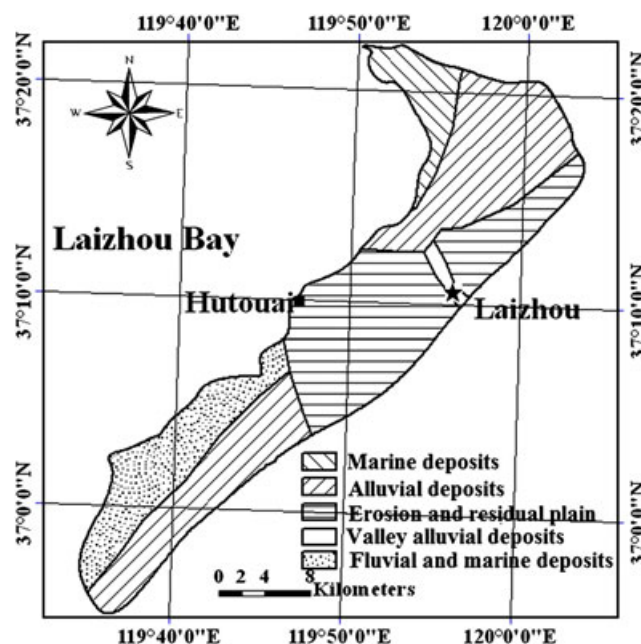
Figure 2. Simplified geological map of the study area (after Han, 1996)

The recent 2009 piezometric map (Figure 3) shows piezometric depressions related to overexploitation of the aquifer with negative piezometric levels on the order of −5 m. This map (Figure 3) shows a multidirectional flow mainly oriented to the piezometric depressions located at north and the west of the study area.

MATERIALS AND METHODS

Field investigation was carried out in August 2009. A total of 32 shallow groundwater samples from long-term groundwater observation wells and drinking wells with depth of 5–40 m, the sample wells located within 10 km from the coastline, were randomly selected for groundwater sampling (Figure. 1).

Water temperature, electrical conductivity (EC) and pH were measured in the field. Major cation concentrations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analysed using inductively coupled plasma-atomic emission spectrometer and atomic absorption spectrometry. The anion concentrations, including Cl^-, SO_4^{2-} and NO_3, were analysed using ion chromatography, and the anion HCO_3^- was analysed using titration (pH 4.8 alkalinity). The value of TDS was calculated from measured major constituents (Fishman and Friedman, 1989).

Ion balance checking was used to carefully inspect the chemical analyses quality. The chemical analyses were
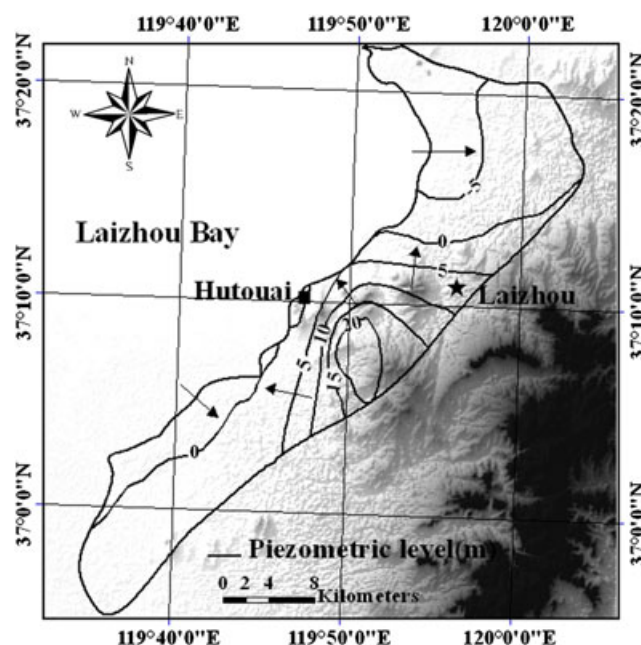

Figure 3. Piezometric map of the shallow aquifer of the study area (August 2009)

tested for charge balance error according to the following equation Freeze and Cherry (1979) described:

$$\%\text{Charge Balance Error} = \frac{\sum z \cdot m_c - \sum z \cdot m_a}{\sum z \cdot m_c + \sum z \cdot m_a} \cdot 100 \quad (1)$$

where z is the absolute value of the ionic valence, m_c is the molality of cationic species and m_a is the molality of the anionic species.

Calculated charge balance errors were less than or equal to $\pm 10\%$, which was an acceptable error for the purpose of this study.

The interpretation of the analytical results was shown numerically and graphically through the saturation index (SI), ionic deviations, piper diagram and binary diagrams. Calcite, dolomite, gypsum and halite SI were calculated using the PHREEQC 2.17 software to verify the salinization phenomena.

