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ORIGINAL ARTICLE

Statistical analysis of groundwater chemistry of the Tarim River lower reaches, Northwest China

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Abstract This study applied a comprehensive quantitative approach including statistical, principal component and gray relation analyses to assess the groundwater chemistry based on monitored data from 840 samples collected from the lower reaches of Tarim River from 2000 to 2009. The main findings were: (1) there were six types of groundwater chemistry in the lower reaches of Tarim River where $Cl{\cdot}SO_4$–$Na{\cdot}Mg$ was the dominant type accounting for 73.57% in all samples. There were linear relationships among chemical parameters, where TDS had significant multiple correlations with Na^+, K^+, Mg^{2+}, Ca^{2+} and Cl^-, respectively. (2) Three principal components (PC1, PC2 and PC3) were extracted. They included comprehensive measurements for salinization, alkalinity and pH, respectively. Most parameters showed decreasing trends during the period of 2000–2009, as well as the scores on PC1, because the concentrations of various chemical substances were diluted due to the uplift of the groundwater table in the lower reaches and the implementation of the ecological water delivery project in 2000. (3) $HCO_3{}^-$ was the most sensitive chemical parameter affected by the groundwater table followed by TA, Mg^{2+}, TH, SO_4^{2-}, K^+, TDS and TS. PC2 was the most sensitive principal component to the change of the groundwater table followed by PC1 and PC3.

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Introduction

Groundwater plays an important role in physical characteristics of the hydrological system. The change in its chemistry has a great impact on the ecological process (Murgai et al. 2001; Cui and Shao 2005). Because precipitation is rare and evaporation is very high in arid areas (Xu et al. 2009), groundwater is very important in maintaining the health of ecosystems and social and economic development. Therefore, the groundwater chemistry and its changes have received recent attention (Li et al. 2010). To utilize and protect valuable groundwater resources effectively and predict the change in groundwater environment, it is necessary to understand the hydrochemical characteristics of the groundwater and its evolution under natural water circulation processes (Zhu et al. 2010).

The Tarim River is in the arid area, northwest China (Fig. 1). The ecosystem and environment of the area have been changed significantly by extensive agricultural exploitation. Irrational exploitation of water resource and rapid development of water utilization over the last 50 years have greatly disturbed the natural distribution of water resources in the Tarim River Basin. Environmental problems such as deforestation, desertification and increased soil salinity have received considerable attention. A more serious situation is that more than 321 km of the watercourse has been drained after the Daxihaizi Reservoir was built in the 1970s (Liu and Chen 2002, 2007). As a consequence, the water table along the dried off

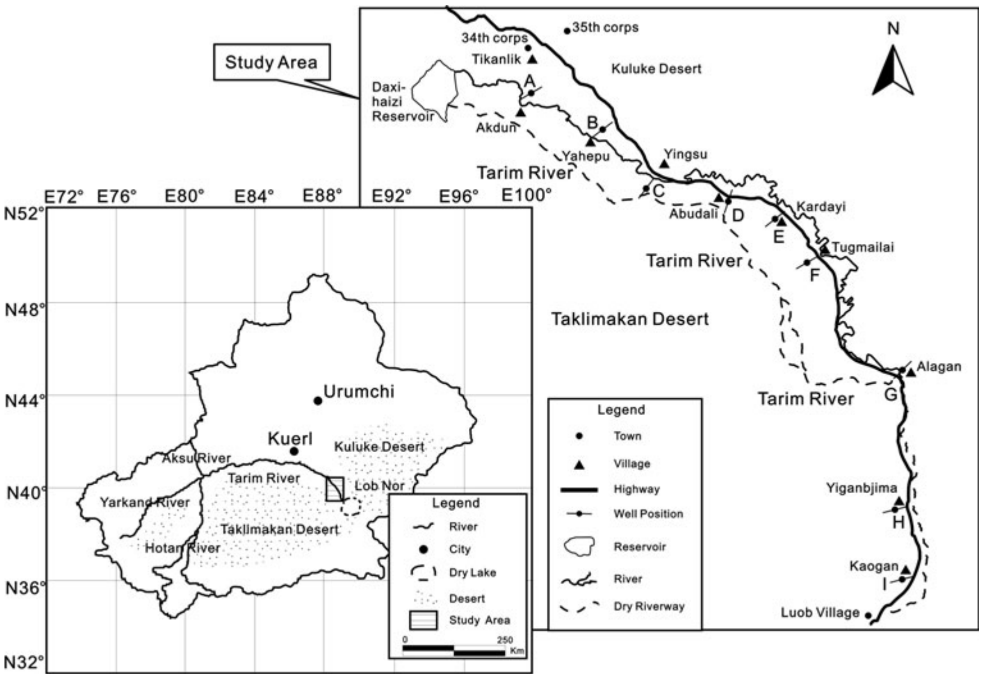

Fig. 1 Location of the monitoring sites for groundwater of the Tarim River lower reaches

watercourse decreased from –2 to –3 m to –4 to –10 m, and the groundwater quality kept on deteriorating. The total dissolved solids (TDS) in groundwater was 1.3 g/L in the 1970s and it reached 4.5 g/L in the 1990s (Chen et al. 2008). During the past five decades, the area of the *Populus euphratica* forest, which is the main tree species of the region, declined from 540 to 52.3 km^2 along the lower reaches of the Tarim River (Feng et al. 2001). The shrub and meadow area decreased by 200 km^2 and the desertification increased by 12,300 km^2 (Feng et al. 2001).

To prevent continued deterioration of the ecosystem and the enlarging desertification along the dried-up watercourse, a water delivery project has been carried out. From May 2000, the water in Boston Lake was intermittently supplied to the dried watercourse. By November 2002, five intermittent water deliveries had been completed, which played a critical role in vegetation recovery (Guo et al. 2002; Li et al. 2003; Xu et al. 2003).

Literature has shown that the groundwater table along the lower reaches of the Tarim River has risen and the ecological environment has improved markedly because of ecological water conveyance since 2000 (Chen et al. 2006, 2008, 2009; Li et al. 2010; Ye et al. 2009). However, few quantitative analyses and assessments of groundwater chemistry during the last decade have been conducted. Therefore, the main objectives of this study are to (a) examine the correlation among chemical parameters, (b) extract the principal components (PCs) of groundwater chemistry; and (c) rank the chemical parameters, PCs and their sensitivities to the groundwater table. Thus, a comprehensive statistical approach including statistical, principal component and gray relation analyses was employed to analyze the groundwater chemistry based on monitored data from the lower reaches of the Tarim River from 2000 to 2009.

