

Analysis on temporal and spatial variations of groundwater hydrochemical characteristics in the past decade in southern plain of Beijing, China

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Abstract: Groundwater utilization and protection are crucial for sustainable urban development. This is especially true for Beijing, where groundwater is an important source for urban water supply. In this study, statistical methods, including descriptive statistics, correlation analysis, principal component analysis, and Piper-Tri-linear diagram, were used in analyzing the temporal and spatial variations of the hydrochemical characteristics of groundwater based on monitored data from the southern plain of Beijing, China. Results indicated consistent changes of groundwater's hydrochemical characteristics in different aquifers in the study area. The percentage of HCO_3^- in total anion increased significantly in the groundwater, and hydrochemical water type evolved gradually from Ca-Mg-Cl- SO_4 based to Ca-Mg- HCO_3 based from period 2005-2007 to period 2013-2015. In shallow groundwater, the concentration of Na^+ , Ca^{2+} , SO_4^{2-} , HCO_3^- , and total dissolved solids (TDS) increased from period 2005-2007 to period 2013-2015, and the greatest change came from HCO_3^- , rising from 428.93 to 528.96 mgL^{-1} . The changes of main ionic concentrations in the deep groundwater were consistent with those in the shallow groundwater for both periods. However, the variations in deep groundwater were less than those in shallow groundwater. The temporal and spatial variations of hydrochemical characteristics reflect the groundwater quality in the study area. This study could facilitate decision-making process on the protection of groundwater resources to ensure its sustainable utilization.

Keywords: Beijing; Groundwater; Hydrochemical characteristics; Temporal and spatial variation; Water quality

Introduction

The formation and distribution of groundwater chemical components, in certain natural geographical and geological conditions, can be used to trace regional groundwater circular pathway and indicate the migration and transformation characteristics of groundwater flow system. Hydrochemical water type is the reflection of groundwater chemical compositions (Gosselin D C *et al.* 2001; Panno S V *et al.* 1994). Groundwater hydrochemistry research is an essential part in the groundwater resources quality assessment. It can provide a better

understanding of changes in quality affected by human activities (Arumugam K and Elangovan K, 2009). It also plays a role in regional groundwater resources exploitation and management as well as relevant environmental protection. Weathering of silicate and carbonate rock leads to significant quantities of mineral ions in groundwater (Mapoma H W T *et al.* 2016). Water-rock interaction is a key factor that affects hydrochemical characteristics of groundwater. For example, high concentration of SO_4^{2-} could result in the dissolution of carbonate. Another factor is cation exchange, a major hydrochemical process conducted in aquifers. In addition, climate change has the potential of recharging groundwater, leading to the evolution of groundwater hydrochemical characteristics (Anwar

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A E, 2010). Using ion concentration ratio to discover the hydrochemical evolution process is an essential method in studying groundwater hydrochemical characteristics (Martos F S *et al.* 1999). With the accelerating urbanization and rapidly growing population, cities and surrounding districts in many developing countries are facing dual challenges of excessive exploitation of groundwater and water quality deterioration (SHI J S *et al.* 2011; WANG Xin-juan *et al.* 2016). This challenge not only seriously affects industrial and agricultural production as well as drinking water security, but also changes groundwater hydrochemical characteristics.

Beijing is a mega city that suffers from severe water shortage of northern China, with an approximate 585 mm average annual precipitation. Since 1999, a persistent drought has caused a nearly 20% reduction of annual precipitation, further aggravating the shortage of water resources. Groundwater, as a major water source for urban water supply, has been exploited in a maximum annual rate of 2.7 billion m³, a volume which accounts for approximate 80% of total water supply for the city. Although South-to-North Water Diversion Project could transfer 1 billion m³ water from the Yangtze River to Beijing annually, groundwater is still withdrawn in around 1.8 billion m³ every year, which accounts for nearly 50% of total water supply in Beijing. Effective utilization and protection of groundwater are of great significance in the socio-economic sustainable development of the whole city (LV Xiao-jian *et al.* 2015). However, due to human activities, such as excessive groundwater pumping, groundwater level is continually descending and water quality has also been affected. It is important to conserve and improve groundwater resources and environment by controlling excessive exploitation of groundwater (SHI J S, 2014) and emission of pollutants, and by utilizing the surface water injection when necessary. The objective of this study is to help understand the evolution process of groundwater hydrochemical characteristic under the influence of human activities and provide a theoretical basis for reasonable exploitation of groundwater by analyzing the temporal and spatial variation of groundwater hydrochemical characteristics in the past decade in Beijing.

1 Materials and methods

1.1 Study area

The study site is the Daxing District (39°26' to 39°50'N; 116°13' to 116°43'E) located in the southern plain of Beijing, covering an area of approximately 1 030 km² (Fig. 1). Average annual precipitation is 514.6 mm, and the average annual evaporation ranges from 980 to 1 100 mm. As it belongs to the Yongding River alluvial plain, the study site is relatively flat (the average slope is approximately 1‰) with elevations varying from 15 to 20 m. The thickness of Quaternary sediment is controlled by paleotopography and basement structure. Generally, it becomes thicker from northwest to southeast. Surface alluvium and diluvium are mainly composed of sand, sandy loam, and silt. The lithological composition of the aquifers is determined by the Yongding River alluviation and basement structure. Aquifers in northwestern region are composed of gravel; those in the middle region of coarse sand and fine sand; those in the southern region of silt. The shallow aquifer system can be divided into three aquifers (aquifers I, II, and III) in vertical direction. Aquifer I is a shallow aquifer whose thickness varies from 5 to 10 m with bottom boundary ranging from 10 to 50 m. The northern area of aquifer I consists mainly of coarse sand and medium sand, and some areas have sand gravel. The southern area contains a mass of medium sand and fine sand, and some areas have coarse sand. The depth for northern area of aquifer II ranges from 25 to 35 m. It is composed of cobble and gravel, with a thickness of about 10-25 m. The southern area of layer II consists of several thin confining aquifers, with the depth ranging from 30 to 40 m and thickness ranging from 10 to 25 m. It mainly includes medium-coarse and fine sand. The northern area of aquifer III is 40-50 m in depth and 10-15 m in thickness, and mainly composed of gravel and medium-coarse sand. The southern area of aquifer III is a multilayered structure with medium-coarse sand and fine sand, which is 10-15 m in thickness. The deep aquifers with a thickness of 200-300 m are mainly located in the south of the study area with Quaternary sediment. The aquifers are mainly composed of medium-coarse, fine sand, and sand gravel in some areas, and most of the aquifers are deeper than 200 m.

Regional groundwater is recharged mainly by precipitation. The main causes of discharge are groundwater exploitation and evaporation, and part

of the groundwater flows into surface waters or depressions.

