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Geochemical characteristics of high-arsenic groundwater in the Kuitun River Basin, Xinjiang, China

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ABSTRACT

To determine the geochemical characteristics and the main factors controlling high-arsenic (As) groundwater in the Kuitun River Basin, factor analysis (FA) and hierarchical cluster analysis (HCA) were applied for quantitative investigation of the relationship among the chemical properties of 50 groundwater samples from the Kuitun River Basin. The results showed that As was positively correlated with redox potential (Eh), pH, and phosphate (PO_4^{3-}) concentration, and FA results showed that As enrichment in groundwater was controlled by factors such as geology, reducibility, and competitive ion adsorption. Samples were classified via HCA into four clusters that corresponded to the source, reducing environment, groundwater runoff, and weak alkaline conditions. The combination of FA and HCA showed that different factors dominated under different conditions. The presence of Fe–Mn minerals and geological influences provided sources for As in groundwater. In contrast, reducing conditions were considered to be the main factor that influenced the study area, and high pH conditions caused environmental As to desorb and dissolve into the groundwater. The competitive adsorption of HCO_3^- with arsenate and arsenite also prompted the release of As into the aquifer.

Keywords: Factor analysis; Hierarchical cluster analysis; Dominating factor; Arsenic

1. Introduction

Arsenic (As) is a transition metal element which is poisonous, carcinogenic, and is ubiquitously distributed in the natural world [1,2]. Drinking high-arsenic water for extended periods can cause diseases such as skin cancer, bladder cancer, liver cancer, and lung cancer [3]. Varying degrees of poisoning due to exposure to As occur in more than 70 countries around the world, and high-As groundwater is an active concern of the international community [4]. In China, health of about 2.3 million people is at high risk by drinking high-As groundwater [5], including more serious problems in Inner Mongolia, Shanxi, Xinjiang, Ningxia, Jilin, and Anhui [6]. With the continuous development of the metallurgy, mining, coal-burning, and arsenic pesticides industries, larger quantities of As are being released into the environment through human activities, leading to As contamination that is highly concentrated in some local areas [7]. Therefore, investigation of the geochemical behaviors of As migration and transformation has become a research hotspot at the global scale.

Many studies have documented the distribution characteristics and enrichment mechanisms of high-As groundwater. For example, Postma et al. [8] reported that As enrichment was generated from the reduction and dissolution of As-containing minerals. Verma et al. [9] reported

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that As-enriched sediments were transported by rivers originating from the Himalayan Mountains and deposited in the downstream basins and delta areas. Wang et al. [10] believed that As-containing minerals are constantly enriched in plain or basin areas, controlled by tectonic movements and deposition, and are regarded as an important source of As in groundwater. Microorganisms undergo metabolic activities with organics buried in sediments, reducing Fe^{3+} to Fe^{2+} and consuming oxygen combined with arsenic iron hydroxide, which leads to the release of As. The behavior of As is controlled by many different factors such as redox conditions, pH, and the presence of organic matter and microbial activities. Although these results can generally explain the distribution and source analysis of As in groundwater, they still have some limitations regarding distribution characteristics of high-As groundwater, enrichment mechanism, and spatial evolution characteristics of groundwater chemistry at specific watersheds.

Factor analysis (FA) and hierarchical cluster analysis (HCA) were used to investigate factors controlling groundwater geochemistry based on a large amount of groundwater chemical data [11–15]. A factorial regression analysis (FRA) model was established by FA and HCA methods, which deepened the understanding of how land use, aquifer lithology, water depth, and other internal factors affected high-As groundwater [16]. Lin [17] used FA and CA to examine the composition source and formation effect of the major components of groundwater hydrochemistry. Zhang et al. [18] studied the deposition conditions of high-As groundwater by FA in the reducing environment with neutral to weak alkaline pH, and reported that microbial action caused the reduction and dissolution of As-containing ferromanganese oxide driven by organic matter. Lu et al. [19] used clustering and FA to sort and extract the hydrochemical data of high-As groundwater in the As poisoning ward, Hangjinhou Banner, Inner Mongolia. FA and HCA not only make full use of the information but also do not particularly rely on individual indicators and exclude inappropriate indicators to scientifically improve the objectivity of the evaluation results.

According to results from investigations of groundwater quality and pollution during 2003–2018 by the groundwater Research Group at Xinjiang Agricultural University, and synthesis of recent literature, the high-As groundwater in Xinjiang is mainly distributed in the fine-soil plains of the Kuitun River Basin [20]. This area is located at the southern edge of the Junggar Basin in Xinjiang (44°40′–45°05′N and 84°15′–84°50′W). The high-As groundwater in this area is protogenetic; and that from the Quaternary strata of the plain has a huge area of high As content (with a maximum value of 887 μg L^{-1}) in groundwater; therefore, it is both unique and representative of the region [21]. After more than 20 y of disease prevention and water reform policies instituted by the government, the drinking water quality in the high-As groundwater area of Xinjiang has been significantly improved. However, As can still get into crops through irrigation and leaching, posing serious threat to human health [22]. In this study, factor analysis (FA) and hierarchical cluster analysis (HCA) were used to investigate the contribution rate of groundwater hydrochemical component content to groundwater As content in Kuitun area. Combined with the hydrogeological characteristics of the study area, the causes of high As concentration in groundwater and the hydrogeological process were comprehensively analyzed. Therefore, exploration of factors that cause enrichment of high-As groundwater and to search for high-quality water sources are highly desirable. The main objectives of this study are as follows: (1) to ascertain geochemical characteristics of high-As groundwater in Kuitun River Basin and (2) to identify the main controlling factors of high-As groundwater in the study area.