Ionic deviations were calculated to better understand the hydrochemical processes that took place in the aquifer. Given the two end-member water samples, the conservative mixture concentration of an ion derives from the following equation (Appelo and Postma 2005):

$$m_{i,mix} = f_{sea} \cdot m_{i.sea} + (1 - f_{sea}) \cdot m_{i.fresh} \quad (2)$$

where m_i is the concentration of the ion i (meq/l); f_{sea} stands for the fraction of seawater; the indexes *mix*, *sea* and *fresh* correspond to the conservative mixture and the end members of seawater and freshwater, respectively.

Any deficit or excess, expressed as negative or positive value of $m_{i,react}$, will constitute ion exchange or redox reactions, which can be simplified as

$$m_{i,react} = m_{i,sample} - m_{i,mix} \quad (3)$$

where $m_{i,sample}$ is the measured concentration of the ion i in the sample.

It is possible to estimate the fraction of seawater of each well based on the Cl⁻ concentration, which is considered as a conservative tracer, namely does not contribute to the ion exchange processes (Tellam 1995):

$$f_{sea} = \frac{m_{Cl^-,sample} - m_{Cl^-,fresh}}{m_{Cl^-,sea} - m_{Cl^-,fresh}} \quad (4)$$

Multivariate analysis of the hydrochemical parameter data sets was performed through factor analysis techniques. The factor analysis was applied on experimental data standardized through z-scale transformation to avoid misclassification because of wide differences in data dimensionality (Liu *et al.*, 2003). Furthermore, the standardization procedure eliminates the influence of different units of measurements and renders the data dimensionless. Factor analysis was performed on correlation matrix of rearranged data for hydrochemical parameters. The factor loadings of the variables with eigenvalues were computed. Data sets were processed using routines taken from SPSS-13.0 statistical software.

RESULTS AND DISCUSSIONS

Hydrochemical characteristics

Table I summarizes the basic statistics of hydrochemical parameters for the analysed groundwater samples from the study area in August 2009. Groundwater samples collected from the study area showed high Cl⁻ contours (Figure 4). The high values of the Cl⁻ of groundwater in the study area relate to the zones characterized by significant piezometric depressions such as the areas of north and west of the study area. In particular, very wide ranges and high standard deviations were easily recognized for most of parameters (Table I). The pH ranged from 5.65 to 7.48, with an average of 7.02, indicating a slight tendency towards a basic composition. EC varied between 591 and 31 600 μS/cm, with an average of 3572.38 μS/cm; the TDS value had a wide range between 249.60 and 5878.30 mg/l with an average of 1233.27 mg/l. The ranges of Na⁺ and Cl⁻ ions also were wide, variations with ranges of 12.27–771.55 mg/l with an average of 143.61 and 42.68-2145.78 mg/l with an average of 404.76 mg/l, respectively. SO₄²⁻ value also showed large variations ranging from 20.49 to 1014.60 mg/l with an average of 181.47 mg/l. Ca²⁺, HCO₃⁻, Mg²⁺ and K⁺ showed least variations with ranges

Table I. Hydrochemical data summary of groundwater in the study area

|	Minimum	Maximum	Average	Standard deviation	Variance
pH	5.65	7.48	7.02	0.32	0.1
Na⁺ (mg/l)	12.27	771.55	143.61	199.17	39 667.321
K⁺ (mg/l)	1.82	139.55	13.95	29.28	857.252
Mg²⁺ (mg/l)	7.70	270.50	46.73	53.35	2846.39
Ca²⁺ (mg/l)	31.48	649.47	135.17	137.80	18 988.83
HCO₃⁻ (mg/l)	91.92	237.83	146.19	37.56	1410.80
SO₄²⁻ (mg/l)	20.94	1014.60	181.47	227.64	51 819.87
Cl⁻ (mg/l)	42.68	2145.78	404.76	476.31	226 866.90
NO₃⁻ (mg/l)	2.44	451.36	129.47	104.15	10 909.17
Electrical conductivity (μS/cm)	591.00	31600.00	3572.38	6448.08	41 580 000.00
Total dissolved solid (mg/l)	249.60	5878.30	1233.27	1233.64	1 521 865.50
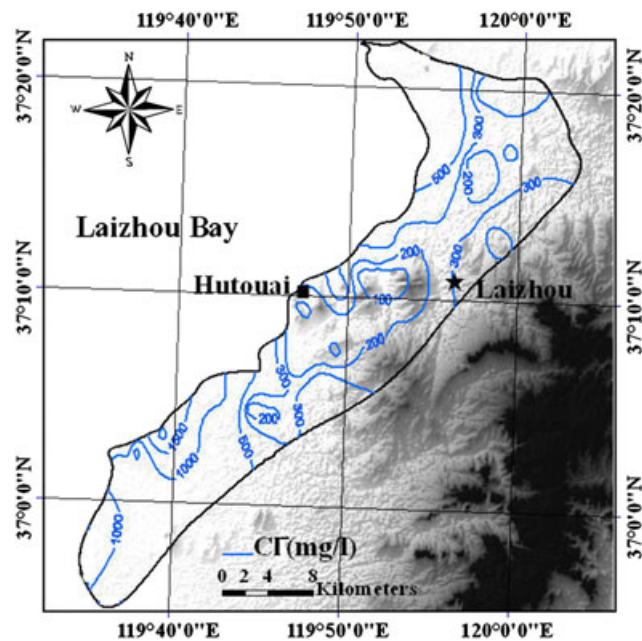
Figure 4. Iso-Cl⁻(mg/l) contour map of the study area (August 2009)