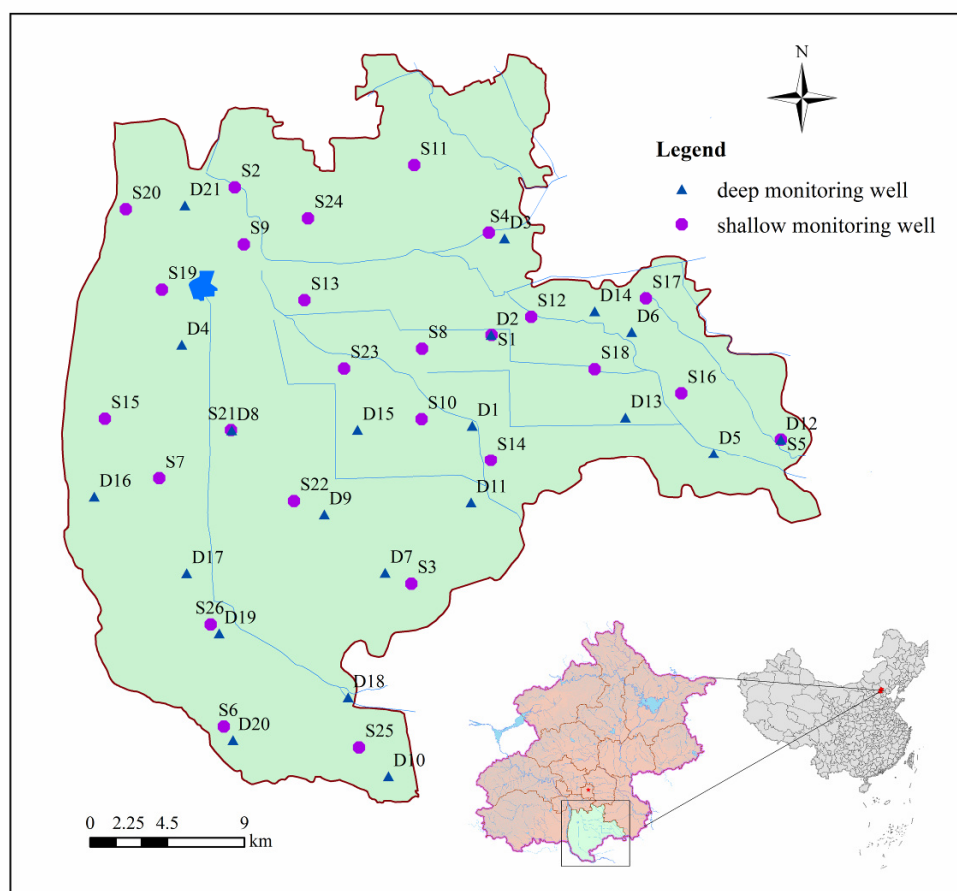


Fig. 1 Location of study area

1.2 Data collection and analysis

In total, 26 shallow and 21 deep groundwater monitoring wells were distributed in the study area (Fig. 1). The shallow wells, with depths ranging from 30 to 150 m, were used to monitor phreatic water and shallow confined water. The deep wells, with depth over 150 m, were used to monitor deep stratum confined water. Water quality samples were collected at monitoring points in wet season (September) once a year, and were finally analyzed in Water Quality Monitoring Center Lab of Beijing Water-affair Authority. The major monitoring indexes included concentration (mg L^{-1}) of potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), total dissolved solids (TDS), as well as pH value and electrical conductivity (EC;

$\mu\text{S cm}^{-1}$). Each chemical index was determined in strict accordance with the Chinese national standard method. pH value was tested with glass electrode method. EC was determined with conductance instrument method. SO_4^{2-} , Cl^- , NO_3^- and F^- were evaluated by Ion chromatography. Ethylenediaminetetraacetate (EDTA) titration was used to measure Ca^{2+} , Mg^{2+} . Flame atomic absorption spectrophotometry (FAAS) was used to measure K^+ and Na^+ . TDS was evaluated with weighing method. The acid titrimetric method was used to measure CO_3^{2-} and HCO_3^- . The relative error of ion balance inspections on water quality monitoring was less than 5%. On the basis of groundwater quality monitored for many years, we selected average data during 2005-2007 and during 2013-2015 to represent the hydrochemical parameters in the earlier period and the later period, respectively. The data were analyzed statistically based on principal component analysis by using SPSS software.

2 Results and discussion

2.1 Descriptive statistics

Table 1 listed the statistical characteristic of groundwater hydrochemical parameters in different layers in the earlier period and the later period. The relatively small coefficients of variation (CV) for HCO_3^- , Ca^{2+} , and Mg^{2+} suggested that their spatial distributions were relatively stable. Meanwhile, both mean and standard deviation (SD) are relatively high, which suggests that these ions were main components that determined the groundwater hydrochemical characteristics. In the shallow groundwater, the concentration of Na^+ , Ca^{2+} , SO_4^{2-} , HCO_3^- , and TDS all increased from the earlier period to the later period. HCO_3^- concentration increased most significantly, from a mean concentration of 428.93 to 528.96 mg L^{-1} . Concentrations of K^+ and F^- showed a slightly downward trend, with the mean concentration of K^+ decreasing from 2.05 to 1.97 mg L^{-1} , and F^- from 0.77 to 0.71 mg L^{-1} . In the deep groundwater, the variations in concentrations of most ions were consistent with those in the shallow groundwater, and the concentrations of all ions in the deep groundwater were lower than those in the shallow groundwater. Compared with that in the earlier period, the mean concentration of HCO_3^- in the later period increased notably from 230.71 mg L^{-1} to 309.24 mg L^{-1} , and the mean concentrations of Na^+ , Ca^{2+} increased slightly. Additionally, the mean concentrations of K^+ and Cl^- decreased insignificantly, and the mean concentrations of these two ions dropped from 1.85 and 26.31 to 1.79 mg L^{-1} and 24.12 mg L^{-1} , respectively.

Table 2 shows the correlation between chemical parameters in groundwater. The pH value had negative relationships with EC, K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , and TDS in both the earlier and the later period, while pH value had a positive correlation with F^- in both the earlier and the later period. EC was positively related to Mg^{2+} , Cl^- , HCO_3^- and TDS in both the earlier ($r=0.929, 0.882, 0.883$ and 0.993) and the later period ($r=0.897, 0.902, 0.865$ and 0.992). The K^+ had negative correlation with Na^+ , HCO_3^- and F^- in the earlier period ($r=-0.138, -0.061$ and -0.253), while it had positive correlation with them in the later period ($r=0.109, 0.163$ and 0.114). The Ca^{2+} had a positive

correlation with TDS in both the earlier ($r=0.812$) and the later period ($r=0.808$), while it had a negative correlation with F^- in both the earlier ($r=-0.250$) and the later period ($r=-0.221$). The Cl^- was positively related to Mg^{2+} and TDS in both the earlier and the later period ($r=0.884, 0.896$ and $r=0.834, 0.901$). The F^- had negative correlations with NO_3^- in both the earlier and the later period ($r=-0.244$ and -0.262). In general, these correlation variances between groundwater hydrochemical parameters in different years indicate the interannual variability of groundwater quality (Seth R *et al.* 2016). The changed correlations between major hydrochemical parameters in the study area from the earlier period to the later period indicated that the groundwater hydrochemical characteristics had changed.