2. Study area

2.1. Location and climate

The Kuitun River Basin is located in the southwestern Junggar Basin, with the Tianshan Mountains to the south, Gurban Tungut Desert to the north, and a terrain stepping down from south to north (Fig. 1). In the southern mountainous area, the lithology of formation is mainly cobble and sandy gravel, and the phreatic water is abundant at depths of over 100 m with a water type of HCO_3–Ca–Na. With the groundwater flowing to the north, the lithology of formation changes to that of an aquifer with a multilayered structure (a phreatic aquifer on the top and a multilayer confined aquifer on the bottom), in which the thickness of the phreatic aquifer is about 26 m, while that of the confined aquifer is 38 m. A plain that narrows to the west between the Southern and Northern Mountainous areas divides the area into a pre-mountain alluvial–proluvial plain, alluvial plain, aeolian plain, and alluvial–lacustrine plain by genesis, with many small streams developed through the pre-mountain alluvial–proluvial plain such as the Kuitun river, Sikeshu River, Guertu River, and Tewule river [23]. The area is a northern temperate arid climate zone with less precipitation and the large temperature difference between day and night, with dry air, large evaporation, and hot summer and cold winter. The average annual temperature is about 7°C, with the highest temperature of 40.3°C and the lowest temperature of –32.3°C. The average annual evaporation ranges from 1,710–1,930 mm [24], which is 10–12.9 times of the precipitation. The plain area mainly has northwest and southwest winds throughout the year, with an average wind speed of 2.4 ms^{-1}.

2.2. Geological and hydrological conditions

Since ancient times, the Kuitun River Basin has undergone many tectonic movements, forming the east–west tectonic system of Tianshan Mountain, the Beishan multi-type system, and the north–west tectonic system. During the Quaternary, the neotectonic movement was still strong, the ascending movement enhanced the erosion of the river to form deep valleys, and terraces with different heights and under different times were formed on both sides of the valley. Influenced by the nasal uplift of Chexi, the coarse particles and strong groundwater runoff are the main recharge runoff areas of groundwater, which mainly accept snowmelt (lateral recharge of groundwater flow), vertical rainfall, and agricultural irrigation water (canal system water, field irrigation, reservoir water) infiltration recharge. Owing to the flat and low-lying terrain, the phreatic position is shallow, and the evaporation becomes the main reason to be considered for drainage [22]. The basin includes two parts: piedmont

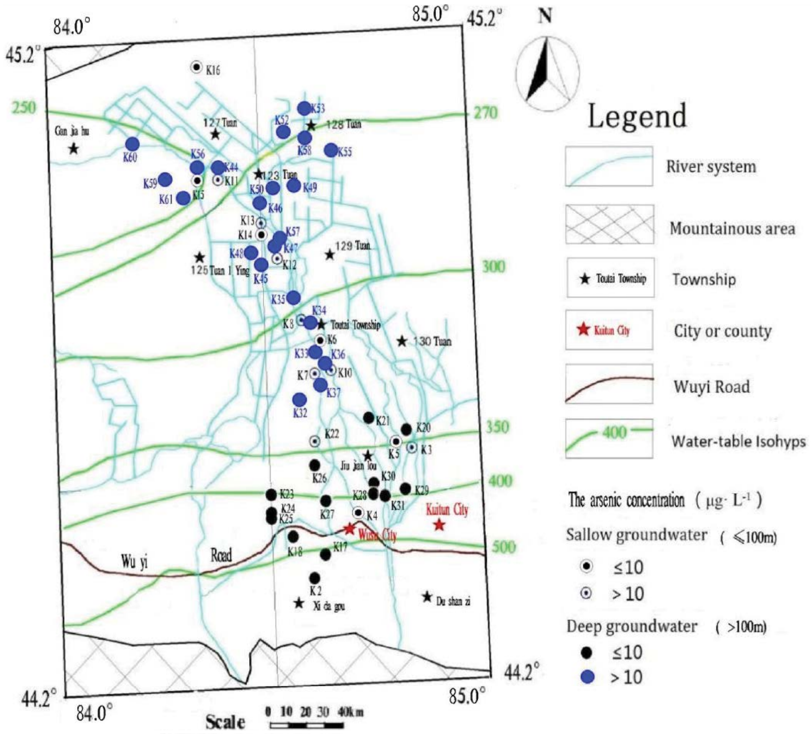

Fig. 1. Locations of study area and sampling sites.

alluvial gravel inclined plain and alluvial lake plain. The former is a singular phreatic aquifer, and is dominated by pebble gravel and sandy pebble gravel in a lithological composition and is highly permeable. The latter has a groundwater burial depth of 60–75 m near the Wuyi Road. Below the groundwater spilling belt of downtown Kuitun, aquifer number gradually increases, and the sediment between the aquifers consists of pebbly loam. There is also a gradual transition to multi-layered phreatic-confined aquifers [25].