of 31.48–649.47, 91.92–237.83, 7.70–270.50 and 1.82–139.55 mg/l, with an average of 135.17, 146.19, 46.73 and 13.95 mg/l, respectively. These wide distributions indicated that chemical composition was affected by complex hydrochemical processes including seawater mixing (Park *et al.*, 2005). The very high NO_3^- concentration (average 129.47 mg/l) is a characteristic of groundwater in the study area. This reflects a considerable degradation of groundwater because of anthropogenic contamination.

To understand the relationship between different ionic species, correlations between major ions were carried out using Spearman's correlation analysis. Table II showed the correlation coefficients between the major ions in groundwater. High positive correlation (>0.75) and significant at P-level 0.05 were obtained, TDS between Na^+, Mg^{2+}, Ca^{2+}, Cl⁻ and SO_4^{2-} , with a correlation coefficient of 0.93, 0.90, 0.89, 0.98 and 0.88, respectively. The high correlation implied that groundwater chemistry was mainly controlled by these ions.

The piper diagram (Piper 1944) was used to distinguish the different groundwater types. Groundwater in the study area has been classified into two hydrochemical facies

(Figure 5), Ca^{2+}-Mg^{2+}-Cl⁻ facies and Na^+-Cl⁻ facies. Most of the groundwater samples belong to Ca^{2+}-Mg^{2+}-Cl⁻ facies, and only three samples belong to Na^+-Cl⁻ facies.

Hydrochemical processes

The Durov diagram (Figure 6) showed occurrence of hydrochemical processes, such as simple dissolution and inverse ion exchange, taking place simultaneously.

The results from the chemical analyses were used to identify the hydrochemical processes and mechanisms in the study area. The Na^+-Cl⁻ relationship often has been used to identify the mechanism for acquiring salinity and saline intrusions in coastal regions (Kim *et al.*, 2003; Kouzana *et al.*, 2009; Russak and Sivan 2010). Conservative seawater–fresh water mixing is expected to show a linear increase in Na^+ and Cl⁻ (Martos *et al.*, 1999). Ratio values of groundwater less than the seawater ratio (0.86) indicate that the fresh groundwater was contaminated with the saline waters (Lee and Song 2006). The relationship between Cl⁻ and Na^+ (Figure 7a) showed that the majority of the samples were positioned lower

Table II. Matrix of correlation coefficients for hydrochemical data in the study area

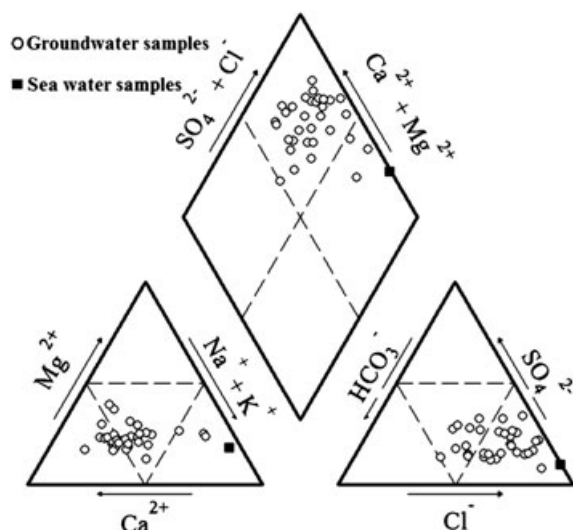|	pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl⁻	SO_4^{2-}	NO_3^-	EC	TDS
pH	1.00										
Na^+	−0.51	1.00									
K^+	−0.37	0.74	1.00								
Mg^{2+}	−0.35	0.84	0.70	1.00							
Ca^{2+}	−0.52	0.77	0.47	0.76	1.00						
HCO_3^-	−0.18	0.52	0.33	0.45	0.36	1.00					
Cl⁻	−0.51	0.93	0.65	0.88	0.85	0.49	1.00				
SO_4^{2-}	−0.40	0.88	0.64	0.84	0.72	0.31	0.84	1.00			
NO_3^-	−0.59	0.25	0.05	0.25	0.47	−0.04	0.30	0.28	1.00		
Electrical conductivity	−0.55	0.82	0.65	0.78	0.73	0.30	0.90	0.73	0.27	1.00	
Total dissolved solid	−0.55	0.93	0.67	0.90	0.89	0.46	0.98	0.88	0.38	0.89	1.00