2.2 Classification of groundwater

Fig. 2 shows the hydrochemical water type in Piper-Tri-linear diagram for water samples collected from shallow and deep groundwater monitoring wells. There was a slight change in hydrochemical water type for both the shallow and the deep groundwater in study area, with the main hydrochemical water types evolving from Ca-Mg-Cl- SO_4 to Ca-Mg- HCO_3 from the earlier period to the later period. The deep groundwater monitoring sites were relatively concentrated in Zone II, while the shallow groundwater monitoring sites were relatively scattered. The ratios of Na^+ and Cl^- were greater than 1 in most groundwater samples (Fig. 4a), indicating that there was a strong water-rock interaction in regional groundwater (Panno S V *et al.* 1994). Increasing populations during the past 11 years (from approximately 886 000 in 2005 to 1.562 million in 2015) have accelerated the groundwater exploitation, resulting in increased depth to groundwater in the phreatic aquifer (from 17.4 to 18.2 m on average). As a result, the water cycle speeds up, spectrometer exchange becomes stronger, and soluble substances in unsaturated and saturated zones dissolve in groundwater. These changes led to increased HCO_3^- concentration in groundwater and finally Ca-Mg- HCO_3 water type was formed. Meanwhile, the mean annual precipitation in the later period was 515 mm, 25% (413 mm) higher than that in the earlier period; consequently, increased rainfall infiltration is another key factor that changes groundwater hydrochemical characteristics.

Table 1 Descriptive statistics parameters of groundwater in study area

Parameters													
		pH	EC	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	NO ₃ ⁻	F ⁻
SGW in earlier period (n=26)	Min	7.2	641	0.8	27.8	53.2	34.8	22.8	25.4	270.0	375.5	0.1	0.3
	Max	7.65	1713	3.8	153.8	155.8	125.3	268.0	198.5	652.3	1176.0	32.9	1.7
	Mean	7.45	1151.42	2.05	68.15	91.55	63.24	95.79	90.30	428.93	754.71	5.13	0.77
	SD	0.13	291.32	0.83	31.37	31.19	19.89	63.94	48.58	90.30	218.91	8.37	0.41
	CV (%)	1.80	25.30	40.25	46.04	34.07	31.46	66.75	53.80	21.05	29.01	163.07	52.71
SGW in later period (n=26)	Min	7.2	585	1.3	20.4	52.1	16.9	11.0	25.5	282.0	389.0	0.5	0.1
	Max	7.6	1755	3.0	196.0	170.0	133.0	291.0	223.5	785.0	1167.0	30.5	1.8
	Mean	7.35	1183.38	1.97	75.22	102.86	60.19	99.13	101.94	528.96	791.81	5.94	0.71
	SD	0.13	289.55	0.49	38.20	35.72	23.76	61.46	58.82	127.07	224.67	7.89	0.46
	CV (%)	1.73	24.47	24.76	50.78	34.73	39.47	62.00	57.70	24.02	28.37	132.92	64.79
DGW in earlier period (n=21)	Min	7.525	526	1.0	23.2	32.5	10.1	12.0	21.8	186.2	320.0	0.1	0.3
	Max	8.05	734	4.1	77.6	70.3	31.7	52.8	80.4	276.0	445.5	3.0	1.5
	Mean	7.74	592.89	1.85	46.95	47.86	21.20	26.31	52.07	230.71	364.82	1.18	0.63
	SD	0.15	53.11	0.63	13.48	9.04	5.85	10.64	17.74	24.64	31.98	0.80	0.26
	CV (%)	1.96	8.96	34.10	28.72	18.90	27.62	40.45	34.07	10.68	8.77	68.01	42.23
DGW in later period (n=21)	Min	7.4	528	1.3	18.8	30.6	16.1	9.2	22.7	216.5	305.0	0.1	0.2
	Max	7.8	958	3.2	118.0	92.5	45.5	73.0	87.9	474.0	606.0	6.4	1.8
	Mean	7.60	623.52	1.79	47.06	51.92	23.71	24.12	51.24	309.24	378.76	1.28	0.60
	SD	0.13	118.28	0.45	22.95	13.45	7.76	15.36	17.68	65.57	84.67	1.37	0.36
	CV (%)	1.66	18.97	25.40	48.77	25.90	32.72	63.65	34.51	21.20	22.35	107.32	60.65

Note: EC in the unit of $\mu\text{S cm}^{-1}$, and other parameters are in the unit of mg L^{-1} ; SGW refers to shallow groundwater and DGW refers to deep groundwater.

Table 2 Pearson's correlation for different parameters in groundwater for the earlier and later period

Parameters	Period	pH	EC	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	NO ₃ ⁻	F ⁻
pH	Earlier	1											
	Later	1											
EC	Earlier	-0.773	1										
	Later	-0.704	1										
K ⁺	Earlier	-0.191	0.156	1									
	Later	-0.304	0.236	1									
Na ⁺	Earlier	-0.280	0.695	-0.138	1								
	Later	-0.106	0.677	0.109	1								
Ca ²⁺	Earlier	-0.817	0.772	0.399	0.218	1							
	Later	-0.857	0.762	0.253	0.134	1							
Mg ²⁺	Earlier	-0.789	0.929	0.006	0.560	0.644	1						
	Later	-0.584	0.897	0.087	0.589	0.558	1						
Cl ⁻	Earlier	-0.622	0.882	0.101	0.570	0.649	0.844	1					
	Later	-0.620	0.902	0.113	0.608	0.626	0.834	1					
SO ₄ ²⁻	Earlier	-0.403	0.625	0.482	0.478	0.671	0.369	0.417	1				
	Later	-0.530	0.737	0.242	0.434	0.779	0.474	0.597	1				
HCO ₃ ⁻	Earlier	-0.779	0.883	-0.061	0.613	0.647	0.914	0.660	0.396	1			
	Later	-0.546	0.865	0.163	0.691	0.523	0.891	0.682	0.436	1			
TDS	Earlier	-0.769	0.993	0.196	0.665	0.812	0.900	0.896	0.662	0.843	1		
	Later	-0.730	0.992	0.270	0.631	0.808	0.856	0.901	0.787	0.812	1		
NO ₃ ⁻	Earlier	-0.406	0.459	0.536	0.145	0.587	0.281	0.433	0.614	0.141	0.516	1	
	Later	-0.585	0.473	0.270	0.105	0.695	0.203	0.372	0.690	0.134	0.541	1	
F ⁻	Earlier	0.078	0.254	-0.253	0.493	-0.250	0.315	0.183	-0.072	0.315	0.188	-0.244	1
	Later	0.192	0.313	0.114	0.675	-0.221	0.430	0.194	0.042	0.543	0.241	-0.262	1

