Influences of natural and anthropogenic processes on the groundwater quality in the Dagujia River Basin in Yantai, China

Henghua Zhu, Jianwei Zhou, Tingting Song, Haibo Feng, Zhizheng Liu, Hongwei Liu and Xiaohua Ren

ABSTRACT

Groundwater plays an important role in water supply and economic development for Yantai city, China. However, the groundwater quality has degraded due to the increase and expansion of agricultural and industrial development. It is urgent to acquire groundwater characteristics and distinguish impacts of natural factors and anthropogenic activities on the groundwater quality. Forty-six groundwater samples collected from different wells showed a great variation of chemical components across the study area. Most wells with higher total dissolved solids, total hardness, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} concentrations were located relatively close to the coastal zone. The factor analysis (FA) and hierarchical cluster analysis results displayed that seawater intrusion was the primary mechanism controlling the groundwater quality in the coastal areas. A three-factor model was proposed based on the FA and explained over 85% of the total groundwater quality variation: Factor 1, the seawater intrusion; Factor 2, the water–rock interaction and Factor 3 (NO_3^-), the human activities. Furthermore, the geographical maps of the factor scores clearly described the spatial distributions of wells affected by natural processes or human activities. The study indicated that both natural processes and human activities are the major factors affecting the chemical compositions of groundwater.

Key words | Dagujia River Basin, factor analysis, groundwater, hierarchical cluster analysis, seawater intrusion

Henghua Zhu
Jianwei Zhou
Haibo Feng
Hongwei Liu
School of Environmental Studies,
China University of Geosciences,
Wuhan, Hubei Province,
China

Henghua Zhu
Zhizheng Liu
Shandong Institute of Geological Survey,
Jinan, Shandong Province,
China

Tingting Song
Shandong Province Guohe Circular Economy Research Center,
Jinan, Shandong Province,
China

Xiaohua Ren (corresponding author)
School of Water Conservancy and Environment,
University of Jinan,
Jinan, Shandong Province,
China
E-mail: *renxiaohua2008@163.com*

INTRODUCTION

Groundwater is a vital provision resource for agriculture, industry, public consumption and rural communities (Ansa-Asare *et al.* 2009). The quality and quantity of groundwater are greatly dependent on environmental and anthropogenic factors, such as regional geological setting, precipitation and human activities (Devic *et al.* 2013; Hamzah *et al.* 2017). Some anthropogenic activities, such as urban development, agricultural production, industrial application, mining, power generation and forestry practices, have caused the deterioration in groundwater quality and quantity (Jiang *et al.* 2009; Khatri & Tyagi 2015; Khatri *et al.* 2017; Habib-ur-Rehman *et al.* 2018). Especially, high abstraction rate or overpumping for the coastal aquifers might lead to seawater intrusion, which could increase the levels of Na, Cl and total dissolved solids (TDS) in the groundwater (Rao *et al.* 2013). The high ionic concentration could limit the groundwater usage. Therefore, it is very important to understand the influencing/controlling factors of groundwater quality for the groundwater management and utilization (Nishikawa 2016).

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As known, the groundwater quality largely depends on the natural processes (such as lithology, hydrogeological conditions, the interaction of water with rock, soil and other types of aquifers, and seawater intrusion), anthropogenic factors (such as agriculture, industry and urban development) and atmospheric input (Jeong 2001; Jiang *et al.* 2009; Huang *et al.* 2013). Many previous studies have reported the influences of natural and anthropogenic processes on the groundwater quality in the coastal areas (Kim *et al.* 2003; Xing *et al.* 2013), arid/semi-arid areas (Jianhua *et al.* 2012; Wu *et al.* 2017; Xiao *et al.* 2018; Yang *et al.* 2018) and karst area (Jiang *et al.* 2009). The relative results suggested that anthropogenic processes played an important role in determining the groundwater chemical components. Generally, the application of water indices analysis, such as the hierarchy method based on the index system (Zhu *et al.* 2018) and the criticality index method (Pimparkar *et al.* 2016), and multivariate statistical techniques, such as hierarchical cluster analysis (HCA) and factor analysis (FA) (Alberto *et al.* 2001; Reghunath *et al.* 2002; Simeonov *et al.* 2004; Omo-Irabor *et al.* 2008; Hynds *et al.* 2014), allows us to better understand the groundwater quality, identify the possible factors and finally offer a valuable tool for managing water resources and rapid solution to pollution problems. For example, the FA method has been widely used to assess and characterize surface water and groundwater, which is useful in identifying the variations induced by natural and anthropogenic factors (Liu *et al.* 2003; Shrestha & Kazama 2007; Jiang *et al.* 2009).

As a typical coastal area, the Dagujia River Basin is located in the middle-north of Yantai city along the Dagujia River, which is one of the most important freshwater resources. Several studies on the evolution of groundwater quality with different technical methods have focused on the Dagujia River Basin (Guo 2005; Li & Liu 2007). However, the previous studies mainly focused on the basic characteristics of groundwater quality, lacking of the analysis of factors affecting the groundwater quality and the relevant affecting mechanisms.

On the basis of analyzing concentrations of the conventional pollutants and minor metal elements, the objectives of this study are to (1) describe the physico-chemical characteristics of the groundwater in the study area and (2) distinguish the impact of natural factors and human activities on the groundwater quality with FA and HCA methods. This study would provide important data and a theoretical basis for groundwater management and utilization and provide references for other coastal areas in China.