3. Materials and methods

3.1. Sample collection and analysis

Through systematic investigation of the underground wells in the study area, representative well water samples were collected. In August 2016, 50 groups of groundwater samples were collected from depths ranging from 18 m to 500 m, as shown in Fig. 1. Field tests were conducted on pH, water temperature, redox potential (Eh), and electrical conductivity (EC). Pumps were run for 10 min prior to groundwater sampling in order to obtain fresh groundwater. Then, the samples were collected in 550 mL polyethylene bottles after first being rinsed three times with the water sample. After filtration through a 0.45 μm membrane [26], the water samples were sealed, stored under low temperature, and sent for testing. All these water samples were entrusted to the Laboratory of Xinjiang Uygur Autonomous Region No. 2, Hydrogeology Group for testing. Plasma emission spectrometer (iCAP6300) was used as the main detection instrument. Na^+ and K^+ ions were determined by flame atomic absorption spectrophotometry; Ca^{2+}, Mg^{2+}, and HCO_3^- were determined by natridium tetradiamide method; Cl- using silver nitrate; SO_4^{2-} by barium sulfate turbidity method, and total dissolved solids (TDS) by weight method. Charge balance error (CBE) was calculated to ensure the accuracy and reliability of groundwater chemical analysis [27,28]. Results for all samples recorded CBE < 5%, indicating results from all analyses were accurate and reliable. The collection, preservation, and inspection of water samples were performed in strict accordance with the 'Technical specifications for groundwater environmental monitoring of China (HL/T164-2004) (Ministry of Ecology and Environmental of China, 2004) [29].

3.2. Research methodology

FA is a statistical method for dealing with dimensionality reduction in a multivariate analysis. It simplifies complex data by decreasing the dimensions without losing important information, rearranging the original parameters to be some new uncorrelated comprehensive components (or factors) [30]. Every new factor is a linear combination of the original variants and is independent, which ensures the accuracy of the description of the data characteristics [31]. Then, the Varimax rotation method is used to rotate the calculated factors to strengthen the variable loadings of closely related variables in each factor. Each component describes the statistical variance of the data being analyzed and is interpreted in terms of correlated variables. The variable loadings are defined by the orthogonal projection of the variable on each factor. Factor selection is based on the significance of the factor (eigenvalue > 1) and the cumulative percentage of the variance of the interpreted data. The final step explains the correlation between each of the factors related to the question being studied. In this study, 13 physical and chemical parameters (As(total), As(III), Eh, pH, EC, F^-, chemical oxygen demand (COD), HCO_3^-, Fe, Mn, NH_4^+–N, SO_4^{2-}, and PO_4^{3-}) of 50 groundwater samples were quantitatively analyzed. After analysis of each physical and chemical parameter, the contribution of each parameter was calculated and the main components were extracted, and then the scores of factors were obtained after rotation. The scores of factors can reflect the relationship between samples and their hydrochemical components, reveal the degree of influence of each chemical component to the samples, or show the similarity of each sample. To comprehensively analyze the influence of each factor on samples and quantify the similarity among samples, the factor scores from each monitoring well were used as the variants in the HCA method and grouped accordingly [32]. Cluster analysis groups data step by step according to the degree of similarity between the observed objects to achieve the purpose of "object clustering", in which the hierarchical cluster analysis (hierarchical cluster analysis, HCA) method is the most widely used method [33]. HCA uses the variance method to define the distance between variable clusters, trying to minimize the sum of squares of any two clusters that may be formed in each step. Then, samples with similar factor scores are grouped. The distribution of groundwater As in Kuitun River Basin was investigated using FA results and its influencing factors were evaluated. The geochemical process of controlling groundwater As occurrence and migration was expounded.

4. Results

4.1. Chemical characteristics of high-arsenic groundwater

According to the analysis of the main chemical groundwater indicators in the Kuitun River Basin (Table 1), the average concentration of total As in the samples was 57.83 $\mu g \cdot L^{-1}$, with a maximum value of 887 $\mu g \cdot L^{-1}$, which far exceeds the World Health Organization Standards for As in drinking water (>10 $\mu g \cdot L^{-1}$). The pH ranged from 7.4 to 9.5, with an average value of 8.16, indicating that the groundwater in the study area was slightly alkaline on the whole; and the average value of Eh was 7.88 mV, indicating a strong reducing environment. The TDS values in the study area were within the range of 114.48–5,211.01 $mg \cdot L^{-1}$, with an average value of 900.47 $mg \cdot L^{-1}$. The maximum value of As(III) was 108.7 $\mu g \cdot L^{-1}$, indicating strong toxicity in this region. The F^- content was high in groundwater, with a range of 0.48–6.1 $mg \cdot L^{-1}$ and an average value of 1.19 $mg \cdot L^{-1}$, which exceeded drinking water standards in China (1 $mg \cdot L^{-1}$). The content of Fe was low, with an average of 80.3 $\mu g \cdot L^{-1}$ and a maximum value of 960 $\mu g \cdot L^{-1}$; and Mn ranged from 50 to 1,719 $\mu g \cdot L^{-1}$. PO_4^{3-} and NH_4^+–N were detected in the high-As groundwater, with average values of 0.17 and 0.39 $mg \cdot L^{-1}$ and maximum values of 0.46 and 1.41 $mg \cdot L^{-1}$, respectively, indicating little anthropogenic influence on groundwater in the study area. In addition to As content, physical and chemical parameters such as Eh, COD, HCO_3^-, SO_4^{2-}, Fe, and NH_4^+–N related to the redox environment also showed significant changes. Fig. 2 shows the scatter diagram of As (total) and these physical and chemical parameters. The correlation between As and Eh was not significant (Fig. 2a), and in alkaline environment, positively charged mineral surface (minerals containing As) was replaced by surface negatively charged colloidal and clay mineral bands, causing de-adsorption of As and resulting in increased As concentration in groundwater. The stronger the reducing activity of the groundwater environment, the higher the As concentration accordingly. The reduced environment was found to be conducive to As release. Moreover, the correlation between arsenic and COD, HCO_3^-, Fe, NH_4^+–N, and SO_4^{2-} was, respectively, not significant (Fig. 2b–f), the concentration of Fe content in this region was low, and the correlation between Fe and As was not significant. It shows that the As concentration in groundwater in this study area was not