Figure 5. Piper diagram of the shallow groundwater and sea water samples of the study area

than the theoretical mixing freshwater– seawater line. In the present study, the molar ratio of Na^+/Cl^- for groundwater samples generally ranged from 0.26 to 0.90, with a mean value of 0.52, almost all values of groundwater samples less than the seawater ratio, indicating that a large proportion of groundwater was affected by seawater intrusion to some degree. Values close to the seawater ratio indicate recent simple mixing of groundwater with seawater (Mercado 1985). The low

values of Na^+/Cl^- samples were especially controlled by an inverse cation exchange between Na^+ and Ca^{2+}-Mg^{2+}.

The plot of $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-+SO_4^{2-}$ will be close to the 1:1 line if the dissolutions of calcite, dolomite and gypsum are the dominant reactions in a system. Ion exchange tends to shift the points to the right because of an excess of $HCO_3^-+SO_4^{2-}$ (Cerling et al., 1989; Fisher and Mulican 1997). If reverse ion exchange is the process, it will shift the points to the left because of a large excess of $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-+SO_4^{2-}$. The plot of $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-+SO_4^{2-}$ (Figure 7b) showed that most of the data plot are above the 1:1 trend except for a few samples, as shown in Figure 7b, indicating that samples were especially controlled by an inverse cation exchange. The plot of $Ca^{2+}+Mg^{2+}$ versus Cl^- (Figure 7c) indicated that concentrations of the two items were roughly the same as Ca^{2+} and Mg^{2+} increase with the increasing salinity that could be the indication of reverse ion exchange in the aquifer for most samples.

The $Ca^{2+}+Mg^{2+}$ / HCO_3^- ratio is used to explain the sources of Ca^{2+} and Mg^{2+} in groundwater. As this ratio increases with salinity, Mg^{2+} and Ca^{2+} are added to solution at a greater rate than HCO_3^-. If Mg^{2+} and Ca^{2+} only originate from the dissolution of carbonates in the aquifer materials and from the weathering of accessory pyroxene or amphibole minerals, this ratio would be about 0.5 (Sami 1992). The plot of $Ca^{2+}+Mg^{2+}$ versus HCO_3^- in Figure 7d showed all the data plot above the 1:1 line, suggesting a carbonate origin for the calcium and another source for bicarbonates, probably dolomite dissolution.
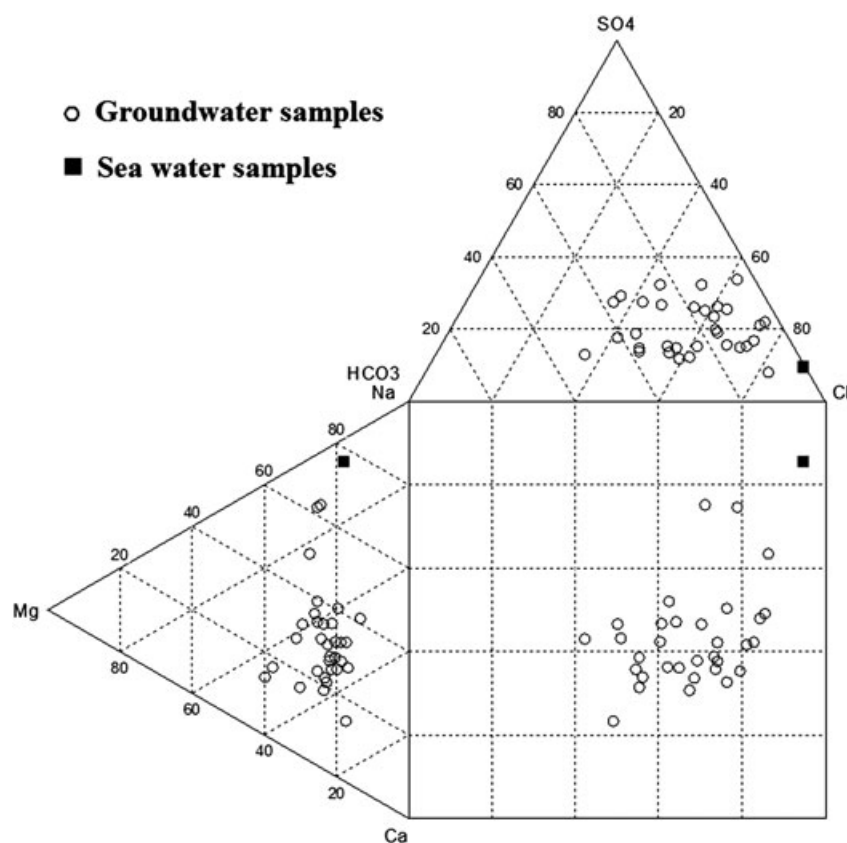