Methodology

Study area

Tarim River is in south Xinjiang, Northwest China, with a length of 1,321 km and watershed area of 102 × 10^4 km^2 (39°00′–41°40′N, 74°30′–88°30′E) (Zhang et al. 2005). It is one of the longest inland rivers around the world, and plays a key role in the development of local society and economy. The Taklamakan Desert, the second largest desert around the world, was named after the Tarim River and Kuluke Desert. It lies to the south of the river and extends across the Tarim Basin. There are Tianshan Mountains to the north of the basin and Karakorum Mountains to the south. The lower reaches of the Tarim River are 321 km in length from Qiala to the Taitema Lake (Fig. 1).

The downstream alluvial plain area lies in the eastern part of the Tarim Basin, and the terrain is relatively flat, with an average altitude of 825 m. Major landform types are alluvial–diluvial, alluvial, eolian and fluvial–lacustrine sedimentation. Simultaneously, the stratum structure is simple, mainly made up of the Pleistocene and Holocene of the quaternary strata, and the surface lithology is dominated by sand, sub-sandy soil and clay (Nishidai and Berry 1990). In addition, the aquifer in this study area is a Quaternary aquifer, and the lithology is single with river–lake facies fine sand and silty fine sand in the majority and eolian sand locally. Divided by water-bearing media, it belongs to a typical chinky aquifer, and while divided by burial condition, it belongs to a phreatic aquifer. Thus, the permeability and water abundance are relatively poor with the permeability coefficient varying from 1.2 to 4.8 m/d, and the single-orifice water inflow is <150 m^3/dm. The study area is in the disconnection river, from Tikanlik to Taitema Lake, which has a warm temperate, extremely arid climate with annual solar radiation of 5,692–6,360 kj/m^2. According to the observation by Tikanlik meteorological station from 1957 to 2005, the average temperature, annual precipitation and annual evaporation are 10.94°C, 34.53 mm and 2,531.45 mm, respectively. Due to years of zero flow, the groundwater table mostly dropped to 8–12 m and both the degree of salinity and mineralization were relatively high.

Data collection and analysis

Nine groundwater monitoring sites along the lower reaches of the Tarim River were selected. They were Akdun (A), Yahepu (B), Yingsu (C), Abudali (D), Kardayi (E), Tugmailai (F), Alagan (G), Yiganbjima (H) and Kaogan (I). Monitoring wells, with a depth of 8–17 m, were laid at an interval of 100–200 m for every monitoring site. There were a total of 40 and distributed within the range of 50–1,050 m from the watercourse. To analyze the changes of the groundwater chemistry components, the groundwater table and collected groundwater samples regularly from each well at each site were measured, and 840 samples were collected and analyzed during the period from 2000 to 2009. The samples were stored in clean and colorless polyethylene plastic bottles, and sealed with paraffin and labeled. The samples were placed in a shaded area until they were sent to the laboratory. The chemical compositions of the samples were analyzed within 2 days in the laboratory. The chemical analyses included total dissolved solids (TDS), total salt (TS), pH, total alkalinity (TA), total hardness (TH), electric conductivity (EC), CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+ and Na^+.

This study adopted appropriate methods to measure each parameter. The pH and electrical conductivity (EC) were measured using pH and pre-calibrated portable conductivity meters (APHA 1995). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined using EDTA titrimetric method (APHA 1995). Chloride (Cl^-) was determined by standard $AgNO_3$ titration. Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were determined by titration with HCl (APHA (American Public Health Association) 1995). Sodium (Na^+) and potassium (K^+) were measured by flame photometry, while sulfate (SO_4^{2-}) by spectrophotometer turbidimetry (APHA (American Public Health Association) 1995). Total hardness (TH) was measured by Ca–Mg conversion method and total alkalinity (TA) by acid–based titration (MEP PRC 2004). TDS and TS were determined by the gravimetric method (MEP PRC 1999).

Classification approach of groundwater chemistry

The chemical characteristics of the groundwater can reflect on the different formation conditions, which are determined by different natural environments. In other words, the chemical composition is similar when the groundwater is formed from the same natural source. At present, there are several common methods used to classify groundwater chemistry, such as Shorclife classification (Wang and Zhang 1995), Brodsky classification (Wang and Zhang 1995), Piper Tri-linear diagram (Wang and Zhang 1995; Piper 1944), etc. In this study, the Brodsky classification and Piper Tri-linear diagram were adopted to analyze the characteristics of groundwater chemistry:

(1) Brodsky classification can be used to classify the groundwater samples into 36 groundwater chemical types, which are denominated by the anions and cations whose milligram equivalent (meq) values are the largest or second largest among the six primary ions, i.e., HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+ (Wang and Zhang 1995). For example, the type of HCO_3·Cl–Na·Mg means that the major anions are HCO_3^- and Cl^-, and the meq value of HCO_3^- is more than Cl^-, while the major anions are Na^+ and Mg^{2+}, and the meq value of Na^+ is more than Mg^{2+}. According to the denomination method, the chemical types of the 840 samples can be determined. Therefore, by counting the number of samples of different chemical types, we can obtain the samples' distribution in different chemical types. Furthermore, the percentages of different chemical types can be obtained by the formula, i.e., the numbers of samples in different chemical types divided by the number of total samples (840 in this paper). Meanwhile, the main type can be judged by the percentages of different types.

(2) Piper's Tri-linear diagram (Piper 1944) has been used to decipher the geochemical evaluation of groundwater. The diagram consists of two triangular fields and a central diamond-shaped field. In the two triangular fields, percentage meq values of major cations and anions are plotted separately and then projected onto the central field for the representation of the overall

characteristics of water. This plot reveals useful properties and relationships for large sample groups and can be drawn by Sigma Plot v.11.

Statistical analysis

Although the chemistry of groundwater in the lower reaches of the Tarim River is affected by various factors, the correlation among variables describing chemical components can still be established, as it was commonly done in many other researches (Xu 2002; Tardy et al. 2004; Giridharan et al. 2008; Chenini and Khemiri 2009; Xu et al. 2010). For the purpose of comparison, this work also conducted regression analysis to examine the correlation among TDS, TS, TA, TH and some ions.

Principal component analysis

Principal component analysis (PCA) is a well-known technique for data compression and information extraction from a large number of variables (Xu 2002), which is suitable for multivariate analysis of groundwater (Mrklas et al. 2006; Mumford et al. 2007; Fernandes et al. 2010). Essentially, PCA extracts a smaller set of underlying new variables that are uncorrelated, mutually independent (orthogonal) and mathematically represented by linear combinations of original variables in the X matrix. These new variables, referred to as principal components (PCs), are calculated to account for much of the variance presenting in the X matrix (Wold et al. 1987; Mumford et al. 2007) and therefore are able to describe major trends in the original data sets. PCA decomposes the data matrix X as the sum of the outer product of vectors t_i and p_i plus a residual matrix E as presented in Eq. 1.

$$X = \sum_{i=1}^{k} t_i \cdot p_i + E \tag{1}$$

where k is the number of samples in the X data set. The t_i vectors are known as scores (i.e., values) on the PCs (i.e., new variables) extracted by PCA. The p_i vectors are known as loadings and contain information on how the variables relate to each other (Wold et al. 1987; Eriksson et al. 2001). The scores (t_i) generated by PCA can be interpreted as projections of the variable to a new space spanned by the PCs (i.e., when the original variables are transformed to PCs, each variable in the X matrix is projected on to the PC space). Generally, the first few principal components can explain most of the variability in the original data.