Table 1
Statistical analysis of contents of major components in groundwater

Index	Units	Mean	SD	Var.	Min.	Max.
As(total)	$\mu g \cdot L^{-1}$	57.83	135.74	18,426.46	5	887
As(III)	$\mu g \cdot L^{-1}$	28.01	25.38	643.95	2.42	108.7
Eh	mV	7.88	95.19	9,061.37	–216	194
pH	–	8.16	0.49	0.24	7.4	9.5
EC	$\mu S \cdot cm^{-1}$	1,070.22	1,390.03	1,932,178.07	110	6,350
TDS	$mg \cdot L^{-1}$	900.47	1,170.15	1,369,270.96	114.48	5,211.01
F^-	$mg \cdot L^{-1}$	1.19	1.08	1.17	0.48	6.41
COD	$mg \cdot L^{-1}$	1.96	1.38	1.897	0.58	9.47
HCO_3^-	$mg \cdot L^{-1}$	142.93	77.04	5,934.47	78.18	486.2
Fe	$\mu g \cdot L^{-1}$	80.30	159.03	25,290.21	15	960
Mn	$\mu g \cdot L^{-1}$	189.88	333.97	111,537.46	50	1,719
NH_4^+–N	$mg \cdot L^{-1}$	0.39	0.49	0.24	<0.04	1.41
SO_4^{2-}	$mg \cdot L^{-1}$	324.57	491.64	241,706.00	13.06	1,962.44
PO_4^{3-}	$mg \cdot L^{-1}$	0.17	0.13	0.018	<0.07	0.46