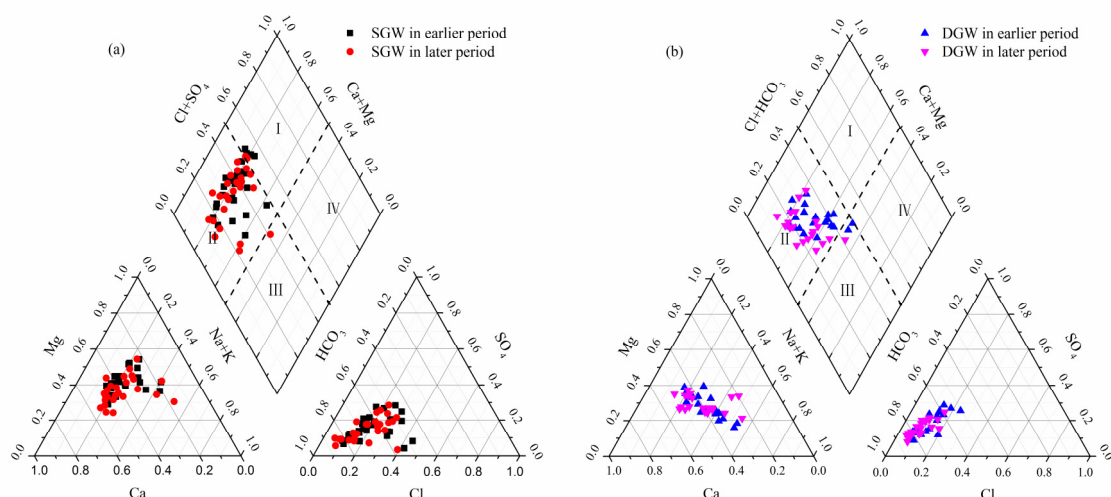


Fig. 2 Hydrochemical type plotted in Piper-Tri-linear diagram

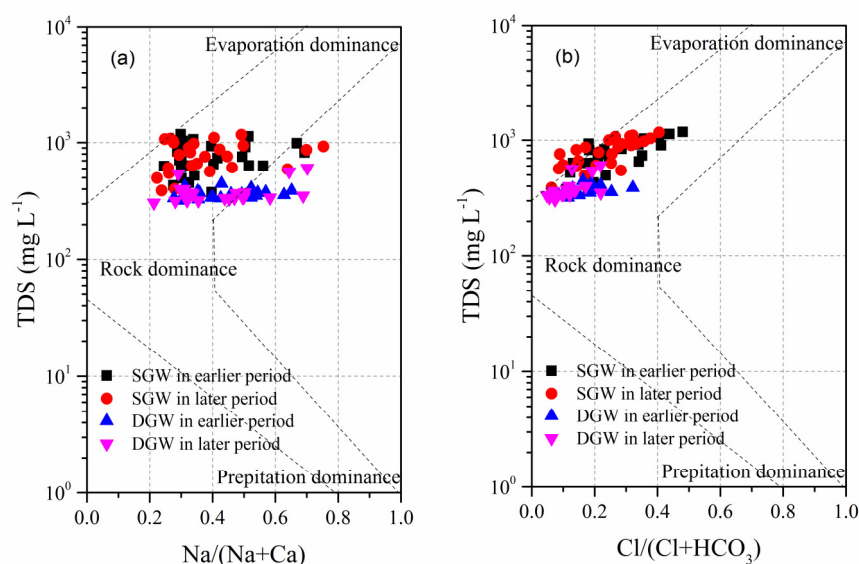


Fig. 3 Gibbs diagram

Gibbs diagram can be used to identify principal mechanisms (evaporation, rock weathering, and precipitation) that control the groundwater hydrochemical water type (Gibbs R J, 1970). In Fig. 3a, the majority of groundwater samples are concentrated in rock interaction area, which illustrates that rock weathering is a major source of groundwater ions in the study area. The similar distribution in the earlier and the later period indicates that rock weathering impacted the concentration of Na^+ and Ca^{2+} slightly. In general, evaporation and precipitation are major factors that influence groundwater hydrochemical evolution, and under these two processes, interactions between recharge sources and rocks in aeration zone could also change the hydrochemical water types (Richter

B C *et al.* 1993). Likewise, Fig. 3b clearly shows that most of the samples are concentrated in rock interaction areas, further suggesting that groundwater hydrochemical types were mainly determined by rock weathering. Compared with the earlier period, the distribution of water samples in the later period was more concentrated within rock interaction areas, which revealed a constantly increasing tendency in the process of groundwater hydrochemical evolution.

2.3 Ionic ratios

Comparison between the chloride concentration and other ionic concentrations may be used as an index of the relative contribution of meteoric salts to those resulting from mineral weathering

(Mahlknecht J *et al.* 2004). Infiltration and lateral inflow are the main ions sources of groundwater in the study area. In addition, the ions may also originate from water interacting with deeper bedrock with a high ionic concentration by interstratification. In arid and semi-arid areas, evaporation will increase the ionic concentration in groundwater, which mainly occurs in low permeable aquifers. The most likely sources of sodium are the dissolution of Na-feldspars, halite, evaporation and cation exchange. Chloride in groundwater originates from the dissolution of halite or is of meteoric origin (Tizro A T and Voudouris K S, 2008). Fig. 4 shows the relationships among major ions in groundwater in the earlier and the later period. The concentration relationships between Na^+ and Cl^- can be used to identify the salinization mechanism in arid and semi-arid areas (Dixon W and Chiswell B, 1992). Without the influence of human intervention, the dissolution of albite and other salt rocks can be a main source of Na^+ and Cl^- with a proportion generally at about 1:1. Most samples in the study area have a Na^+/Cl^- ratio ranging from 0.45 to 5.2 in the earlier period and 0.56 to 8.1 in the later period, and the average ratios were 2.11 and 2.37, respectively. Besides the weathering and the dissolution of albite, Na^+ in the aquifer may also come from the surface infiltration (Fig. 4a). The ratio of $\text{Ca}^{2+}/\text{Cl}^-$ tends to increase in both periods (Fig. 4b); the range was 0.56-7.01 in the earlier period and 0.57-10.36 in the later period, and the averages were 2.92 and 3.65 respectively. There