STUDY AREA

The study area, named the Dagujia River Basin, is located in the middle-north of Yantai city in China and covers an area of about 2,435 km^2 (Figure 1). It lies between latitudes 37°2′31.478″–37°37′51.592″ N and longitudes 120°44′1.857″–121°26′27.636″ E. The Dagujia River is the second largest river of Yantai and occupies an important position in the water supply and economic development of Yantai city. Geomorphologically, the area is composed of about 40% low mountains, 40% hills and 20% valley plain. The annual mean temperature of the area is about 11.5 °C (Liu *et al.* 2007). The main way of groundwater recharge is atmospheric precipitation, and the annual average precipitation is 677.95 mm (Zeng *et al.* 2017).

The Quaternary strata are the main characteristics of the Dagujia River Basin, and the groundwater source is mainly alluvial sand and sand–gravel pore water with the total area of 63.3 km^2 (Tao *et al.* 2018). Up to now, five groundwater resources have been exploited. The hydrogeological map in the previous study showed that from bottom to top, the three-layer strata are in the following order: confined aquifer (mainly, sand, gravel and pebble), relative water-blocking layer (silty sand and silt) and porous aquifer (fine silt, silt and a part of medium sand) (Tao *et al.* 2018). Due to the difference of topography, stratigraphic lithology, runoff condition and distance from the sea, the hydrochemical type of the groundwater changes from HCO_3–Ca·Mg to Cl–Na from south to north in the Dagujia River Basin (Kou 2013).

METHODOLOGY

Sampling

Forty-six groundwater samples, including 7 confined samples and 39 phreatic samples, were collected from

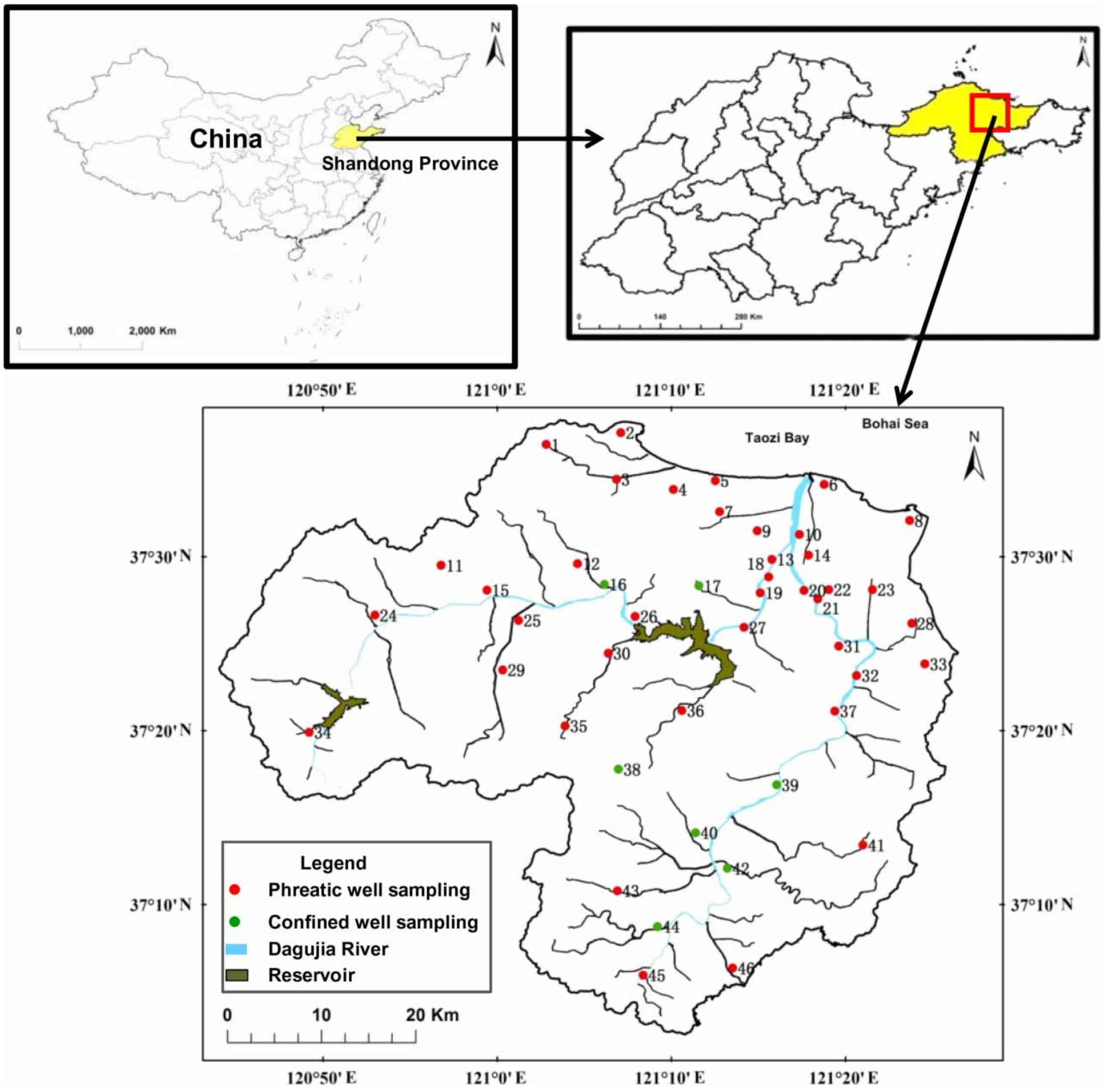

Figure 1 | Location of the study area and groundwater sampling sites.

different wells in 22–27 May 2014, and the location of the wells is illustrated in Figure 1. The sampling depth ranges from 1.7 to 100 m. Before the samples were collected, the wells were pumped out for about 30 min to remove stagnant or polluted water. The collected samples were stored at 4 °C. The selected groundwater parameters include pH, electrical conductivity (EC), turbidity, alkalinity (Alk), TDS, total hardness (TH), Ca^{2+}, K^{+}, Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, F^{-}, NO_3^{-}, As, Pb, Cr, Hg, Zn, Cd, Se, Mn, Fe and Al. The indices pH, EC and turbidity were measured in the field, and other indices were analyzed in the laboratory. The physico-chemical analyses of all samples were performed according to the *National Sanitary Method for Determination of Drinking Water (GBT 5750-2006)*, and the related analysis methods are listed in Table S1 in Supplementary Materials.