To characterize the groundwater chemistry in the lower reaches of the Tarim River, three PCs, i.e., the first, second and third PCs were extracted from 14 parameters for 840 water samples in this paper.

Gray relation analysis

From the viewpoint of gray system theory (Deng 1989), the groundwater in the lower reaches of the Tarim River is a typical gray system (Xu 2002). Therefore, the gray relation analysis method was used to study the sensitivity of the groundwater chemical parameters and PCs to the change of groundwater table.

In a gray relation analysis, variables of series are represented as reference series and influenced series. The gray relation is the indefinite relationship among the two types of series data, and the aim here is to compute the affecting degree of influence series to reference series. A parameter called gray relation degree is used to represent the propinquity of two series. If the relation degree of one series is higher than that of others, this particular series is deemed to place greater influence on the reference series and will be chosen for modeling (Deng 1985).

The principle of gray relation analysis is as follows. For reference series $\{Y_1\ (t),\ t = 1,\ 2,\ldots\ldots\}$, i.e., groundwater table, and influenced series $\{Y_i\ (t),\ i = 1,\ 2,\ldots;\ t = 1,\ 2,\ldots\ldots\}$, i.e., the first, second and third PCs characterizing chemistry of groundwater, the following formula is used to calculate relation parameters [$\xi_{1i}(t)$] of two series (Deng 1985):

$$\xi_{1i}(t) = \frac{\min\limits_i \min\limits_t |Y_1(t) - Y_i(t)| + k \max\limits_i \max\limits_t |Y_1(t) - Y_i(t)|}{|Y_1(t) - Y_i(t)| + k \max\limits_i \max\limits_t |Y_1(t) - Y_i(t)|} \tag{2}$$

where k is a gray parameter with a value range between 0 and 1, and often assigned a value of 0.5 for calculation.

With the computed relation parameters, the gray relation degree (γ_{1i}) of each influence series [$Y_i\ (t)$] to reference series [$Y_1\ (t)$] can be calculated:

$$\gamma_{1i} = \frac{1}{n} \sum_{t=1}^{n} \xi_{1i}(t) \tag{3}$$

It needs to be pointed out that the data of each series should be normalized before conducting the gray relation analysis. There are several methods for normalizing the data, and this paper used the following:

$$y_i(t) = \frac{Y_i(t) - \min\limits_t Y_i(t)}{\max Y_i(t) - \min\limits_t Y_i(t)} \quad i = 1, 2, \ldots, m \tag{4}$$

That is to say, $y_i\ (t)$, instead of $Y_i\ (t)$, should be used in Eq. 1 for computation.

Results and discussions

Major chemical parameters and types of groundwater

The basic statistical parameters and the *t* test results for 840 samples are shown in Table 1. Overall, the groundwater in the lower reaches of the Tarim River shows slight alkalinity, with a mean pH of 7.66 ± 0.02 and a mean TA of 0.601 ± 0.010 g/L. Besides, the mean TH is 2.692 ± 0.133 g/L and the mean EC is 5.08 ± 0.49 ms/cm, while the mean TDS and TS are 5.333 ± 0.450 and 5.148 ± 0.433 g/L. As for the anions of CO_3^{2-}, HCO_3^-, Cl^- and SO_4^{2-}, the contents are 0.002 ± 0.000, 0.363 ± 0.006, 2.047 ± 0.233 and 1.002 ± 0.052 g/L, respectively. Similarly, the contents for cations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ are 0.180 ± 0.009, 0.220 ± 0.012, 1.299 ± 0.140 and 0.036 ± 0.002 g/L, respectively.

Table 2 shows the distribution of major chemical types for samples from the lower reaches of the Tarim River according to the Brodsky classification (Wang and Zhang 1995). As can be seen from Table 2, divided only by anion, there were mainly three chemical types of groundwater in the study area, in which $Cl\cdot SO_4$ takes up 80.24% of the total samples acting as the leading one, $HCO_3\cdot SO_4$ 11.19% and $SO_4\cdot Cl$ 8.33%. Based only on cations, the groundwater chemical types were divided into three types, in which Na·Mg, Mg·Na and Na·Ca account for 89.29, 5.24 and 3.93%, respectively. Taking both anions and cations into account, the chemical types of groundwater in the study area were mainly divided into six types as follows: $Cl\cdot SO_4$–Na·Mg accounts for the largest proportion of 73.57%, $HCO_3\cdot SO_4$–Na·Mg accounts for 9.64%, $SO_4\cdot Cl$–Na·Mg accounts for 5.95%, and the three others, i.e., $Cl\cdot SO_4$–Mg·Na, $Cl\cdot SO_4$–Na·Ca and $HCO_3\cdot SO_4$–Mg·Na, account for 3.45, 2.38 and 1.07%, respectively. It is clear that $Cl\cdot SO_4$–Na·Mg is the major chemical type of groundwater in the lower reaches of the Tarim River. Furthermore, the result has also been verified by the Piper diagram (Fig. 2).

Table 1 Basic statistical analysis of groundwater chemistry for 840 samples from the Tarim River lower reaches

	Mean	Std. Error of Mean	Std.	Skewness	Kurtosis	*t*	Samples	Sig. (2-tailed)
TA (g/L)	0.601	0.010	0.293	1.293	2.505	59.545	840	0.000
TH (g/L)	2.692	0.133	3.865	3.646	14.280	20.187	840	0.000
pH	7.66	0.02	0.51	1.372	12.442	438.434	840	0.000
EC (ms/cm)	5.08	0.49	14.15	10.044	141.510	10.404	840	0.000
TDS (g/L)	5.333	0.450	13.050	6.030	42.187	11.845	840	0.000
TS (g/L)	5.148	0.433	12.547	6.142	44.575	11.892	840	0.000
CO_3^{2-} (g/L)	0.002	0.000	0.012	8.878	91.168	4.583	840	0.000
HCO_3^- (g/L)	0.363	0.006	0.175	1.217	2.298	60.177	840	0.000
Cl^- (g/L)	2.047	0.233	6.762	6.949	58.111	8.774	840	0.000
SO_4^{2-} (g/L)	1.002	0.052	1.511	3.648	15.282	19.216	840	0.000
Ca^{2+} (g/L)	0.180	0.009	0.249	5.171	36.093	20.907	840	0.000
Mg^{2+} (g/L)	0.220	0.012	0.338	3.523	12.903	18.832	840	0.000
Na^+ (g/L)	1.299	0.140	4.064	6.738	53.858	9.264	840	0.000
K^+ (g/L)	0.036	0.002	0.069	6.340	43.323	15.287	840	0.000