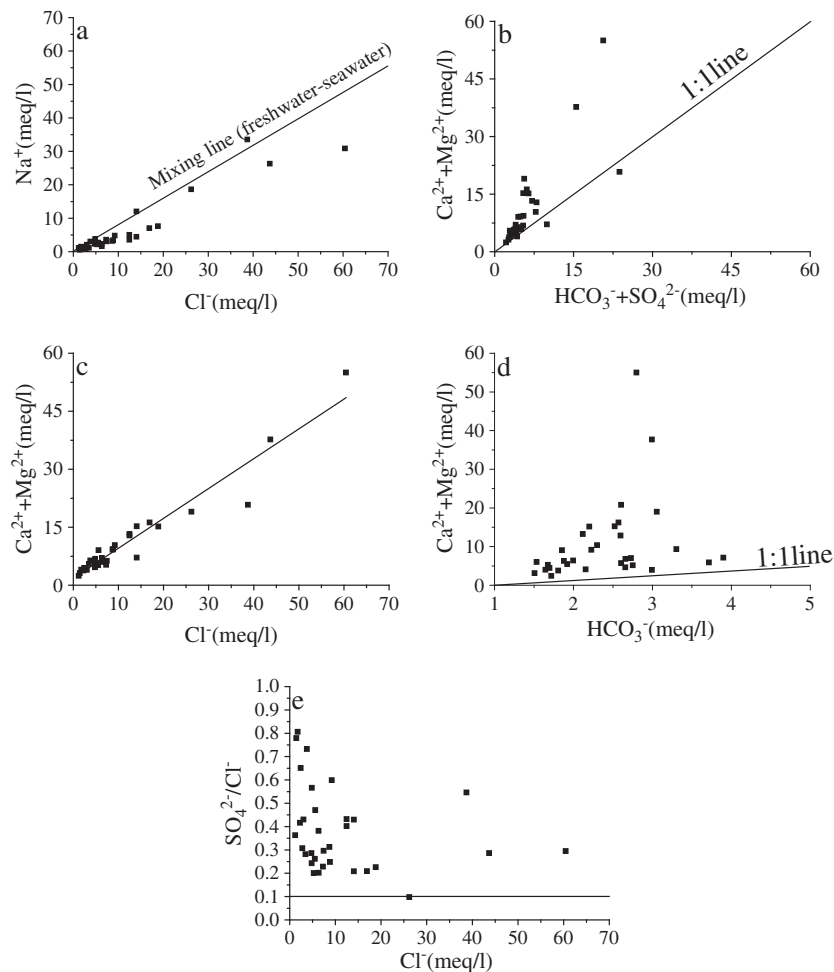Figure 6. Durov diagram of the shallow groundwater and sea water samples of the study area

Figure 7. Ions scatter diagram of groundwater in the study area

In fact, many samples presented an excess of calcium and/or Mg^{2+} and a deficit of sodium compared with chlorides. When seawater intrudes a freshwater aquifer, an inverse cation exchange occurs, and sodium is captured by the exchanger (clay); while Ca^{2+} and/or Mg^{2+} is released, water quality changes from Na-Cl rich to $Ca-Cl_2$ rich and/or $Mg-Cl_2$ rich (Kouzana *et al.*, 2009).

The SO_4^{2-}/Cl^- ratio of the majority of the samples were greater than that of the seawater sample (0.10) (Figure 7e); thus, the enrichment of these points with SO_4^{2-} suggested other sources including the dissolution of gypsum and agricultural pollution where some of these water points recorded high NO_3^- content. The SO_4^{2-}/Ca^{2+} ratio for the majority of the samples was less than 1. The deficit of SO_4^{2-} over Ca^{2+} reflected extra sources of Ca^{2+}; inverse cation exchange and calcite precipitation were regarded as the factors that released the Ca^{2+} from groundwater and increased its content.