As shown in Table S2, the groundwater type of wells 16, 17, 38, 39, 40, 42 and 44 is confined water, while that of other wells is phreatic water. The three wells 2, 17 and 44, five wells 16, 29, 33, 38 and 41 and the other wells are screened in the carbonate, igneous and metamorphic, and loose rock aquifers, respectively. It also can be seen that from Table S2, the utilization of well water is mainly for drinking, agricultural irrigation, industry and domestic water.

Multivariate statistical methods

Factor analysis

FA, one of the multivariate statistical methods, is used to classify the groundwater chemical compositions with multivariate patterns by obtaining the general relationship for the measured chemical variables. The first step was to standardize the raw groundwater data. Let x_i, …, x_P denote P variables, each with N observations. The jth observation of the ith variable is named $X_{i,j}$, where $i = 1$, …, P and $j = 1$, …, N. The mean value and standard deviation were denoted as x_m and S_i, respectively. The jth observation of the ith variable is computed in the following equation:

$$Z_{ij} = (X_{i,j} - X_m)/S_i \qquad (1)$$

where Z_{ij} is the jth value of the standardized variable Z_i. The average and variance of Z_i are 0 and 1, respectively, for all i values.

Then, the correlation coefficient ($r_{x,y}$) is computed in the following equation, and the correlation matrix is obtained as follows:

$$r_{x,y} = \frac{\sum (x - x_m)(y - y_m)}{\sqrt{[\sum (x - x_m)]^2 [\sum (y - y_m)]^2}} \qquad (2)$$

Finally, the data were transformed into factors, and the eigenvalue and the percent of variance associated with each factor were obtained. The number of factors extracted is determined in a way that reduces the data by using the inherent interdependences. Therefore, a small number of factors could be remained and account for about the same amount of all original data.

Furthermore, to emphasize the relation of the effects of the factors, the contribution of each factor at each well (factor scores) is computed by SPSS. The comprehensive factor score (F) can be calculated based on the factor scores, which is shown in the following equation:

$$F = \sum_{i=1}^{m} F_i W_i \qquad (3)$$

Here, F is the comprehensive factor score, F_i denotes the factor score of the ith factor, m is the number of the extracted factors, and W_i is the weight of the ith factor, which is expressed as follows:

$$W_i = \frac{\lambda_i}{\sum_{i=1}^{m} \lambda_i} \qquad (4)$$

where λ_i is the corresponding eigenvalue of the ith factor.

Hierarchical cluster analysis

HCA, one of the most commonly used multivariate statistical methods, could group the factors into clusters on the basis of similarities within a cluster and dissimilarities between different clusters (Zhang *et al.* 2012; Huang *et al.* 2013; Abu-Alnaeem *et al.* 2018). The results of HCA can help in interpreting the hydrochemical data and patterns.

The selected variables for FA and HCA were pH, EC, TDS, Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and NO_3^-.

Interpolation analysis

The spatial distribution of factors (Figure 2) is derived from space interpolation analysis with the inverse distance weighting method.

RESULTS AND DISCUSSION

Physico-chemical characteristics

Fifteen physico-chemical parameters were detected and are shown in Tables 1 and 2. The pH of the groundwater samples varies from 6.84 to 8.07. The majority of the groundwater samples is moderately mineralized, suggested by its moderate to high EC values from 549 to 4,000 μS/cm. The highest EC value is found at both wells 5 and 9, which is probably ascribed to their short distances to the coast. A wide range in TDS concentrations from 396.92 to 19,436.22 mg/L with an average of 1,141.45 mg/L is recorded for all the groundwater samples. Notably, the maximum concentrations of TDS (19,436.22 mg/L), TH (3,676.21 mg/L), K^+ (172.5 mg/L), Na^+ (5,875 mg/L), Ca^{2+} (306.69 mg/L), Mg^{2+} (706.75 mg/L), Cl^- (1,0684.75) and SO_4^{2-} (1,575.19 mg/L) are all found in the well 5,