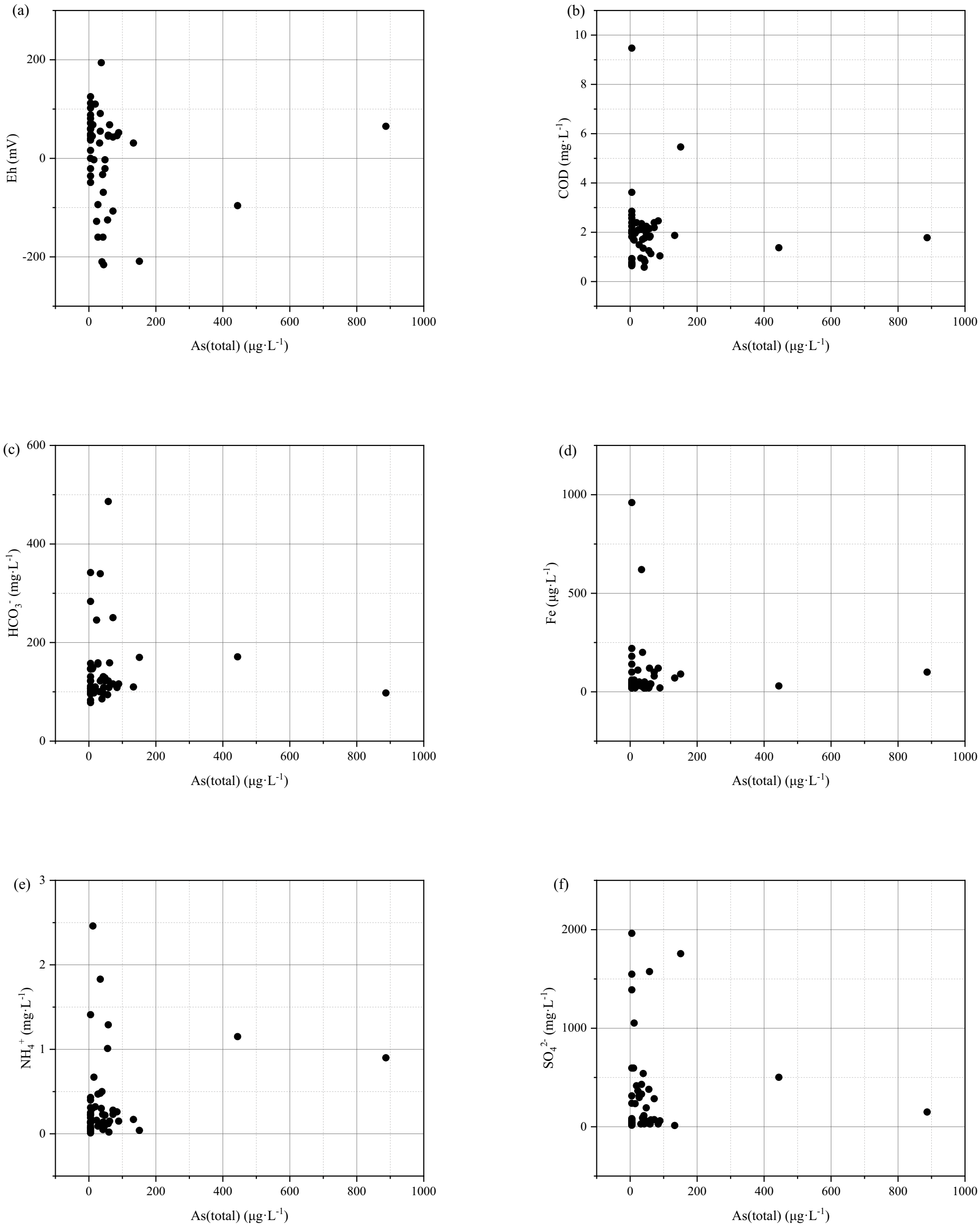

Fig. 2. Diagrams of (a) Eh-As, (b) COD-As, (c) HCO_3^--As, (d) Fe-As, (e) NH_4^+-As, and (f) SO_4^{2-}-As in the study area.

just affected by Fe oxide mineral reduction. The increase of As content in the groundwater in this region with reduced SO_4^{2-} concentration (Fig. 2f) indicates that the oxidation mechanism containing arsenic sulfide cannot provide a reasonable explanation for the formation of high-As water in the region. Therefore, As enrichment in groundwater in the region is not only largely related to pH and Fe–Mn oxide minerals, but also affected by SO_4^{2-} reduction and sulfide mineral precipitation. Figs. 3 and 4 demonstrate that the cations in the high-As groundwater samples in this area are relatively concentrated at the Na^+ end, and the anion distribution is relatively dispersed, mainly close to the HCO_3^- and SO_4^{2-} end, indicating that the high-As groundwater in this area is significantly affected by evaporation concentration and mineral weathering. It indicates that the As concentration in groundwater was not only related to the redox environment [34], but also affected by other factors such as hydrogeological conditions [35], cation exchange, human activity, and water–rock interactions [36].

4.2. *Factor analysis of arsenic influencing factors in groundwater*

In this study, SPSS 23.0 software was used to conduct FA on 14 different geochemical parameters, and the results are shown in Table 2 and Fig. 3.

Based on the correlations between different physical and chemical parameters of groundwater, the correlation between As (total), pH, and PO_4^{3-} was found to be significant. This was because the chemical structure and properties of phosphate and arsenate are similar, and they both

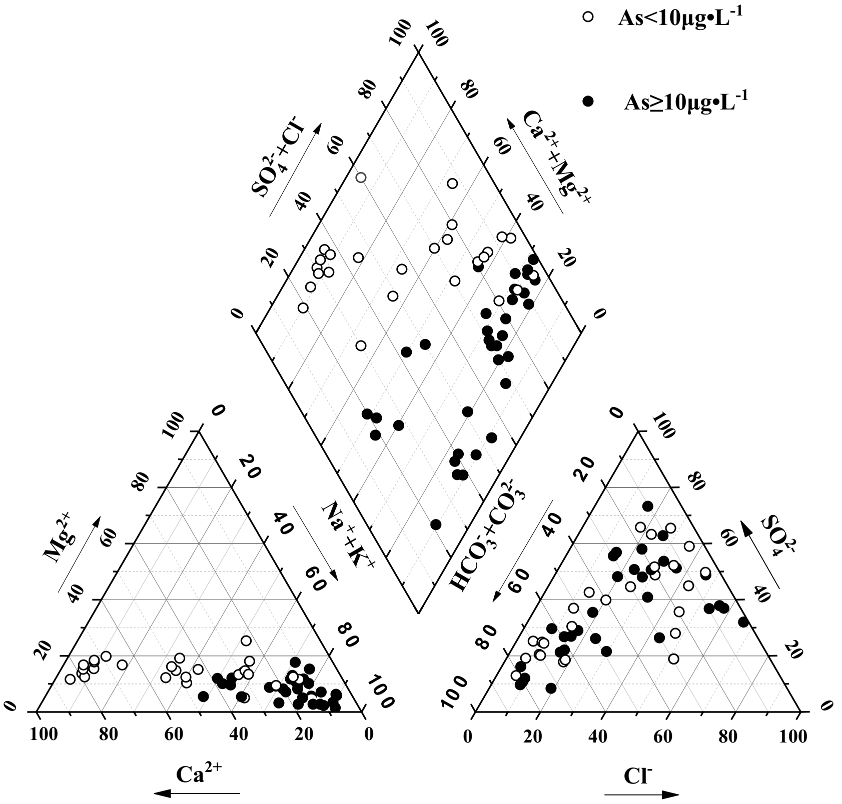

Fig. 3. Piper diagram of groundwater in study area.