Table 2 Distribution of major chemical types for samples of groundwater

	$HCO_3^- + Cl^-$		$HCO_3^- + SO_4^{2-}$		$SO_4^{2-} + HCO_3^-$		$SO_4^{2-} + Cl^-$		$Cl^- + SO_4^{2-}$		$Cl^- + HCO_3^-$		Total	
	Num	Percent	Num	Percent	Num	Percent	Num	Percent	Num	Percent	Num	Percent	Num	Percent
$Ca^{2+} + Mg^{2+}$	0	0.00	0	0.00	0	0.00	3	0.36	0	0.00	0	0.00	3	0.36
$Ca^{2+} + Na^+$	0	0.00	0	0.00	0	0.00	2	0.24	5	0.60	0	0.00	7	0.83
$Na^+ + Ca^{2+}$	0	0.00	4	0.48	1	0.12	8	0.95	20	2.38	0	0.00	33	3.93
$Na^+ + Mg^{2+}$	0	0.00	81	9.64	1	0.12	50	5.95	618	73.57	0	0.00	750	89.29
$Mg^{2+} + Ca^{2+}$	0	0.00	0	0.00	0	0.00	1	0.12	2	0.24	0	0.00	3	0.36
$Mg^{2+} + Na^+$	0	0.00	9	1.07	0	0.00	6	0.71	29	3.45	0	0.00	44	5.24
Total	0	0.00	94	11.19	2	0.24	70	8.33	674	80.24	0	0.00	840	100

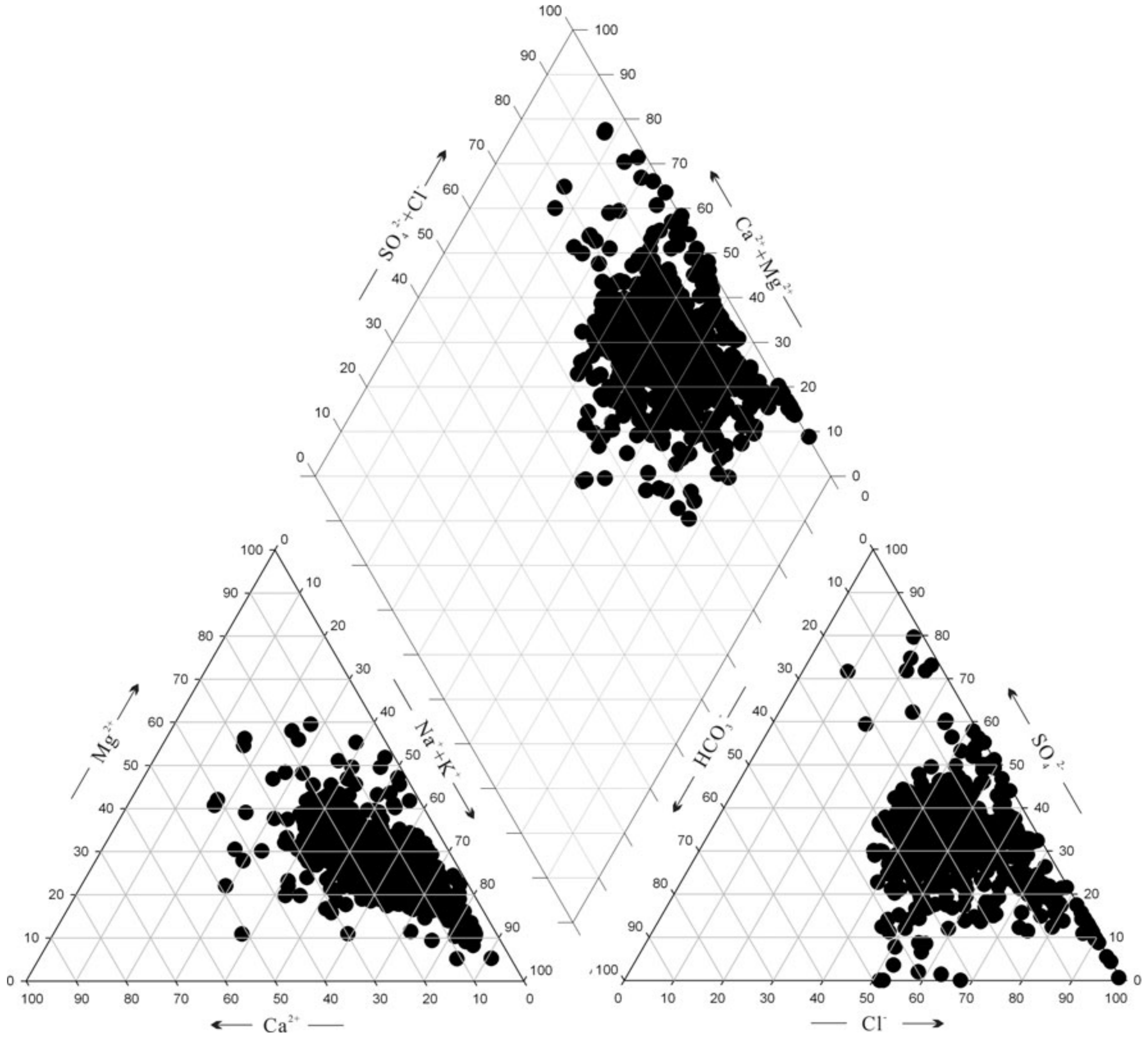

Fig. 2 Piper diagram of groundwater chemistry

Correlation among major chemical parameters of groundwater

One of the groundwater characteristics in the lower reaches of the Tarim River is the linear relationship among the principal ions, which is similar to the groundwater in the proximity of the River Cooum, Chennai, India (Giridharan et al. 2008).

The good relationship between $Na^+ + K^+$ and Cl^- (Fig. 3a) shows that Cl^- and most of $Na^+ + K^+$ are derived from dissolution and weathering of disseminated halite. The slope of TA and HCO_3^- (Fig. 3b) indicates that the bicarbonate in the groundwater is dominant, and the groundwater in the downstream of the Tarim River is slightly alkaline. It is well known that HCO_3^- is the dominant species at a pH range of 7.5–8.0, while the groundwater in the lower reaches of the Tarim River has a mean pH of 7.66 ± 0.02, in accordance with the conclusion from the relationship between TA and HCO_3^-.