This behavior was confirmed by the calculation of deficit or excess of each ion. In fact, the samples showed Na^+ deficiencies ($Na_{react} < 0$), and the Ca^{2+} and Mg^{2+} in were excess (Ca_{react}, $Mg_{react} > 0$) (Figure 8). The opposite evolution of Na_{react} and $Ca_{react} + Mg_{react}$ indicated that a deficit of Na^+ was compensated by corresponding excess in $Ca^{2+}+Mg^{2+}$. The most logical explanation for this excess of Ca^{2+} and Mg^{2+} is an inverse cation exchange.

This confirms the mixture of freshwaters with seawater. The higher the deviation, the more important are the processes modifying the content of the mixing.

From the plots of SI against TDS for all the investigated waters (Figure 9), most of the groundwater samples were saturated with respect to calcite and dolomites, suggesting that these carbonate mineral phases are present in the corresponding host rock, and carbonate mineral may have influenced the chemical composition of groundwater. This leads to an increase of Ca^{2+}, Mg^{2+} and
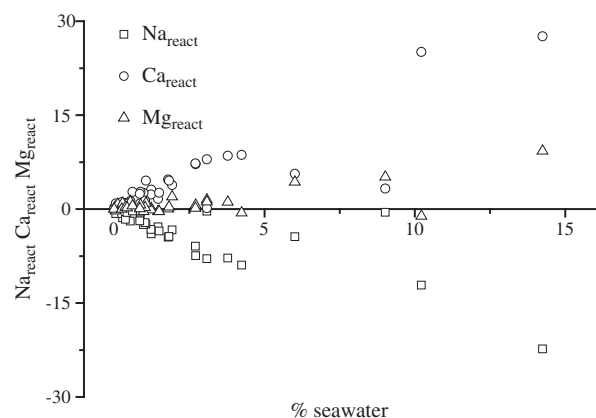
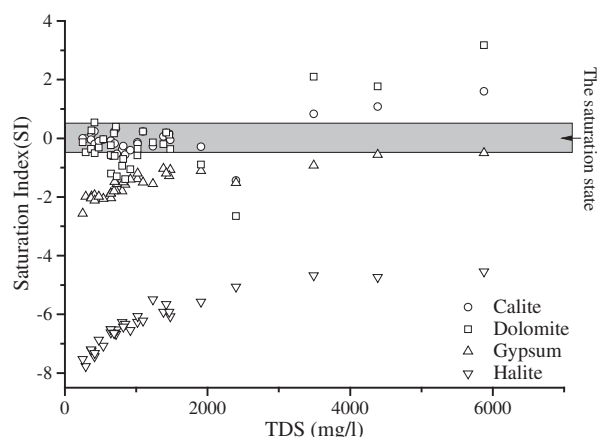Figure 8. Na_{react}, Ca_{react} and Mg_{react} relation with percentage of seawater

Figure 9. Plots of saturation indices with respect to calite, dolomite, gypsum and halite *versus* total dissolved solid

HCO_3^- in the aquifer. All of the groundwater samples were under-saturated with respect to gypsum and halite (Figure 9), suggesting that evaporate mineral phases are minor or absent in the host rocks. The enrichment of groundwater in Ca^{2+} as a result of both Na^+–Ca^{2+} cation exchange and dissolution of calcite and dolomite in the unsaturated zone (caused by nitrification and an increase in CO_2 concentration) created favourable conditions for calcite precipitation.

In addition to the natural mineralization processes mentioned above, anthropogenic pollution also plays a significant role in the salinization of groundwater in the study area. Indeed, the concentrations of nitrate in groundwater samples are relatively high in the studied area. The nitrate concentrations in the studied aquifer showed a large range of variation, from 2.42 to 451.36 mg/l. About 82% of the groundwater samples exceeding the maximum World Health Organization admissible nitrate concentration limit in drinking water (50 mg/l). The

examination of the nitrate distribution map (Figure 10) revealed that high nitrate concentrations appeared to be related to agricultural land-use patterns and suggested that the application of nitrogen fertilizers led to increased nitrate leaching. Consequently, the districts, characterized with high nitrate concentrations that exceeded 50 mg/l, showed the presence of agricultural influences that introduced a long-term risk of groundwater pollution by excess fertilizers and pesticides leached downward. Indeed, the positive relationship between NO_3^- and SO_4^{2-} (Figure 11) suggested that both N and S were used in the study area in the form of $(NH_4)_2SO_4$- fertilizers (Bohike *et al.*, 2007; Moussa *et al.*, 2011). Moreover, some groundwater samples showed a well-defined relationship between NO_3^- and Ca^{2+} (Figure 12), highlighting that both elements mostly originated from the excessive use of $Ca(NO_3)_2$- fertilizers (Stigter *et al.*, 2006).