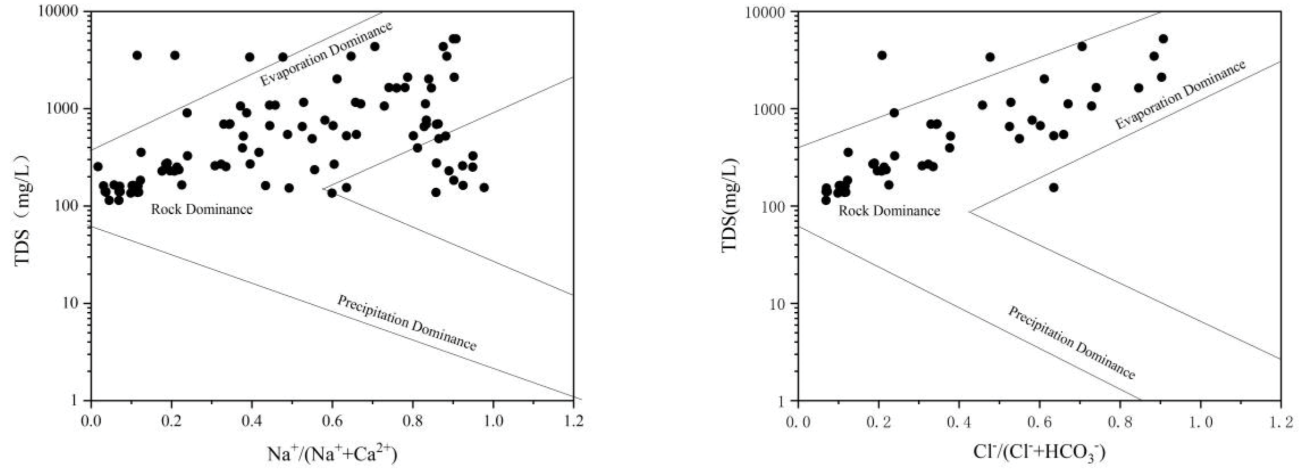

Fig. 4. Gibbs diagram in Kuitun River Basin.

have affinity toward iron oxide, resulting in the phosphate being strongly competitive with arsenate [37]. It indicates that the acid–base properties, reducing conditions, and competitive adsorption of ions showed a great influence on the migration of As in groundwater. The contents of EC and SO$_4^{2-}$, Mn, and HCO$_3^-$ also showed significant correlation with each other, which revealed that the dissolved ion was related to the reducing environment in groundwater. Taking eigenvalues of factors close to or over one as the principal component, five principal component factors (P1, P2, P3, P4, P5) were extracted that explained 25.467%, 19.267%, 16.481%, 14.637%, and 11.048% of the total variance, respectively, with the cumulative contribution rate reaching 86.9% (Table 2). It indicates that the five principal components encompassed 86.9% of the information from the 14 variables representing the chemical components in groundwater, ultimately reducing the amounts of variables needed. After proper rotation, the factor loading matrix of the principal components can be represented as shown in Fig. 5.

The first principal component was highly positively correlated with As, pH, F$^-$, NH$_4^+$, and PO$_4^{3-}$, accounting for 25.467% of the total variance. The pH could influence the

Table 2
Rotated factor loadings of principal components on variables

Component matrix after rotation					
Index	Composition				
	P1	P2	P3	P4	P5
As	0.966	0.195	−0.066	−0.021	0.078
As(III)	0.076	0.754	−0.407	−0.152	0.305
Eh	−0.073	−0.532	0.086	0.413	0.484
pH	0.637	−0.222	−0.311	−0.179	0.477
EC	−0.150	−0.103	0.969	−0.034	−0.084
TDS	−0.137	−0.088	0.975	0.004	−0.043
F^-	0.979	−0.055	0.025	−0.042	0.012
HCO_3^-	0.038	0.184	−0.052	0.889	−0.152
COD	−0.078	0.856	0.105	0.290	0.118
Fe	−0.111	−0.013	0.025	0.949	0.003
Mn	0.107	0.040	−0.122	−0.102	0.806
NH_4^+	0.680	−0.172	−00.183	0.117	−0.397
SO_4^{2-}	0.117	0.917	−0.116	0.089	−0.254
Percentage variance	25.467	19.267	16.481	14.637	11.048
Accumulate	25.467	44.735	61.215	75.852	86.900

Rotation method: maximum variance method of Caesar normalization.
Rotation converges after 5 iterations.

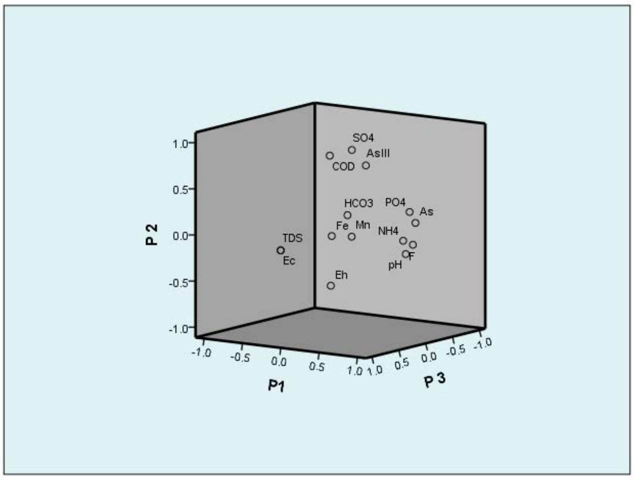

Fig. 5. The index load diagram of three main components.