It can be seen from the slopes of $Ca^{2+}$and Mg^{2+} with TH (Fig. 3c, d) that the average ratio of Ca^{2+}:TH is 0.2935 and the average ratio of Mg^{2+}:TH is 0.7169. Furthermore, it is well known that TH is the sum of Ca^{2+} and Mg^{2+}. Therefore, the average percentages of Ca^{2+} and Mg^{2+} in the groundwater are 29.35% and 71.69%, respectively. It can be indicated from the slope of TH and SO_4^{2-} (Fig. 3e) that there is a good relationship between TH and SO_4^{2-} and the average ratio of SO_4^{2-}:($Ca^{2+} + Mg^{2+}$) is 0.7516. Therefore, the dissolution of sulfate mineral could exert a control on Ca^{2+} and Mg^{2+}. If Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- are derived from simple dissolution of calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$] and gypsum ($CaSO_4$), with the reactions of Eqs (5), (6) and (7) (Tyagi et al. 2009; Garrels and Mackenzie 1971; Holland 1978), then a charge balance should exist between cations and anions, i.e., the ratio of ($SO_4^{2-} + HCO_3^-$):($Ca^{2+} + Mg^{2+}$) is 1. However, as indicated in Fig. 3f, the slope of $SO_4^{2-} + HCO_3^-$ with TH is 0.7713, i.e., a majority of the water samples in the

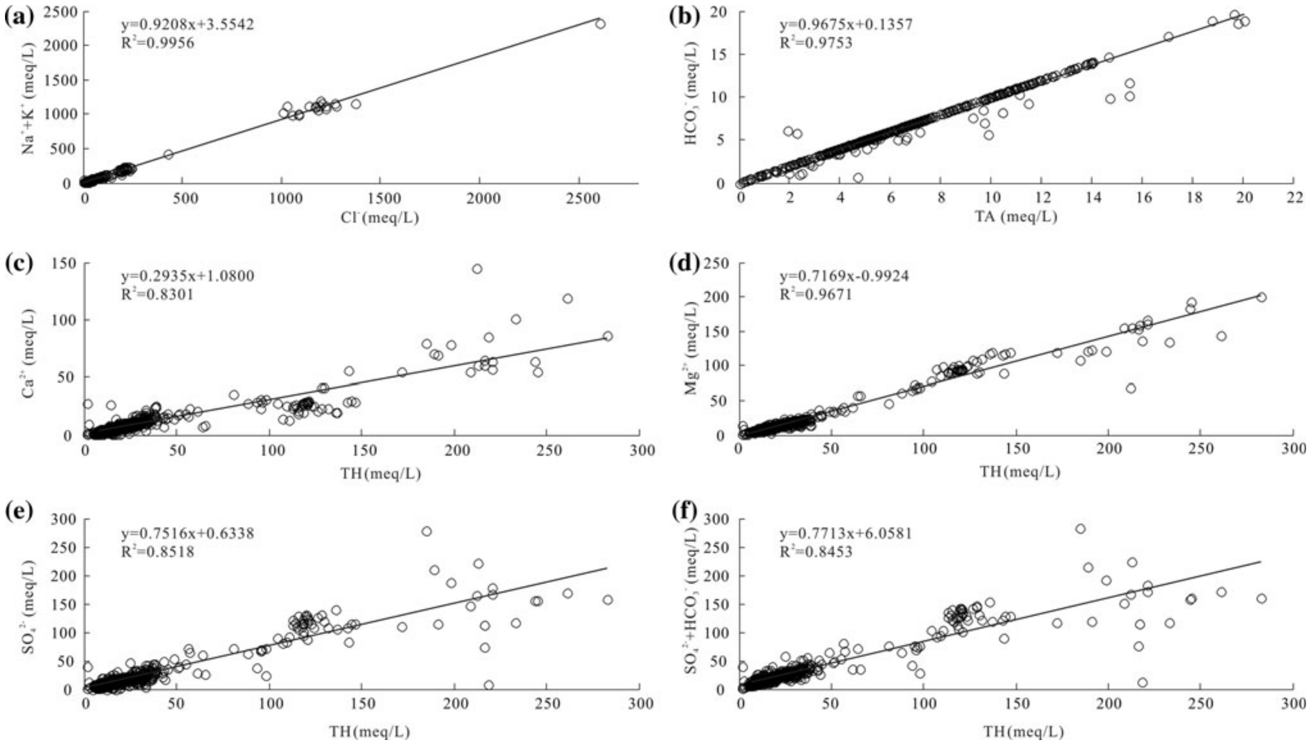

Fig. 3 The correlation of groundwater chemical components

study area have ($SO_4^{2-} + HCO_3^-$):($Ca^{2+} + Mg^{2+}$) equivalent ratios smaller than 1. Therefore, there must exist other anions balancing the excess of $Ca^{2+} + Mg^{2+}$.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad (5)$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad (6)$$

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \qquad (7)$$

Stepwise regression analysis was performed by taking TDS as a dependent variable and other parameters as independent variables. The results are shown in Table 3 and indicate that the screened independent variables are Na^+, Mg^{2+}, Ca^{2+}, Cl^- and K^+. The *t* test results for the partial regression coefficient of the first four independent variables, i.e., Na^+, Mg^{2+}, Ca^{2+}, Cl^-, are all highly significant (Sig. = 0.0000), as well as the independent variable, i.e., K^+, shows high significance (Sig. = 0.0495). It indicates that Na^+, Mg^{2+}, Ca^{2+}, Cl^- and K^+ are the main chemical variables to affect TDS.

Principal component for groundwater chemistry

Some studies (Mrklas et al. 2006; Mumford et al. 2007; Fernandes et al. 2010) indicate that PCA is applicable to multivariate analysis of groundwater. For extracting the PCs of groundwater chemistry in the lower reaches of the Tarim River, data from 840 sample points were used to perform PCA for the original variables. The first three principal components (see Table 4) were picked up, with the cumulative contribution rate being up to 88.893%; that is to say, the three PCs already contained 88.893% information of the 14 original variables.

Table 3 The correlation between TDS and cations in groundwater chemical components

Dependent variable	Independent variable and constant	Coefficients	*t*	Sig.
TDS	Na^+	3.2598	54.8818	0.0000
	Mg^{2+}	5.6050	64.1187	0.0000
	Ca^{2+}	3.1437	21.6392	0.0000
	Cl^-	−0.3577	−10.2380	0.0000
	K^+	−1.1016	−1.9672	0.0495
	Constant	0.0758	3.3480	0.0009

Table 4 Eigenvalues and cumulative contribution rate of PCs

PCs	Eigenvalue	Contribution rate (%)	Cumulative contribution rate (%)
1	8.857	63.261	63.261
2	2.238	15.985	79.246
3	1.351	9.648	88.893
4	0.581	4.152	93.045
5	0.460	3.284	96.330
6	0.218	1.557	97.887
7	0.140	1.003	98.890
8	0.081	0.576	99.466
9	0.069	0.494	99.961
10	0.004	0.028	99.988
11	0.001	0.007	99.995
12	0.001	0.004	99.999
13	0.000	0.001	100.000
14	0.000	0.000	100.000

One parameter and the corresponding principal component will have a more significant correlation if the absolute value of load factor is closer to 1. Meanwhile, it will present a positive correlation when the coefficient is positive or a negative correlation when the coefficient is negative. It can be seen from Table 5 that PC1 has larger positive load factors on the variables of TH, EC, TDS, TS, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and K^+, which indicates that PC1 is the comprehensive measurement for the salinization of groundwater. PC2 has larger positive load factors on the variables of TA and HCO_3^-, indicating that PC2 is the comprehensive measurement for the alkalization of groundwater. PC3 has larger positive load factors on the variables of pH and CO_3^{2-}, indicating that PC3 is the comprehensive measurement for the pH of groundwater.