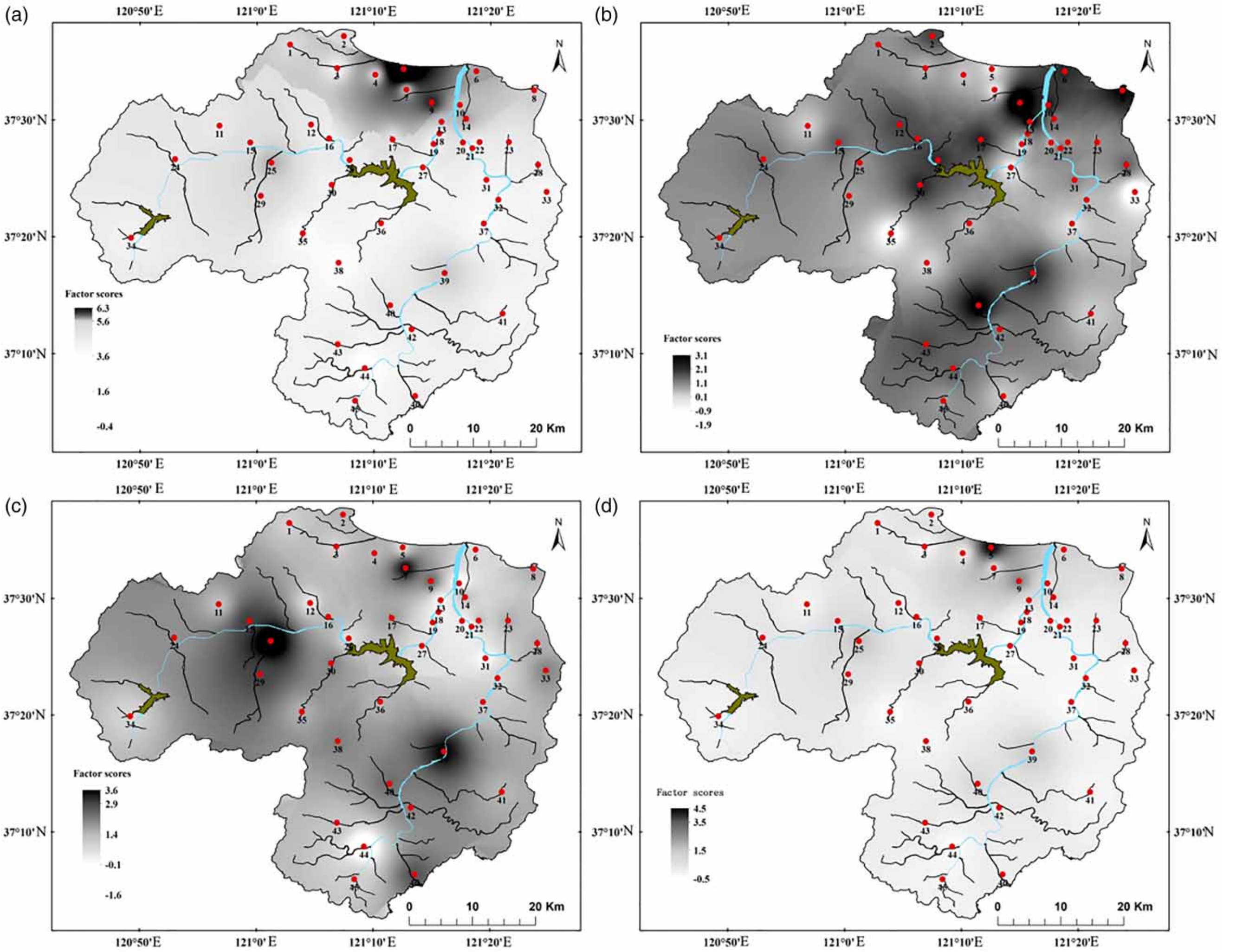

Figure 2 | Maps of the geographical distribution for (a) Factor 1, (b) Factor 2, (c) Factor 3 and (d) the comprehensive factor (*F*). Please refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/aqua.2019.113.

which is closest to the coastal line in the north, suggesting that these values are probably related to seawater intrusion.

Concentrations of minor elements (As, Pb, Cr, Hg, Zn, Cd, Se, Mn, Fe and Al) were also detected and are displayed in Table S3. As expected, the concentrations of minor elements in most groundwater wells are low. The relatively high pH (>6.5) in the majority of the groundwater samples reduces the solubility of most minor elements, whose solubility in water strongly relies on pH (Appelo & Postma 2005; Lin *et al.* 2011). However, Mn and Al in several samples showed the elevated concentrations. The concentrations of Mn in wells 8, 14 and 20 are 0.58, 1.26 and 0.61 mg/L, respectively, which all exceed the WHO limits (0.4 mg/L) in *Guidelines for Drinking-Water Quality* (WHO 2009), and Mn values in four well samples (wells 6, 8, 14 and 20) are higher than the limit value (0.3 mg/L) in the *Drinking Water Sanitary Standard (GB 5749-2006)*. Additionally, the elevated concentration of Al (0.26 mg/L) is found in only one well sample (well 2), which indicates that the well 2 is not suitable for drinking.

Assessment of contributions by FA

Variables for FA in the study were pH, EC, TDS, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and NO_3^-. The correlation matrix for the 11 parameters is displayed in Table 3. As

Table 1 | Physico-chemical characteristics of the 46 groundwater samples in the study area (all values are in mg/L except for pH, turbidity (NTU) and EC (μS/cm))