absorption of arsenic acid and arsenious acid to colloid and clay minerals, leading to the release of As [40]. Presence of NH_4^+ in the northern basin groundwater indicates a strong reducing environment (Table 2). The second principal component was highly positively correlated with As(III), COD, and SO_4^{2-}, accounting for 19.267% of the total variance. Presence of As(III) indicates that the groundwater environment is in a reducing state. The large buried depth of groundwater, dissolved oxygen is continuously consumed in the process of runoff, eventually forming a reducing environment. The SO_4^{2-} could provide a supply for the desulphidation of groundwater [38], leading to low concentrations of Fe and Mn in groundwater. Moreover, 16.481% of the total variance can be explained by the third principal component, which is highly positively correlated with EC and TDS. The TDS indicates a strong concentration effect influenced by evaporation. The fourth principal component is positively correlated with HCO_3^- and Fe. Under slightly alkaline conditions, HCO_3^- could cause the competitive adsorption of As and its ion. With the S^{2-} generated from desulphidation, it is quite easy to precipitate iron sulfide with Fe^{2+}, which could decrease the Fe and Mn contents in groundwater [39]. The fifth principal component is positively correlated with Mn and Eh. This may be related to the effect of Mn-containing minerals on high-As groundwater. Notably, 86.9% of the total variance was explained using these factors; therefore, HCO_3^-, TDS, SO_4^{2-}, pH, COD, and NH_4^+ could be thought of as representing the characteristic elements of As in groundwater in the Kuitun River Basin. The three-dimensional distribution diagrams of characteristic loading for the first, second, and third principal components are mainly drawn to contribute to understanding the relative importance of variates in each component. The figure illustrates that besides the COD being in the plane with coordinate axis of P3 and P2, other factors are all in the plane with coordinate axis of P1 and P2. This illustrates that the formation of a high-As environment in the study area was influenced by multiple factors, among which the influence of organic matter was more significant. This could be attributed to the influence of geological conditions such as the Xihu uplift, Dushanzi anticline, or Liushisihu nose-like uplift, or acceptance of the accumulation of organic matter such as fragments, mud, or coal-containing gypsum from the Tianshan Mountain mountainous area, which is the main source of As ions in water.

4.3. Cluster analysis of arsenic influencing factors in groundwater

Based on FA, HCA was carried out to quantify the similarity between samples. The centroid clustering method was used in the HCA, the spacing was calculated by using square Euclidean distance, the factor score obtained by the FA was used as the variable for statistical grouping [38], and finally all the cluster column diagrams were displayed in the horizontal direction. The output tree diagram reflecting the entire process of clustering is shown in Fig. 6, which can further determine the degree of difference between factors.

When the distance was over 10, samples could be divided into two clusters, with K14, K9, K47, and K52 as one cluster, and the remaining in the other. When the distance was between 5 and 10, 50 samples could be divided into four clusters, among which K14, K9, and K47 still constitute one cluster; K52 is by itself; K60, K13, K56, K36, and K16 are a third cluster; and the remaining samples are in the fourth cluster. When samples were classified into two clusters, the classification precision was not accurate enough, thus the latter classification method was adopted. K14, k9, k47 were recorded as category I; k52 as category II; K60, K13, k56, k36, k16 as category III; and other monitoring well samples as category IV.

The first category is mainly composed of monitoring wells in the upper and middle reaches of the study area. The