Factor analysis

Factor analysis was applied to obtain correlations among the hydrochemical constituents of groundwater samples (Brown 1998; Liu *et al.*, 2008). The factors with eigenvalues greater than 1 were selected and rotated iteratively using the varimax method. The variables used for factor analysis were pH, Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, EC and TDS. Table III presents the eigenvalues, the percentage of variance, the cumulative eigenvalue and the cumulative percentage of variance associated with each other. It reveals that the first three factors, where eigenvalues exceeded one, explain 86.98% of the total variance. For factor loadings, a high positive loading was defined as greater than 0.75, and a moderate loading was defined as 0.50–0.75. Loadings of less than 0.3 were considered insignificant (Liu *et al.*, 2003).

Factor 1 has a high loading of TDS, EC, Cl^-, Mg^{2+}, Na +, K^+, Ca^{2+} and SO_4^{2-}, accounting for 62.58% of the total
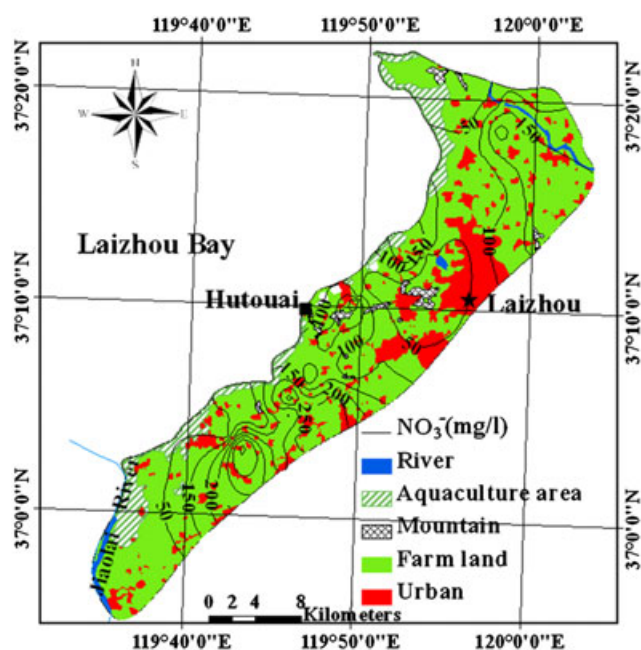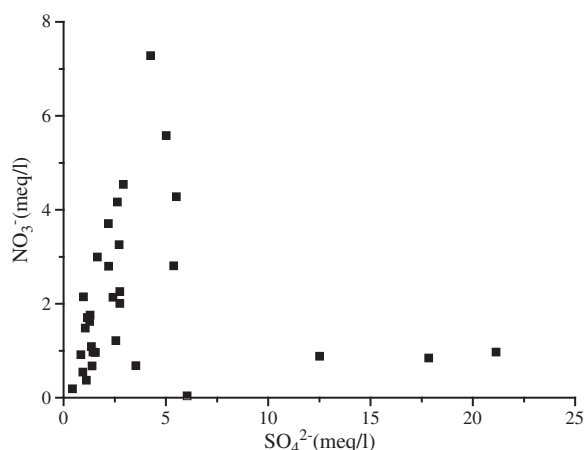

Figure 10. Iso-NO_3^-(mg/l) contour map of the study area (August 2009)

Figure 11. SO_4^{2-} relationship with NO_3^-

variance (Table III). TDS, EC, Cl⁻, SO_4^{2-}, Na⁺, K⁺ and Mg^{2+} are the major solutes in seawater. The TDS is positively correlated with the concentration of ions, which can thus be indirectly calculated from TDS. Therefore, TDS can be regarded as a water salinization index. This particular pattern in conjunction with high positive loadings of TDS, EC, Cl⁻, SO_4^{2-}, Na⁺, K⁺ and Mg^{2+} reflects the influence of seawater intrusion on pollution of groundwater and can thus be termed 'the seawater salinization factor'. The strong positive loading of Ca^{2+} on 'seawater intrusion' factor is not attributed directly to seawater intrusion but to secondary processes such as ion exchange, which becomes more evident in the more salinized water. The close relationship of Ca^{2+} with the 'seawater intrusion' factor also has been detected by Morell *et al.*, (1996), Kim *et al.* (2005) and Papatheodorou *et al.* (2007).