was a negative correlation between $\text{Mg}^{2+}/\text{Cl}^-$ and Cl^- (Fig. 4c), and the regression lines for the earlier period and the later period were close, suggesting that the ratio of $\text{Mg}^{2+}/\text{Cl}^-$ was relatively stable. Statistics results showed the ratio of $\text{Mg}^{2+}/\text{Cl}^-$ in the earlier period and the later period ranged from 0.79 to 5.83 and 0.82 to 6.96 respectively, with average values of 2.61 and 2.85. The relationship between SO_4^{2-} and Cl^- also changed and the ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ tended to increase in the shallow groundwater, and was observed similarly in the deep groundwater (Fig. 4d). HCO_3^- and Cl^- present a good correlation (Fig. 4e) in both the earlier and the later period. The sites in deep groundwater were concentrated more than those in the shallow groundwater. Statistics showed that the ratio of $\text{HCO}_3^-/\text{Cl}^-$ ranged from 1.08 to 12.26 in the earlier period and from 1.46 to 19.81 in the later period respectively, with the average values of 4.66 and 6.74. This indicated that HCO_3^- concentration changed a lot and HCO_3^- was a major ion that determines the variation in groundwater hydrochemical characteristics. The variation of $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ indicates the Ca^{2+} and Mg^{2+} sources in groundwater. The ratio of $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ changed significantly, decreasing from 1.26 in the earlier period to 1.07 in the later period. The $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-$ and Cl^- demonstrated a significant difference in regression lines for the two periods (Fig. 4f), indicating that the groundwater hydrochemical characteristics were altered in the shallow groundwater, but not in the deep groundwater.

Table 3 Initial eigenvalues and loadings of selected factors after Varimax rotation for earlier and later period

	Component	Initial eigenvalues			Rotation sums of squared loadings		
		Total % of variance	% Cumulative	Total % of variance	% Cumulative	Total % of variance	% Cumulative
SGW in earlier period	1	5.649	47.078	47.078	5.284	44.031	44.031
	2	3.323	27.692	74.771	2.862	23.846	67.877
	3	1.170	9.753	84.524	1.998	16.647	84.524
SGW in later period	1	5.373	44.773	44.773	4.426	36.879	36.879
	2	3.459	28.825	73.598	4.332	36.097	72.976
	3	1.136	9.463	83.061	1.210	10.085	83.061
DGW in earlier period	1	5.671	47.260	47.260	5.658	47.148	47.148
	2	3.542	29.520	76.780	3.170	26.418	73.566
	3	1.040	8.666	85.446	1.426	11.880	85.446
DGW in later period	1	5.863	48.857	48.857	5.268	43.902	43.902
	2	3.100	25.834	74.691	3.065	25.543	69.445
	3	1.434	11.948	86.639	2.063	17.194	86.639

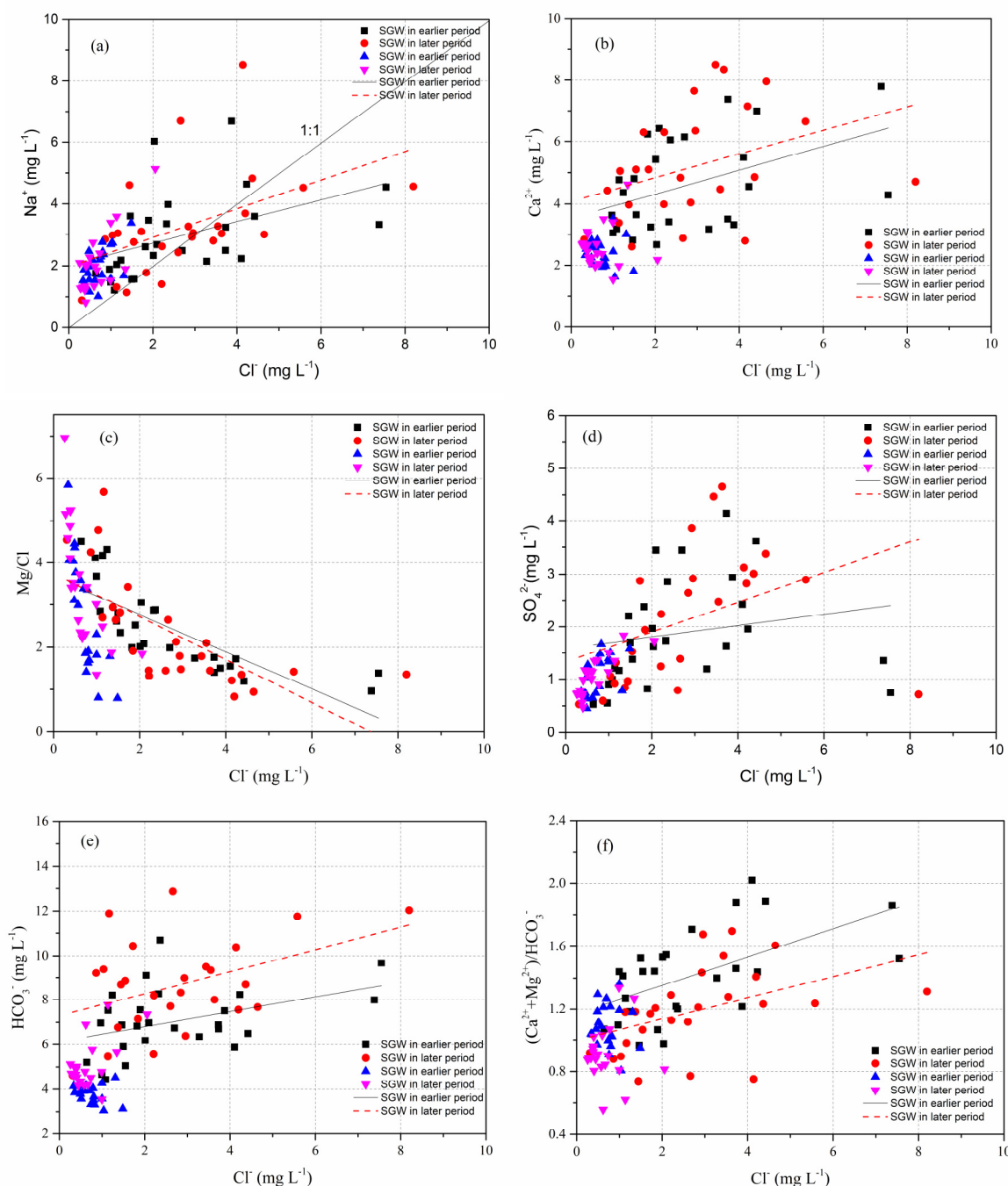


Fig. 4 Relation of major ions in groundwater

2.4 Principal component analysis

Principal component analysis is a widely used method of mathematical statistics multivariate analysis (Matiatos I *et al.* 2014; Voutsis N *et al.* 2015; Moya C E *et al.* 2015). It integrates numerous variables, many of which are correlated with each other, into one or a few principal components reflecting variable observational information. Meanwhile, these produced principal components are independent of each other. As a popular method,

Type-R principal component analysis divides variables into different groups according to their correlations, and variables in the same group are strongly correlated. This method can eliminate independent and repetitive hydrochemical components, and classify numerous complicated variables into a few common components. Each principle component represents a basic combination of hydrochemical components, which can be used to explain sophisticated relationship between hydrochemical parameters.