Table 5 Load factors of principal components

Original variables	Principal components (PCs)		
	PC1	PC2	PC3
TA	0.1174	0.9770	−0.0353
TH	0.9564	0.1721	−0.0806
PH	−0.3487	0.1671	0.7435
EC	0.8243	−0.2219	0.1680
TDS	0.9851	−0.0833	0.0948
TS	0.9847	−0.0847	0.0974
CO_3^{2-}	−0.0704	0.2688	0.8051
HCO_3^-	0.1275	0.9611	−0.1414
Cl^-	0.9603	−0.1580	0.1381
SO_4^{2-}	0.8695	0.2309	−0.1397
Ca^{2+}	0.9397	−0.0110	−0.0549
Mg^{2+}	0.9134	0.2383	−0.0890
Na^+	0.9648	−0.1441	0.1361
K^+	0.9162	−0.1021	0.0850

Differences among sites of groundwater chemistry

Table 6 shows the average values of various chemical parameters at different sites between 2000 and 2009. TA is at maximum of 0.935 g/L in the upstream site A, while it is at minima of 0.380 g/L in the downstream site H. Although there are differences in pH of different sites, the variations are not very obvious with the minimum of 7.36 at site I and the maximum of 7.97 at site G. TDS, TS and TH all present the maximum at site I with values of 37.351, 35.855 and 10.299 g/L, respectively, and show the minimum at site H with values of 1.642, 1.593 and 1.211 g/L, respectively. At the same time, CO_3^{2-} shows a smaller value at every site, and HCO_3^- has the similar permutation with TA at every site. The minimums of the ions, such as Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and K^+, have occurred at site H, while the maximums at site I. The mean values of ion content and mineralization degree at different sites are different, and this mainly depends on the soil salinity and groundwater table. The distribution of salinity at the soil profile is that as it is closer to the ground surface, the soil salinity content is higher and, with the rising groundwater table, more and more salt is dissolved into the water, increasing ion content and salinity (Chen et al., 2005). According to related works (Chen et al. 2005) about the relationship between water chemistry changes and groundwater table in the lower reaches of the Tarim River, the major ions and salinity in groundwater will rise when the groundwater table is around -4 m. Simultaneously, this regular pattern was shown obviously in Table 6. For example, at site A, the average groundwater table is −3.28 m near the ground surface, and the average value of ion content and mineralization is greater than that at site B, D, E, G and H. However, the ion content and mineralization at site C and F are a little higher than those at site A, which may be connected with salinity in the soil. The values of most chemical parameters in site I are the largest among the nine sites. The reason for this is the non-dilution effect seen from Fig. 4, which indicates that when the groundwater table is lower than −9 m, the lower the groundwater table, the higher is the concentration of salinity. Therefore, site I with the average groundwater table at −8.91 m will have the highest concentration of salinity among the nine sites. It was also shown that, among the nine sites, the values of various chemical parameters in site F are the closest to the average values, so it can serve as the representative site in the lower reaches of the Tarim River.

Judging from the principal components, although the average scores of the first, second and third principal

Table 6 Chemical parameters at different sites

	A	B	C	D	E	F	G	H	I
TA (g/L)									
Mean	0.935	0.550	0.617	0.598	0.525	0.602	0.640	0.380	0.480
Std.	0.255	0.093	0.390	0.156	0.132	0.179	0.420	0.085	0.164
TH (g/L)									
Mean	2.785	1.341	3.834	1.432	1.507	2.710	1.449	1.211	10.299
Std.	1.518	0.576	4.426	0.765	0.818	2.463	0.803	0.519	9.651
pH									
Mean	7.55	7.69	7.54	7.72	7.64	7.75	7.97	7.78	7.36
Std.	0.30	0.28	0.78	0.34	0.32	0.24	0.63	0.25	0.44
EC (ms/cm)									
Mean	3.58	2.41	5.18	2.17	2.53	4.75	2.21	1.79	34.24
Std.	1.86	0.82	10.43	0.88	1.61	3.79	0.95	0.66	46.59
TDS (g/L)									
Mean	3.464	2.008	6.111	2.010	2.570	4.650	1.943	1.642	37.351
Std.	2.147	0.684	7.479	0.853	2.063	3.641	0.734	0.902	40.310
TS (g/L)									
Mean	3.377	1.966	5.898	1.971	2.504	4.436	1.906	1.593	35.855
Std.	1.942	0.669	7.162	0.831	1.980	3.385	0.739	0.865	38.876
CO_3^{2-} (g/L)									
Mean	0.000	0.000	0.002	0.000	0.000	0.000	0.014	0.000	0.000
Std.	0.000	0.001	0.008	0.002	0.001	0.000	0.033	0.000	0.000
HCO_3^- (g/L)									
Mean	0.570	0.335	0.374	0.364	0.320	0.367	0.362	0.232	0.293
Std.	0.156	0.057	0.240	0.095	0.081	0.109	0.228	0.052	0.100
Cl^- (g/L)									
Mean	0.883	0.515	1.981	0.520	0.870	1.548	0.452	0.462	18.905
Std.	0.843	0.216	2.635	0.241	1.000	1.474	0.210	0.336	21.641
SO_4^{2-} (g/L)									
Mean	0.906	0.509	1.650	0.482	0.498	1.072	0.502	0.408	3.458
Std.	0.480	0.239	2.010	0.303	0.301	0.826	0.422	0.274	3.550
Ca^{2+} (g/L)									
Mean	0.231	0.107	0.205	0.111	0.111	0.176	0.098	0.088	0.707
Std.	0.119	0.051	0.191	0.057	0.050	0.149	0.098	0.033	0.723
Mg^{2+} (g/L)									
Mean	0.199	0.098	0.347	0.107	0.116	0.224	0.118	0.094	0.825
Std.	0.118	0.045	0.435	0.063	0.072	0.214	0.059	0.051	0.794

Table 6 continued

	A	B	C	D	E	F	G	H	I
Na^+ (g/L)									
Mean	0.563	0.379	1.306	0.362	0.568	1.016	0.339	0.292	11.46
Std.	0.420	0.131	1.713	0.157	0.611	0.805	0.158	0.227	12.917
K^+ (g/L)									
Mean	0.025	0.023	0.034	0.025	0.021	0.033	0.022	0.018	0.207
Std.	0.017	0.007	0.028	0.011	0.009	0.026	0.007	0.009	0.219
Groundwater table (m)									
Mean	−3.82	−4.88	−5.34	−4.88	−6.6	−4.91	−6.87	−6.14	−8.91
Std.	1.23	1.53	1.40	1.05	1.76	0.93	1.95	1.00	2.00

components have no obvious regularity in change at different sites (see Fig. 5), it can be determined that the variation of the three principal components is not very large on the average scores from site B to site F, that is, sites B, C, D, E and F. In other words, the chemical properties of groundwater are basically the same in the middle reach sites, whereas site A in the upper reaches and site I in the lower reaches show larger differences. Moreover, the second principal component, i.e., integrated alkaline, at site A, has higher scores while the first principal component, i.e., integrated salinity, at site I, has the highest scores.