Factor 2 explains 12.76% of the total variance (Table III), with high positive loadings of HCO_3^- and moderate negative loading of pH. This factor describes factor dilution of groundwater by water recharge and/or mineralization by water–soil/rock interaction. The fresh water caused by rainfall or river water recharge into the aquifer during the sampling period dissolves carbonate rocks. In addition, the presence of carbonate rocks, such as calcite and dolomite, in the sediments causes the high
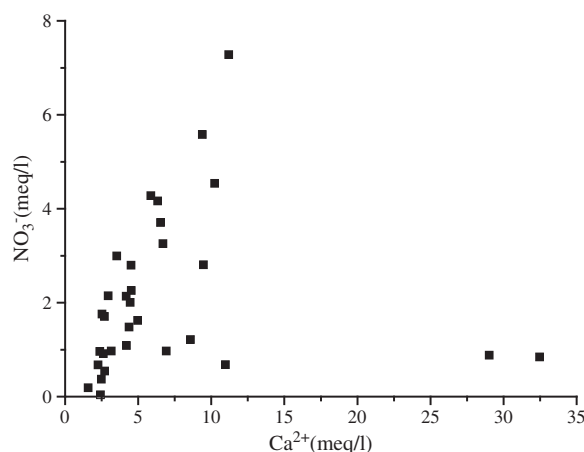
Figure 12. Ca^{2+} relationship with NO_3^-

HCO_3^- concentrations throughout the aquifer. The negative loading for pH may be caused by the biogenic or organic control from marine sediment of the pH value (Mondal *et al.*, 2010).

Factor 3 explains 11.64% of the total variance and is associated with high negative loadings of NO_3^- and moderate loading pH. The NO_3^- pollution is serious in the study area as discussed above because of extensive agricultural activities in the region, superficial N sources such as fertilizer, and domestic wastewaters, all of which significantly influence the groundwater quality through soil infiltration. The inverse relationship between NO_3^- and pH represents the nitrification process (Koh *et al.*, 2007; Papatheodorou *et al.*, 2007). Through the nitrification process, NO_3^- is enriched, and H⁺ is produced as a by-product, leading to a decrease of pH in the groundwater (Kim *et al.*, 2005).

Three factors with different factor loadings indicated that three different contributions were involved in determining the chemical composition of groundwater in this coastal area.

CONCLUSIONS

In this study, hydrochemical methods and factor analysis were applied to identify the mechanisms of groundwater salinization in the eastern coastal aquifer of Laizhou Bay.

The hydrochemical characteristic of coastal aquifers in the study area seems to be influenced by various processes as indicated by very wide ranges and high standard deviations of most hydrochemical parameters, such as EC, TDS, Na⁺, Cl⁻ and SO_4^{2-}. Groundwater in the study area has been classified into two chemical facies, Ca^{2+}-Mg^{2+}-Cl⁻ facies and Na⁺-Cl⁻ facies. Most of the groundwater samples belong to Ca^{2+}-Mg^{2+}-Cl⁻ facies, and only three samples belong to Na⁺-Cl⁻ facies.

The hydrochemical results show that different processes determine the major ionic composition of groundwater in the study area. The most remarkable process is that of the inverse cation exchange, characteristic of the changes of the theoretical mixture of seawater-freshwater, which is carried out between clays and the aquifer water. This exchange consists in the release of Ca^{2+} and/or Mg^{2+} and the adsorption of Na⁺ in the aquifer. The SI, suggesting that carbonate mineral may have influenced the chemical composition of groundwater and evaporate mineral phases, are minor or absent in the host rocks. Nevertheless, groundwater is severely polluted by nitrates (exceeding 50 mg/l) because of the over-fertilization in the study area.

Factor analysis allowed the reduction of the original variables to three factors that explained almost 86.98% of the total variance. In comparing the results of factor analyses for the data sets, three main hydrochemical processes were determined to control groundwater chemistry in the study area, including seawater intrusion, chemical weathering water–soil/rock interaction and nitrate contamination.

Table III. Loading of the components obtained from factor analysis

	F1	F2	F3
pH	−0.07	**−0.73**	**0.53**
Na^+	**0.92**	0.23	0.12
K^+	**0.83**	0.29	0.12
Mg^{2+}	**0.93**	0.14	0.03
Ca^{2+}	**0.91**	0.08	−0.12
HCO_3^-	0.22	**0.80**	0.26
Cl^-	**0.98**	0.18	−0.02
NO_3^-	−0.05	−0.07	**−0.93**
SO_4^{2-}	**0.90**	−0.06	0.09
Electrical conductivity	**0.94**	0.07	0.07
Total dissolved solid	**0.99**	0.15	−0.05
Eigenvalues	6.88	1.40	1.28
% Variance	62.58	12.76	11.64
Cumulative %	62.58	75.34	86.98

The hydrochemical processes in the coastal zone are complex. This study shows that the factor analysis and hydrochemical methods are useful tools for interpreting complex water quality data and the origin of groundwater salinity. The information consequently obtained represents a base for future hydrochemical work that will be useful in the planning, protection and decision making regarding groundwater management in the study area.

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