In order to identify the variation in groundwater hydrochemical characteristics from the earlier period to the later period, principal component analysis was used to analyze the monitored water data. Based on the criterion of eigenvalue >1.0 , three principal components were derived from the earlier period and the later period, respectively (Fig. 5 and Table 3), and their cumulative contribution achieved 84.524% and 83.061% in the shallow groundwater and 85.446% and 86.639% in the deep groundwater, respectively. This makes them reasonable reflection of the main information of original data. In the earlier period, the cumulative

variance contribution rate of the shallow and the deep groundwater reached 84.524% and 85.446% after rotation, with the first principal component contribution rate of 44.031% and 47.148%, the second one of 23.846% and 26.418%, and the third one of 16.647% and 11.880%, respectively. In the later period, the cumulative variance contribution rate of the shallow and the deep groundwater reached 83.061% and 86.639%, with the first principal component contribution rate of 36.879% and 43.902%, the second one of 36.097% and 25.543%, and the third one of 10.085% and 17.194%, respectively.

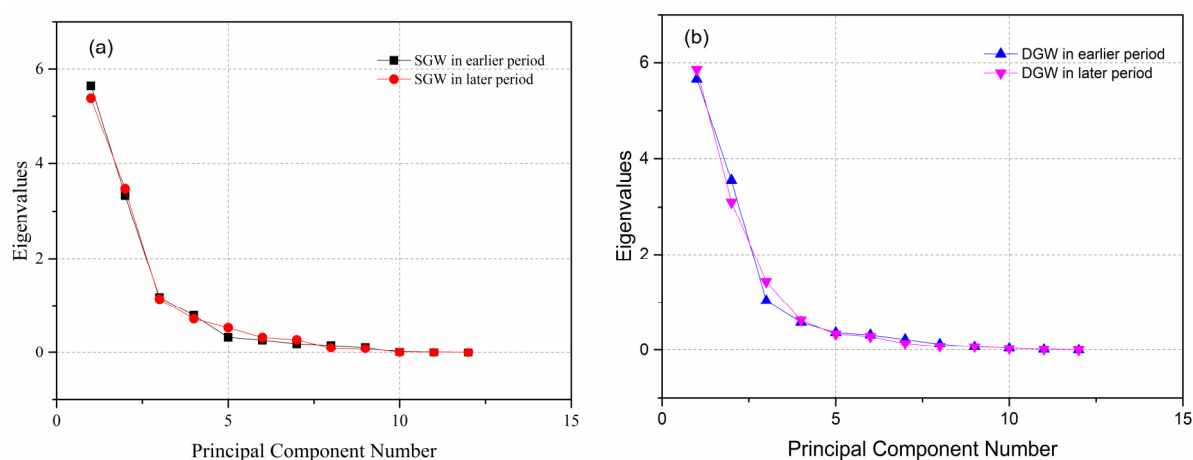


Fig. 5 Screen plot

In shallow groundwater, EC, Mg^{2+} , TDS, and Cl^- all had heavy loadings for Component 1, SO_4^{2-} , NO_3^- , and K^+ for Component 2, and F^- for Component 3; these parameters were positively correlated with their respective Components in the earlier period. HCO_3^- , Na^+ , Mg^{2+} , and EC all had heavy loadings for Component 1, Ca^{2+} and pH value for Component 2, and K^+ for Component 3; these parameters were positively correlated with their respective Components in the later period, except for pH value. In deep groundwater, HCO_3^- , Mg^{2+} , pH value, Ca^{2+} , Na^+ , NO_3^- , and SO_4^{2-} all had heavy loadings for Component 1, EC and TDS for Component 2, and F^- for Component 3; these parameters were positively correlated with their respective Components in the earlier period, except for pH value, Na^+ , and F^- . Cl^- , EC, TDS, SO_4^{2-} , and Na^+ all had heavy loadings for Component 1, Ca^{2+} , NO_3^- , and pH value for Component 2, and K^+ for Component 3; these parameters were positively correlated with their respective Components in the

later period, except for pH value. These results suggested that groundwater hydrochemical characteristics were affected by over-exploitation of groundwater, pollutant emission, and other human activities from the earlier period to the later period.

Fig. 6 shows the relationship of the major ion contents in the shallow groundwater (Fig. 6a and b) and deep groundwater (Fig. 6c and d) in the earlier period and the later period for Component 1, 2 and 3. The tendencies in the earlier and the later period are basically the same. Compared with earlier period, TDS, pH value, Cl^- , Na^+ , Ca^{2+} , and F^- in the later period varied distinctly; particularly the contribution value of TDS for Component 1 and pH value for Component 2 had changed significantly, with the former decreasing from 0.906 in the earlier period to 0.687 in the later period and the latter increasing from -0.186 in the earlier period to -0.884 in the later period. Moreover, the contribution value of Cl^- for Component 1 had significantly reduced from 0.824 in the earlier

period to 0.642 in the later period. The contribution of F^- for Component 1, 2, and 3 also changed significantly, with values increasing or decreasing

from 0.193, -0.291, 0.886 in the earlier period to 0.754, -0.541, 0.190 in the later period.