Changes in groundwater chemistry from 2000 to 2009

The site F is not only in the middle location along the lower reaches of the Tarim River (Fig. 1), but also its groundwater table and chemistry parameters are basically on average among the nine sites according to the analysis in the previous part (Differences among sites of groundwater chemistry). Therefore, to reflect the changes of the chemical property of groundwater with time, this paper will choose site F as a representative site to conduct the statistical analysis with the result shown in Fig. 6. As has been seen from Fig. 6, the parameters (i.e., TDS, TS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-) show a decreasing trend with years during the period of 2000–2009. The main reason is that the lower reaches of the Tarim River is a salt accumulation zone, where there is a high salt content in the soil and groundwater (Chen et al. 2005). Moreover, due to the implementation of the ecological water delivery project since 2000, in the lower reaches, the groundwater tables were uplifted and the concentrations of various chemical substances were diluted. In other words, the lower the groundwater table, the higher is the concentration of salinity, which has been discussed in the previous part (Differences among sites of groundwater chemistry). This result is consistent with the studies of Xu et al. (2008) and Li et al. (2010).

It can be seen from Fig. 7 that PC1 (i.e., the scores on integrated salinity) shows a decreasing trend with years. Moreover, the PC2 and PC3 (i.e., the scores on integrated alkalinity and pH) show a trend toward increase first and then decrease with subsequent years. The reason for the decrease of the three PCs is also the dilution effect as discussed above.

Sensitivity of hydrochemistry to groundwater table

Recent studies have shown that there is a certain correlation between the groundwater chemistry and the groundwater table in the lower reaches of the Tarim River (Chen et al. 2008, 2009; Li et al. 2010). However, which chemical

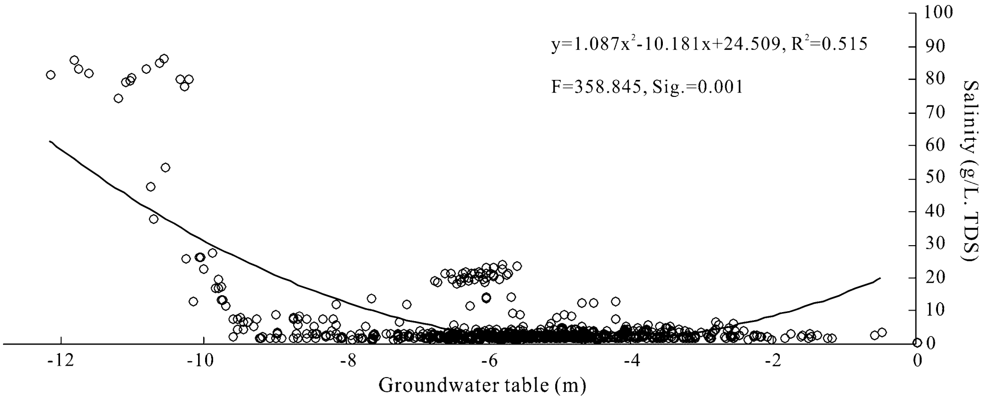

Fig. 4 Relation between groundwater salinity and groundwater table

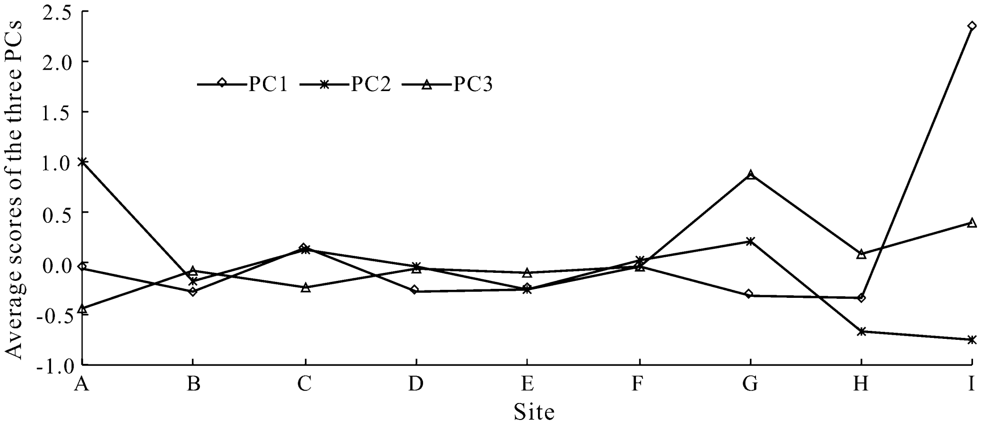

Fig. 5 Changes in scores on principal components of groundwater chemistry at different sites

parameters are more sensitive to the groundwater table, and which are less? To answer these questions, the gray relation analysis was performed by taking the groundwater table as a reference variable and the compositions of different chemical substances and the principal component as affected variables. The results are shown in Tables 7 and 8.

As shown in Table 7, the chemistry parameters can be sorted by the sensitivity to the water table. HCO_3^-, TA, Mg^{2+}, TH, SO_4^{2-}, K^+, TDS and TS are classified as the more sensitive parameters, while pH, EC, CO_3^{2-} and Ca^{2+} are less sensitive.

Table 8 indicates that PC2 (i.e., integrated alkalinity) is the most sensitive to the ground water table, followed by PC1 (i.e., integrated salinity) and then by PC3 (i.e., pH), which is the least sensitive. It is observed that the results from Tables 7 and 8 are consistent and mutually supportive. This result is consistent with the actual situation. For the groundwater chemistry process in the arid area of the Tarim River lower reaches, water is not only the solvent of alkaline substances but also the carrier for its migration. Therefore, PC2 (i.e., integrated alkalinity) and PC1 (i.e., integrated salinity) are more sensitive to groundwater table. As PC3 (i.e., pH) has a relationship with the regional environmental backgrounds, it is comparatively less sensitive to the groundwater table. This result was also supported by comparable study (Zhang et al. 2003).