Well	pH	EC	TDS	Alk	Turbidity	TH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
1	7.62	766	703.97	182.01	4.9	373.19	18	77	93.68	33.82	93.04	199.52	221.96	0.33	60.27
2	7.88	1,357	855.985	264.79	13.7	470.62	1.7	115	107.06	49.37	183.02	123.39	322.85	0.15	95.24
3	7.98	750	515.645	193.87	0.6	314.68	1.15	49.5	82.53	26.38	66.46	78.76	236.37	0.19	70.06
4	8.07	1,022	690.3	184.42	0.2	337	36	80	86.99	29.08	133.94	73.51	224.84	0.31	119.37
5	7.74	4,000	19,436.22	141.83	6.4	3,676.21	172.5	5,875	306.69	706.75	10,684.75	1,575.19	172.96	0.12	22.7
6	7.77	2,445	1,546.225	243.52	0.2	442.8	8.1	400	94.79	50.05	576.67	231.03	296.91	0.23	21.6
7	7.89	1,432	1,031.82	89.83	0.9	453.96	0.85	139.25	150.56	18.94	186.09	189.02	109.54	<0.10	266.45
8	7.41	1,370	888.31	271.89	0.1	467.87	18.25	115	107.06	48.69	167.68	144.39	331.5	0.42	101.66
9	7.58	4,000	4,082.47	293.16	0.9	1,320.09	7.3	1,012.5	295.53	141.35	2,096.05	321.86	357.44	0.7	5.7
10	7.8	1,904	1,144.45	292.06	N.D.	370.38	14.5	261	63.57	51.4	367.96	184.3	356.16	0.49	7.5
11	7.85	807	555.69	148.93	N.D.	331.4	4.5	46	88.1	27.05	59.3	148.19	181.6	0.48	77.38
12	7.48	967	644.295	226.95	0.2	356.47	5.3	77.6	98.14	27.05	135.99	118.14	276.73	0.37	20.4
13	7.64	940	839.94	368.78	0.7	428.89	65.5	71	91.45	48.69	87.93	120.76	449.68	0.13	72.48
14	7	1,579	1,250.78	94.59	7.4	607.15	8	182.5	121.56	73.72	342.53	412.16	115.3	0.18	7.25
15	7.61	1,320	793.595	208.04	0.7	462.32	1.9	67	117.1	41.26	96.11	90.31	253.67	0.21	233.72
16	6.84	763	491.01	160.74	N.D.	269.04	21.25	41	73.16	20.97	54.19	85.67	196.02	0.14	78.7
17	6.88	1,199	664.1	179.66	N.D.	424.43	1.85	55.2	97.47	43.96	103.27	152.82	219.08	0.2	87.69
18	7.84	770	527.665	222.7	N.D.	325.89	4.4	47.5	78.07	31.79	63.38	124.97	271.53	0.3	23.25
19	7.92	640	403.19	144.63	N.D.	250.63	3.35	32.5	62.45	22.99	44.9	98.71	176.32	0.43	40.55
20	7.67	986	656.37	146.58	3.6	314.68	3.5	102.5	72.49	32.46	155.41	170.65	178.72	0.2	9.36
21	7.82	733	486.405	248.72	N.D.	295.22	3.8	54.6	71.37	28.41	59.86	90.84	303.27	0.37	17.8
22	7.52	747	587.58	160.74	2.7	350.92	3.85	54	90.33	30.43	93.04	123.39	196.02	0.23	79.3
23	7.6	864	661.925	174.96	N.D.	354.82	1.5	84	94.79	28.68	130.88	100.96	213.31	0.19	94.06
24	7.56	1,034	651.325	193.87	N.D.	392.65	1	55	103.72	32.46	69.53	125.04	236.37	0.3	127.25
25	7.85	1,570	1,122.03	163.15	0.3	682.31	5.5	58	185.13	53.43	93.04	201.45	198.9	<0.10	408.25
26	7.37	932	586.44	241.12	0.3	387.1	7.4	48	95.91	35.84	71.57	129.67	294.02	0.26	34.09
27	7.89	549	429.55	127.66	0.1	261.79	3.3	36.5	65.8	23.67	48.06	108.83	155.66	0.34	49.7
28	7.52	1,072	697.895	208.04	0.5	350.92	0.5	100	82.53	35.17	113.49	112.89	253.67	0.33	105.1
29	7.82	1,361	816.14	163.15	0.3	476.23	2.7	70	117.1	44.64	145.19	99.57	198.9	0.18	217.62
30	6.93	926	562.475	193.87	0.4	384.3	2.25	31	94.79	35.84	53.17	81.04	236.37	0.16	133.94
31	7.59	733	469.495	191.47	5.6	286.86	6.1	54	71.37	26.38	95.09	78.76	233.49	0.32	6
32	7.65	670	463.455	151.29	0.1	292.41	2.6	38.3	75.84	25.02	61.35	102.39	184.49	0.27	52.1

(*continued*)

Table 1 | continued

Well	pH	EC	TDS	Alk	Turbidity	TH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
33	7.96	675	498.705	85.13	0.7	239.52	1	48.5	73.6	13.53	44.99	81.38	103.77	0.11	158.25
34	7.56	824	515.05	167.85	N.D.	317.49	1.7	48	80.3	28.41	72.59	127.35	204.66	0.21	44.78
35	7.8	603	396.925	99.29	0.2	233.91	5	25	59.11	20.97	34.76	67.15	121.07	0.19	109.88
36	7.76	603	495.705	174.96	0.2	334.2	3.8	24	81.41	31.79	36.81	85.67	213.31	0.18	107
37	7.58	596	434.19	108.75	1.1	247.87	1.6	40	65.8	20.29	55.21	102.39	132.6	0.14	67.35
38	7.52	580	488.87	113.5	1.5	250.68	1.35	46.2	78.07	13.53	49.08	53.26	138.36	<0.10	156
39	7.38	1,294	1,025.935	224.6	0	590.43	12.4	80	149.44	52.75	125.76	134.3	273.85	0.21	305
40	7.16	1,648	815.45	250.33	0	402.21	2.55	125	91.57	42.15	145.57	61.59	305.22	0.15	180.25
41	7.98	611	504.595	177.31	0.3	320.24	4.7	30.5	84.76	26.38	51.12	68.26	216.19	0.16	109.16
42	7.75	788	613.335	208.04	0.8	362.08	1	51.5	115.98	17.58	66.46	70.88	253.67	0.25	146.07
43	7.37	839	539.78	220.3	0	333.35	15.75	39.4	90.46	26.09	47.49	87.06	268.6	0.28	78.9
44	7.81	920	533.16	295.37	0.4	107.45	3.35	162.5	23.17	12.04	45.43	80.12	329.64	2.57	14.05
45	7.6	698	521.73	179.66	2	323.09	2.4	45.5	80.3	29.76	67.48	110.26	219.08	0.22	64.04
46	7.75	686	611.01	146.58	0	395.46	2.4	22.5	107.06	31.11	40.9	91.89	178.72	0.21	211.5
WHO limit (WHO 2009)	–	–	1,000	–	5	–	–	200	–	–	250	500	–	1.5	50

N.D., not detected.