Table 4 Rotated factor matrix extracted from principal component analysis

SGW in earlier period				SGW in later period			
Variable	Component 1	Component 2	Component 3	Variable	Component 1	Component 2	Component 3
EC	0.950	0.304	0.026	HCO_3^-	0.897	-0.047	-0.087
Mg^{2+}	0.912	-0.149	0.059	Na^+	0.856	-0.104	0.250
TDS	0.906	0.397	-0.064	Mg^{2+}	0.844	0.175	-0.341
HCO_3^-	0.825	-0.278	0.133	EC	0.802	0.593	-0.010
Cl^-	0.824	0.159	-0.094	F^-	0.754	-0.541	0.190
Na^+	0.715	0.133	0.577	Cl^-	0.642	0.537	-0.268
pH	-0.703	-0.186	0.559	Ca^{2+}	-0.009	0.929	0.047
SO_4^{2-}	0.274	0.843	-0.051	pH	0.014	-0.884	0.038
NO_3^-	0.135	0.828	-0.199	NO_3^-	-0.125	0.764	0.353
K^+	-0.243	0.828	-0.237	SO_4^{2-}	0.252	0.752	0.323
F^-	0.193	-0.291	0.886	TDS	0.687	0.718	0.040
Ca^{2+}	0.417	0.518	-0.660	K^+	-0.037	0.215	0.825
DGW in earlier period				DGW in later period			
Variable	Component 1	Component 2	Component 3	Variable	Component 1	Component 2	Component 3
HCO_3^-	0.924	0.034	-0.086	Cl^-	0.966	0.038	0.118
Mg^{2+}	0.905	0.120	0.273	EC	0.903	0.135	0.385
pH	-0.895	0.043	0.210	TDS	0.901	0.115	0.372
Ca^{2+}	0.894	0.245	-0.288	SO_4^{2-}	0.889	-0.086	-0.243
Na^+	-0.882	0.265	-0.014	Na^+	0.806	-0.534	0.064
NO_3^-	0.831	0.194	0.067	Mg^{2+}	0.692	0.291	0.481
SO_4^{2-}	-0.806	0.482	-0.088	F^-	0.578	-0.425	0.529
EC	0.091	0.872	0.428	Ca^{2+}	0.049	0.983	0.041
TDS	0.001	0.862	0.433	NO_3^-	0.318	0.880	-0.180
K^+	0.349	0.785	-0.053	pH	0.248	-0.851	-0.294
Cl^-	-0.366	0.740	-0.006	K^+	0.021	0.020	0.814
F^-	-0.068	0.291	0.911	HCO_3^-	0.539	0.096	0.637

Under normal circumstances, groundwater hydrochemical characteristics are codetermined by lithology, groundwater runoff velocity, geochemical reaction characteristics, human activities (including groundwater exploitation and pollutant emission), and other factors (Mahlknecht J *et al.* 2004). Because of years of continuous drought, precipitation dropped sharply in recent years, resulting in decreased groundwater level and changed hydrodynamic conditions. At the same time, in the processes of rainfall and irrigation, because of the strong water-rock interaction and

spectrometer exchange, ionic concentration was increased in groundwater. With rapidly expanding urbanization and increasing populations, the influence of human activities on the groundwater system increased continuously, especially activities such as the emission of domestic sewage, rubbish, and other pollutants and the excessive application of agricultural fertilizers. These all led to increased ionic concentration in surface water and soil, which further affected the groundwater hydrochemical characteristics through infiltration.

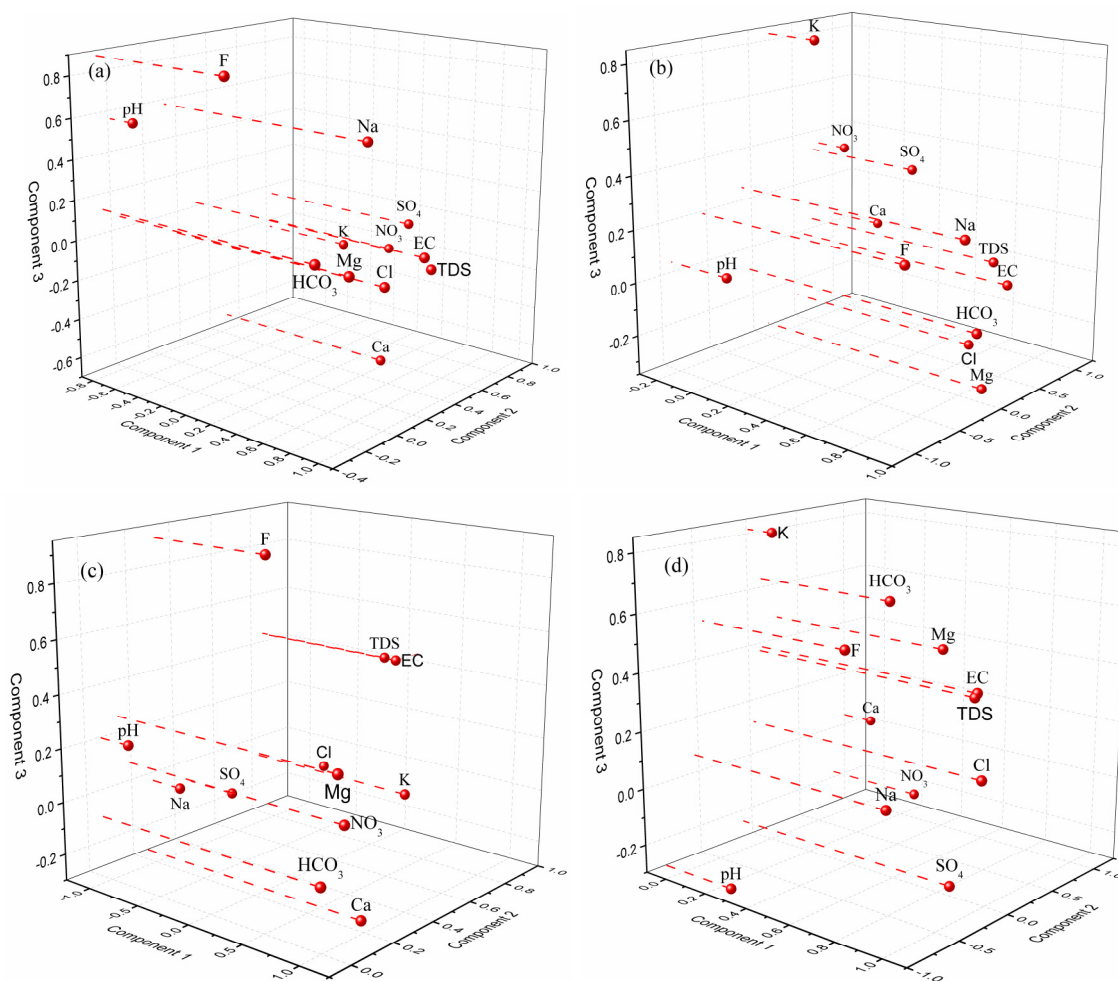


Fig. 6 Component plot

3 Conclusions

In this study, statistical analyses, including descriptive statistics, correlation analysis, principal component analysis, and Piper-Tri-linear diagram, were used to analyze the temporal and spatial variations of groundwater hydrochemical characteristics of Beijing. With the accelerating urbanization, the groundwater hydrochemical characteristics of different aquifers in the study area changed considerably as a result of over-exploitation of groundwater, pollutant emission, and other human activities. The proportion of HCO_3^- in total anion of groundwater increased distinctly from period 2005-2007 (earlier period) to period 2013-2015 (later period), and the major hydrochemical types evolved from Ca-Mg-Cl-SO_4 to Ca-Mg-HCO_3 . In the shallow groundwater, the concentrations of Na^+ , Ca^{2+} , SO_4^{2-} , HCO_3^- , TDS