Conclusions

The main findings of this study are as follows:

(1) There are six groundwater chemical types in the lower reaches of the Tarim River, i.e., $Cl{\cdot}SO_4$–$Na{\cdot}Mg$, $HCO_3{\cdot}SO_4$–$Na{\cdot}Mg$, $SO_4{\cdot}Cl$–$Na{\cdot}Mg$, $Cl{\cdot}SO_4$–$Mg{\cdot}Na$, $Cl{\cdot}SO_4$–$Na{\cdot}Ca$ and $HCO_3{\cdot}SO_4$–$Mg{\cdot}Na$. It can clearly be seen that $Cl{\cdot}SO_4$–$Na{\cdot}Mg$ is the dominant chemical type of groundwater in the lower reaches of the Tarim River.

(2) In the view of the average situation in the 2000s, the groundwater has slight alkalinity with a mean pH of 7.66. Furthermore, there is a linear relationship among the chemical parameters including highly significant correlation between TA and HCO_3^-, and between $Na^+ + K^+$ and Cl^-. Simultaneously, Ca^{2+}, Mg^{2+} and SO_4^{2-}exist in higher correlation. The stepwise regression analysis indicates that Na^+, Mg^{2+}, Ca^{2+}, Cl^- and K^+ are the main substance components correlated with TDS.

Fig. 6 Changes in major chemical parameters at site F with years

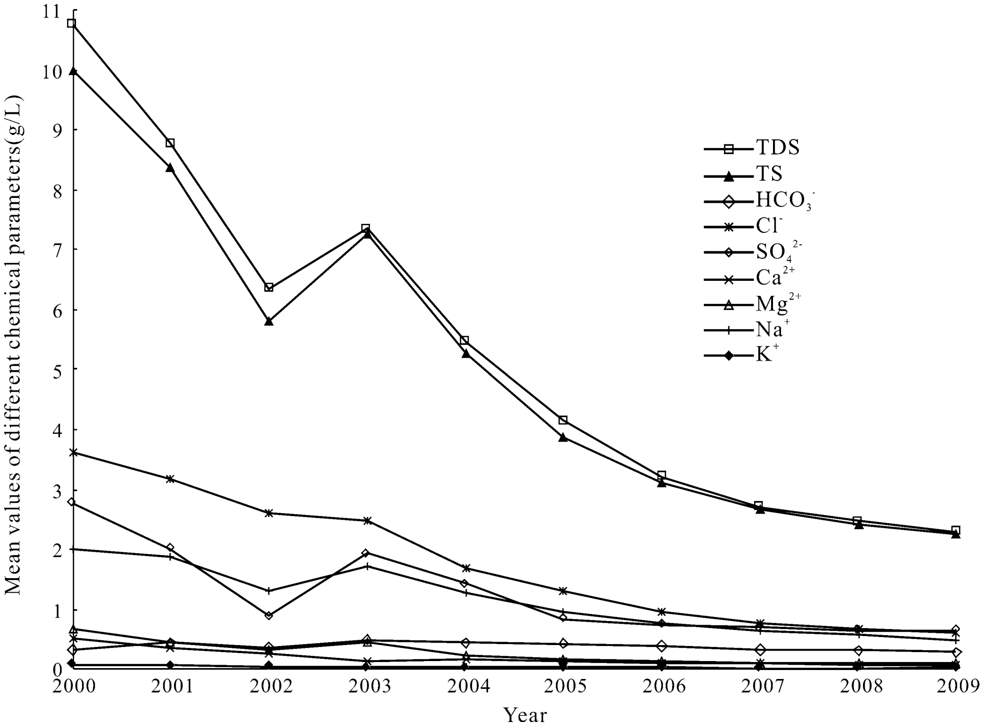

Fig. 7 The average scores on the three principal components at site F during the period of 2000–2009

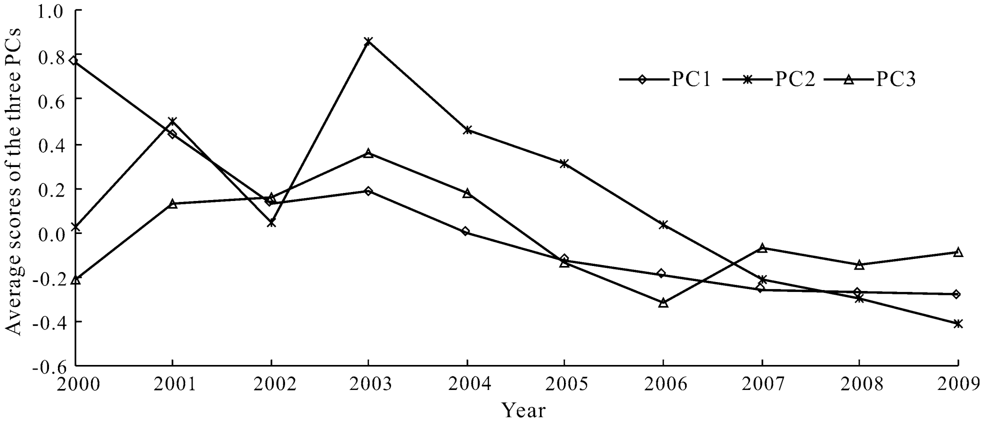

Table 7 Gray relation degree between groundwater table and chemistry composition

	TA	TH	pH	EC	TDS	TS	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Gray relation degree	0.710	0.646	0.512	0.523	0.568	0.564	0.540	0.713	0.552	0.611	0.550	0.681	0.554	0.570
Order	2	4	14	13	7	8	12	1	10	5	11	3	9	6

(3) Three principal components (PCs) of groundwater chemistry were extracted, including 88.89% information of the 14 original variables. PC1 is the comprehensive measurement for salinization, PC2 is the comprehensive measurement for alkalinity and PC3 is the comprehensive measurement for pH.

(4) TDS, TS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^-, as well as the scores on PC1, showed decreasing trends during the period of 2000–2009. This was due to dilution effect by uplifting and continuous rising of groundwater tables in the lower reaches by the implementation of the ecological water delivery project since 2000.

(5) The chemical parameters show no strong regularity among sampling points. The groundwater chemical properties of the B, C, D, E and F sites, in the middle reaches, are basically similar. There are larger differences between site A in the upstream and site

Table 8 Gray relation degree between groundwater table and principal component of chemistry

	PC1	PC2	PC3
Gray relation degree	0.591	0.810	0.533
Order	2	1	3

I in the downstream, with highest scores on PC2 at site A and highest scores on PC1 at site I.

(6) HCO_3^- is most sensitive to the change in groundwater table, followed by TA, Mg^{2+}, TH, SO_4^{2-}, K^+, TDS and TS. Furthermore, pH is the most insensitive parameter than EC and CO_3^{2-}. For the principal components, PC2 is the most sensitive one to the change in the groundwater table, next PC1 and then PC3.

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