Table 2 | Statistics of physico-chemical parameters of 46 groundwater samples in the study area (all values are in mg/L except for pH, turbidity (NTU) and EC (μS/cm))

Parameter	Minimum	Maximum	Mean	Standard deviation
pH	6.84	8.07	7.60	0.29
EC	549	4,000	980.49	402.12
TDS	396.92	19,436.22	1,141.45	2,810.86
Alk	85.13	368.78	187.53	60.58
Turbidity	0	13.7	1.49	2.77
TH	107.45	3,676.21	448.48	515.71
K^+	0.5	172.5	10.59	26.77
Na^+	22.5	5,875	220.03	865.30
Ca^{2+}	23.17	306.69	98.75	50.64
Mg^{2+}	12.04	706.75	49.02	101.06
Cl^-	34.76	10,684.75	375.56	1,583.08
SO_4^{2-}	53.26	1,575.19	154.74	223.83
HCO_3^-	103.77	449.68	228.00	72.82
F^-	0.11	2.57	0.31	0.37
NO_3^-	5.7	408.25	95.84	85.80

seen from Table 3, high correlation coefficients are found between most of the corresponding two variables, indicating that the selected variables could be classified by FA. The eigenvalues, the percent of variance, the cumulative eigenvalue and the cumulative percentage of variance associated with each other are shown in Table 4. Generally, the maximum number of factors is extracted based on the Kaiser criterion (Jiang *et al.* 2009), taking factors only into account with eigenvalues higher than 1. Accordingly, three factors were selected and then rotated based on the Varimax with the Kaiser Normalization method. The corresponding factor loadings and communality of the variables for the three factors are listed in Table 5.

From Table 4, it can be noted that the first three factors account for about 85.09% of the total variance, which indicates that it is reasonable and suitable to extract the first three factors as the main factors. As listed in Table 5, the communalities of all variables except pH and HCO_3^- were higher than 0.80. The different factor loadings in Table 5 suggest different contributions in identifying the chemical compositions of the groundwater samples.

The terms 'strong', 'moderate' and 'weak' were used to denote the absolute factor loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively (Liu *et al.* 2003). Factor 1 consists of EC, TDS, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}, accounting for about 63.12% of the total variance. As known, EC, TDS, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} are the primary parameters in seawater (Liu *et al.* 2003). The previous study by Zeng *et al.* (2017) showed that the increase in the Cl^- concentration was in positive correlation with the seawater intrusion in the Dagujia River Basin. Moreover, as seen from Table 3, EC is positively connected with TDS, K^+,

Table 3 | Matrix of correlation coefficients for the groundwater data of the Dagujia River Basin

	pH	EC	TDS	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HO_3^-	NO_3^-
pH	1.000										
EC	−0.048	1.000									
TDS	0.050	**0.730**	1.000								
K^+	0.038	**0.556**	**0.899**	1.000							
Na^+	0.059	**0.712**	**0.998**	**0.899**	1.000						
Ca^{2+}	−0.031	**0.848**	**0.734**	**0.561**	**0.701**	1.000					
Mg^{2+}	0.020	**0.721**	**0.997**	**0.905**	**0.994**	**0.729**	1.000				
Cl^-	0.054	**0.720**	**0.999**	**0.895**	**0.999**	**0.719**	**0.995**	1.000			
SO_4^{2-}	0.001	**0.724**	**0.976**	**0.877**	**0.972**	**0.719**	**0.979**	0.972	1.000		
HO_3^-	−0.063	−0.264	−0.048	0.089	−0.052	0.056	−0.033	−0.056	−0.104	1.000	
NO_3^-	0.056	−0.070	−0.136	−0.156	−0.170	0.205	−0.138	−0.169	−0.173	−0.208	1.000

Kaiser–Meyer–Olkin measure of sampling: adequacy = 0.557.
Bartlett's test of sphericity: approximate $\chi^2 = 1{,}467.686$, df = 55, Sig. = 0.000.
Bold values are the greater values.

Table 4 | Eigenvalues, the percent of variance, cumulative eigenvalue, the cumulative percentage of variance for the FA in the Dagujia River Basin

Factor	Eigenvalue	Percent of variance	Cumulative eigenvalue	Cumulative percentage of variance
1	6.947	63.12	6.949	63.12
2	1.288	11.71	8.235	74.86
3	1.125	10.23	9.36	85.09
4	0.959	8.72	10.319	93.82
5	0.472	4.29	10.791	98.10
6	0.102	0.93	10.893	99.03
7	0.073	0.66	10.966	99.70
8	0.030	0.27	10.996	99.97
9	0.003	0.03	10.999	100.00
10	0.00001554	0.00	10.999	100.00
11	0.000003342	0.00	10.999	100.00

Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}. Therefore, EC can be noted as a water salinization index. The association of EC, TDS, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} could reflect the influence of seawater intrusion on groundwater pollution (Liu *et al.* 2003). Factor 1 can be termed as 'the seawater intrusion factor'.

The previous studies showed that overpumping of groundwater was the main cause of seawater intrusion (Lambrakis *et al.* 1997; Liu *et al.* 2003). In this study, it can be seen from Figure 2(a) that the wells with high scores, shown as the dark colors, are likely distributed in the north of the study area, which is closer to the coast. Coincidently, the areas with dark colors are the main residential and agricultural lands (shown in Figure S1). The finding confirms that overpumping of groundwater for domestic water and agricultural water is the major cause of seawater salinization in the study area. Especially, the highest score at well 5 suggests heavy seawater salinization. The spatial distribution of Factor 1 (Figure 2(a)) indicates that the well locations are corresponding to the seawater intrusion.