increased, and HCO_3^- changed the most whose mean level increased from 428.93 to 528.96 mg L^{-1} . In addition, the concentration of F^- showed a slightly downward trend, the mean concentration of F^- decreased from 0.77 to 0.71 mg L^{-1} . In the deep groundwater, the changes in most of the ionic concentrations were consistent with those in the shallow groundwater from the earlier period to the later period, yet the variations were less than those in the shallow groundwater. HCO_3^- increased significantly with mean concentration increasing from 230.71 to 309.24 mg L^{-1} . The annual ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$ varied greatly, with a mean value of 1.26 in the earlier period and 1.07 in the later period. The values were bigger than 1 in the majority of the monitoring wells, which reflects significant effects by human activities. The temporal and spatial variations of hydrochemical characteristics can be used as indicators of groundwater quality. It should be understood that

groundwater resources are very precious yet are easily affected by human activities. In order to ensure the security of water supply, it is necessary and urgent to take further effective measures to protect groundwater resources.

Acknowledgments

This study is supported by the National Natural Science Foundation of China (41572240). Thanks are also given to colleagues at the Water Quality Monitoring Center Lab of Beijing Water-affair Authority for their support on water quality data. Furthermore, we thank the editors and anonymous reviewers of this article for their valuable review and suggestions.

References

- Anwar A E. 2010. Hydrogeochemical characteristics and evolution of groundwater at the Ras Sudr-Abu Zenima Area, Southwest Sinai, Egypt. *Journal of King Abdulaziz University: Earth Science*, 21(1): 79-109.
- Arumugam K, Elangovan K. 2009. Hydrochemical characteristics and groundwater quality assessment in Tirupur Region, Coimbatore District, Tamil Nadu, India. *Environmental Geology*, 58(7): 1509-1520.
- Borůvka L, Vacek O, Jehlička J. 2005. Principal component analysis as a tool to indicate the origin of potentially toxic elements in soils. *Geoderma*, 128(3): 289-300.
- Dixon W, Chiswell B. 1992. The use of hydrochemical sections to identify recharge areas and saline intrusions in alluvial aquifers, southeast Queensland, Australia. *Journal of Hydrology*, 130(1-4): 299-338.
- Gibbs R J. 1970. Mechanisms controlling world water chemistry. *Science*, 170(3962): 1088-1090.
- Gosselin D C, Harvey F E, Frost C D. 2001. Geochemical evolution of ground water in the Great Plains (Dakota) aquifer of Nebraska: Implications for the management of a regional aquifer system. *Ground Water*, 39(1): 98-108.
- Green T R, Taniguchi M, *et al.* 2011. Beneath the surface of global change: Impacts of climate change on groundwater. *Journal of Hydrology*, 405(3): 532-560.
- Hajalilou B, Khaleghi F. 2009. Investigation of hydrogeochemical factors and groundwater quality assessment in Marand Municipality, northwest of Iran: A multivariate statistical approach. *Journal of Food, Agriculture & Environment*, 7(3&4): 930-937.
- LV Xiao-jian, LI Yu, LI Zhi-ping. 2015. Thoughts on the coordinated development between groundwater resources and urbanization in Beijing. *Urban Geology*, (S1): 8-12.
- Mahlknecht J, Schneider J F, *et al.* 2004. Groundwater recharge in a sedimentary basin in semi-arid Mexico. *Hydrogeology Journal*, 12(5): 511-530.
- Mapoma H W T, Xie X, *et al.* 2016. Hydrochemical characteristics of rural community groundwater supply in Blantyre, southern Malawi. *Journal of African Earth Sciences*, 114: 192-202.
- Martos F S, Bosch A P, Calaforra J M. 1999. Hydrogeochemical processes in an arid region of Europe (Almeria, SE Spain). *Applied Geochemistry*, 14(6): 753-745.
- Matiatos I, Alexopoulos A, Godelitsas A. 2014. Multivariate statistical analysis of the hydrogeochemical and isotopic composition of the groundwater resources in northeastern Peloponnesus (Greece). *Science of the Total Environment*, 476-477: 577-590.
- Moya C E, Raiber M, *et al.* 2015. Hydrochemical evolution and groundwater flow processes in the Galilee and Eromanga basins, Great Artesian Basin, Australia: A multivariate statistical approach. *Science of the Total Environment*, 508: 411-426.
- Panno S V, Hackley K C, *et al.* 1994. Hydrochemistry of the mahomet bedrock valley aquifer, East-Central Illinois: Indicators of recharge and groundwater flow. *Ground Water*, 32(4): 591- 604.
- Qusai Y Al-Kubaisi, Sarkawt G S. 2009. Hydrochemical evaluation of the groundwater in Fatah Umar-Hazar Kani area, northeast Iraq. *Iraqi Bulletin of Geology and Mining*, 5(1): 87-99.
- Rajendra P, Sandashivaiah C, Ranganna G. 2009. Hydrochemical characteristics and evaluation of groundwater quality of Tumkur Amanikere Lake Watershed, Karnataka, India. *E-Journal of Chemistry*, 6(S1): 211-218.
- <http://gwse.iheg.org.cn>

- Richter B C, Kreitler C W, Bledose B E. 1993. Geochemical techniques for identifying sources of groundwater salinization. NEW York: CRC Press. 593-598.
- Seth R, Mohan M, *et al.* 2016. Water quality evaluation of Himalayan Rivers of Kumaun region, Uttarakhand, India. *Applied Water Science*, 6(2): 137-147.
- SHI J S, LI G M, *et al.* 2014. Evolution mechanism and control of groundwater in the North China Plain. *Acta Geoscientica Sinica*, 35(5): 527-534.
- SHI J S, WANG Z, *et al.* 2011. Assessment of deep groundwater over-exploitation in the North China Plain. *Geoscience Frontiers*, 2(4): 593-598.
- Tizro A T, Voudouris K S. 2008. Groundwater quality in the semi-arid region of the Chahardouly basin, West Iran. *Hydrological Processes*, 22(16): 3066-3078.
- Voutsis N, Kelepertzis E, *et al.* 2015. Assessing the hydrogeochemistry of groundwaters in ophiolite areas of Euboea Island, Greece, using multivariate statistical methods. *Journal of Geochemical Exploration*, 159: 79-92.
- WANG Xin-juan, LI Peng, *et al.* 2016. Effect of over exploitation on underground water quality in the upper part of Chaobai River alluvial fan in Beijing. *Geoscience*, 30(2): 470-477.