Table 5 | Factor loadings and communality of the variables after Varimax rotation

Variable	Factor 1	Factor 2	Factor 3	Communalities
pH	0.039	**−0.505**	−0.057	0.260
EC	**0.786**	**0.425**	0.171	0.828
TDS	**0.994**	−0.060	−0.037	0.992
K^+	**0.895**	−0.026	−0.162	0.828
Na^+	**0.988**	−0.078	−0.080	0.988
Ca^{2+}	**0.788**	0.246	0.449	0.883
Mg^{2+}	**0.991**	−0.041	−0.043	0.986
Cl^-	**0.990**	−0.072	−0.069	0.990
SO_4^{2-}	**0.979**	−0.074	−0.054	0.967
HCO_3^-	−0.015	**0.829**	−0.247	0.748
NO_3^-	−0.124	−0.122	**0.927**	0.889

Extraction method: principal component analysis.
Rotation method: Varimax with Kaiser Normalization.
Bold values are the greater absolute values.

Factor 2, explaining 11.71% of the total variance, is composed of pH, EC and HCO_3^-. The 'strong' positive loading of HCO_3^- indicates that the variable is related to the water–rock interaction. The negative loading of pH and positive loading of EC also support the water–rock interaction hypothesis (Jiang *et al.* 2009). The EC value reflects the amounts of dissolved ions, and the pH of groundwater denotes the H^+ concentration in groundwater. However, H^+ could be absorbed by the water–rock interaction process (Pacheco & Weijden 1996). Therefore, Factor 2 is assumed to be termed as 'the water–rock interaction factor'.

Factor 3, accounting for about 10.23% of the total variance, mainly includes NO_3^-. As known, no lithologic source was found for NO_3^-, and atmospheric deposition was not generally regarded as a main source of NO_3^- in the groundwater (Jiang *et al.* 2009). Generally, NO_3^- could be introduced into the groundwater by urea fertilization in farmlands. The extra amount of fertilizer could not be absorbed and quickly degraded in the soil and then could migrate down to the groundwater (Jiang *et al.* 2009). Moreover, NO_3^- could be introduced by the sewage generated from the residential areas. Hence, the high concentration of NO_3^- in the study area was probably derived from the anthropogenic processes. Noticeably, the land-use type (Figure S1) around the wells with high NO_3^- concentrations is mainly agricultural land and urban land, and the surroundings possibly affecting the groundwater quality (Table S2) are some livestock farms and farmlands, which could provide an evidence for that anthropogenic processes could cause high NO_3^- concentration in groundwater. Therefore, the Factor 3 is assumed to be the indicative of human activities.

Table 6 | Factor scores for the three-factor model

Well	Factor 1	Factor 2	Factor 3	*F*	Order
1	−0.09417	−0.23217	−0.46461	−0.15768	25
2	−0.08001	0.67341	−0.11655	0.01927	15
3	−0.29290	−0.59027	−0.47749	−0.35601	38
4	−0.05362	−0.78002	−0.11499	−0.16095	26
5	6.33892	−1.19655	−0.61280	4.46644	1
6	0.28033	0.97414	−0.63096	0.26627	5
7	0.06948	−1.19306	2.24328	0.15702	10
8	−0.01325	1.39651	−0.03843	0.17772	8
9	1.47693	3.10084	0.89296	1.63020	2
10	0.06129	1.13877	−1.26592	0.05004	13
11	−0.20330	−0.89327	−0.23071	−0.30154	31
12	−0.19392	0.66513	−0.74472	−0.14191	23
13	0.07025	1.83413	−1.06761	0.17621	9
14	0.30027	0.08799	−0.16525	0.21511	6
15	−0.12766	0.40309	1.43569	0.13328	11
16	−0.27147	0.61144	−0.18097	−0.13910	22
17	−0.16258	1.05732	0.19991	0.04886	14
18	−0.25757	−0.07445	−0.99610	−0.32114	33
19	−0.32822	−1.18051	−0.78636	−0.50056	45
20	−0.17095	−0.62743	−0.87801	−0.31875	32
21	−0.31719	0.22020	−1.15982	−0.34452	36
22	−0.23646	−0.29902	−0.15081	−0.23477	28
23	−0.22798	−0.18289	−0.00319	−0.19476	27
24	−0.18899	0.18284	0.36429	−0.07132	17
25	0.18307	−0.20055	3.60184	0.54119	3
26	−0.19978	0.94470	−0.66729	−0.09848	18
27	−0.32175	−1.36638	−0.64848	−0.50477	46
28	−0.22630	0.33655	−0.02001	−0.12405	20
29	−0.07334	−0.38638	1.35775	0.05559	12
30	−0.28518	1.01777	0.49923	−0.01160	16
31	−0.30623	−0.08389	−1.06068	−0.36631	39
32	−0.30503	−0.65567	−0.51829	−0.37891	40
33	−0.32075	−1.89493	0.53140	−0.43495	41
34	−0.26041	−0.25739	−0.53788	−0.29334	29
35	−0.35892	−1.57380	−0.04516	−0.48838	44
36	−0.30978	−0.58468	−0.09341	−0.32160	34
37	−0.34288	−1.11239	−0.33671	−0.44803	42
38	−0.37330	−0.95609	0.56640	−0.34055	35
39	0.02486	0.95541	2.26728	0.42243	4
40	−0.16524	1.60291	0.83260	0.19800	7
41	−0.30247	−0.85275	−0.11027	−0.35509	37
42	−0.25333	0.02347	0.50006	−0.12469	21
43	−0.23102	0.62914	−0.30065	−0.12102	19
44	−0.41641	0.36714	−1.57932	−0.44836	43
45	−0.28904	−0.24732	−0.43687	−0.30107	30
46	−0.24399	−0.80101	1.14760	−0.15338	24

To emphasize the relation of the mentioned influences of seawater intrusion, geochemical processes and human activities on the chemical compositions of groundwater, the contribution of each factor at each well (factor scores) is analyzed and listed in Table 6, and the corresponding maps are illustrated in Figure 2.

As illustrated in Figure 2(a), the dark degree denotes for the score of Factor 1 for different wells, and the area with darker color represents a higher pollutant concentration included in Factor 1. The wells with high scores, shown as the dark colors, are likely distributed in the north of the study area, which is closer to the coast. Especially, the highest score at well 5 suggests heavy seawater salinization. It can be obtained that the distance to the sea probably affects the score of the wells, and thus the spatial distribution of Factor 1 indicates that the well locations are corresponding to the seawater intrusion. Figure 2(b) gives the geographical distribution of Factor 2 for all the 46 wells. The high scores at wells 8, 13 and 40, which are the darkly shaded areas, indicate the strong water–rock interaction. Figure 2(c) shows three wells 7, 25 and 39 with high scores, indicating that high concentrations of NO_3^- are detected in these groundwater samples. It can be seen from the land-use map (Figure S1) that the land types around these wells are mainly agricultural and residential lands, which are in good accordance with the spatial distribution of Factor 3. The distribution of the comprehensive factor (*F*) (Figure 2(d)) displays that the highest score with the darkest color is found at well 5, suggesting that the groundwater quality of the well 5 is most affected by the natural and anthropogenic processes. The distribution of different factors is in good accordance with the groundwater physico-chemical quality of different wells.

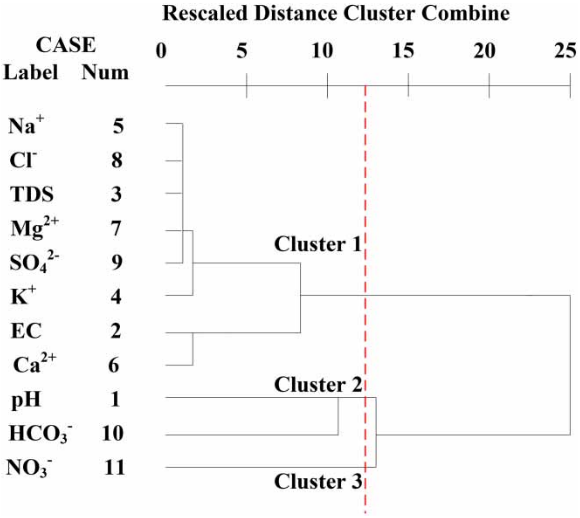

Figure 3 | Rescaled distance cluster combine result.

Assessment of contributions by HCA

Except the FA method, the HCA method was also proved to be effective to cluster the variances based on the chemical similarity. The wells with similar hydrochemical characteristics were classified into the same group. The results using HCA are shown in Figure 3.

As illustrated in Figure 3, three clusters were obtained by selecting the phenon line with a linkage distance of 13. The selection of the phenon value is on the basis of yielding the lowest number of groups which could elucidate most satisfactory results of the difference in chemical characteristics (Cloutier *et al.* 2008; Monjerezi *et al.* 2011). Cluster 1 includes parameters of Na^+, Cl^-, TDS, Mg^{2+}, SO_4^{2-}, K^+, EC and Ca^{2+}, which are exactly as the terms contained in Factor 1. Therefore, Cluster 1 could be the indicator of the seawater intrusion. The parameters pH and HCO_3^- are classified as Cluster 2. The difference between Cluster 2 and Factor 2 is that EC is not included in Cluster 2. As mentioned, EC has a 'weak' positive loading for Factor 2, which indicates that parameters pH and HCO_3^- are the main factors affecting the Factor 2. Since factors HCO_3^- and pH are concerned in the water–rock interaction (Lin *et al.* 2011; Huang *et al.* 2013), the Cluster 2 could be termed as 'the water–rock interaction factor'. As Factor 3, Cluster 3 is comprised of NO_3^-, which is mainly generated from anthropogenic processes (fertilizer application and domestic sewage discharge) (Huang *et al.* 2013). Accordingly, Cluster 3 could be assumed to be the indicative of human activities. It can be noted that the results from HCA are generally consistent with those from FA, suggesting that both of the two methods are valuable tools to understand the possible pollution sources of groundwater.

CONCLUSIONS

The physico-chemical characteristics of groundwater in the Dagujia River Basin were studied to clarify the situation of groundwater quality and speculate the possible factors affecting the groundwater quality. A mass of 46 groundwater samples were collected and analyzed, and the results showed that several groundwater quality indices in some wells (such as wells 2, 6, 8, 14 and 20) are out of WHO limits and the standards of *GB 5749-2006*, indicating that these wells are not suitable for drinking. A great variation of chemical components was found across the study area, where the wells with high TDS, TH, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} concentrations were inclined to be located close to the coastal zone. The FA and HCA results showed that seawater intrusion was the primary mechanism controlling the groundwater quality in the coastal areas. A three-factor model was proposed based on FA and explained over 85% of the total groundwater quality variation. Factor 1 was denoted as 'the seawater intrusion factor', consisting of EC, TDS, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} and accounting for 63.16% of the total variance. Factor 2 mainly included pH, EC and HCO_3^-, explaining about 11.71% of the total variance, which was thought to be related to the water–rock interaction. Factor 3 (NO_3^-) was assumed to be the indicative of human activities. Additionally, the geographical maps of the factor scores clearly illustrated the spatial distributions of wells affected by natural processes or anthropogenic processes. Three clusters were also generated from HCA, which were generally consistent with the results from FA. The results showed that both natural processes and human activities are the major factors affecting the groundwater quality. The results could provide references for the local government to protect groundwater ecology and allocate water resources.

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SUPPLEMENTARY MATERIAL

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