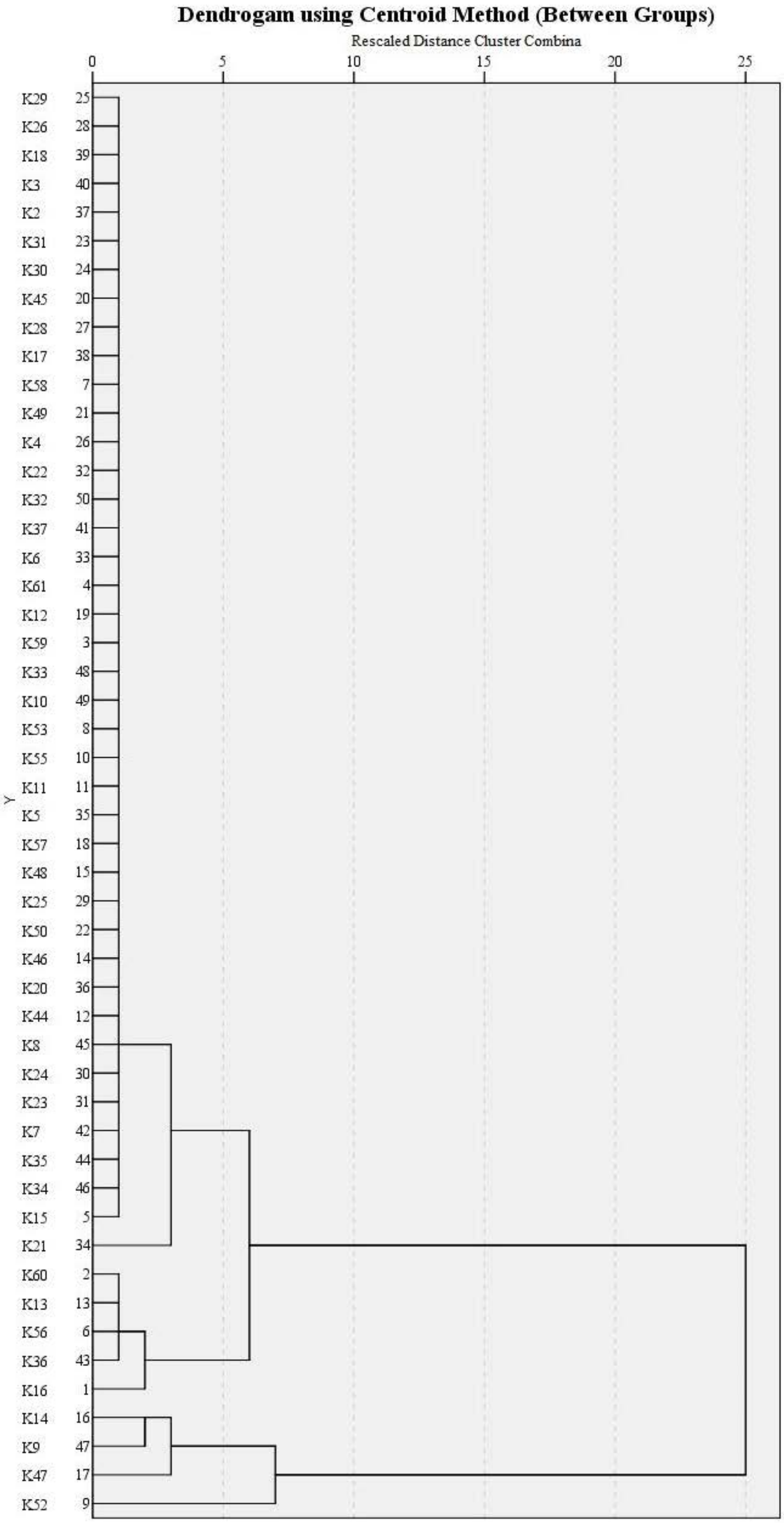

Fig. 6. Dendrogram for groundwater samples.

second and third categories are mostly located in the middle and lower reaches, and the fourth category mainly includes the wells in the lower reaches except for several wells with particularly high As concentration. In order to quantify the changes between clusters and summarize the characteristics of different cluster samples, the minimum, maximum, and mean values of physicochemical parameters were obtained as presented in Table 3. In the study area, the average concentration of As exceeded 10 μg·L^{-1} and increased successively in four classifications. The pH was between 7.4 and 9.5, and the average value of the fourth cluster was slightly higher than those of the other three clusters, indicating that with the increase in the pH, the activity of As increased. The reducing environment (Eh and SO$_4^{2-}$) of the second cluster was the strongest, while the third and fourth clusters were both in a low-oxidation environment.

A strong reducing environment provided conditions for the release of As into groundwater. The content of NH$_4^+$–N in the third cluster was higher than that in the first and second clusters, which might be related to human activities (irrigation and fertilization), although the influence was weak. Irrigation activity increases the reducibility near the surface and leads to an increase in deduction and dissolution of arsenic iron oxides, which leads to the release of As [41,42]. The contents of HCO$_3^-$, Fe, and Mn in the first cluster were higher than those in the other three clusters, which might be related to microbial activity. The microorganisms reduce Fe and Mn and release As, at the same time, they oxidize the organic matter in the aquifer and generate HCO$_3^-$, and might be related to the competitive absorption of As to the surface of iron and manganese oxides [43], which provides a material basis for the source of As in groundwater.

5. Discussion

5.1. Chemical factors affecting the presence of high-arsenic groundwater

The chemical composition of groundwater resulted from a long-term interaction between groundwater and its external environment. The chemical composition exhibited an influence on the cause of presence of As in groundwater. The results of FA and HCA indicate that the concentration of As was related to the redox parameters (Fig. 2 and Table 3). Research of the influence of reducing conditions indicates that the surface geology plays an important role in determining As concentration in groundwater.

Fig. 5 and Table 3 clearly present the dominant factors in different groups. The first group of samples was mainly concentrated in the middle and upper reaches. The concentration of NH$_4^+$ was high and the average value of Eh was negative, indicating a strong reducing environment. Compared with other groups, this group exhibited a higher concentration of HCO$_3^-$, which could compete with As for adsorption, releasing As into the groundwater. However, Fig. 2c shows that As is not significantly correlated with HCO$_3^-$. This might be related to microorganism activity. Although the microorganisms release As on the surface of iron ore in the reducing environment, organic matter in the aquifer is reduced to produce a large amount of HCO$_3^-$. The second group of samples showed the smallest Eh and the strongest reduction environment, and it was located at downstream. Under reducing conditions, Fe–Mn oxide minerals were reduced to form low-cost Fe^{2+} and Mn^{2+}. As the minerals dissolved and coexisted, As was also released into groundwater, resulting in As enrichment.

Table 3
Basic description of physicochemical parameters of groundwater in four clusters

Index	Units	I (*N* = 3)			II (*N* = 1)		
		Min.	Max.	Mean	Min.	Max.	Mean
As(total)	μg·L^{-1}	5	42	17.33	–	27.3	27.3
Eh	mV	–160	81	–33.33	–	–94	–94
pH		7.4	7.8	7.63	–	8.1	8.1
HCO$_3^-$	mg·L^{-1}	283.42	486.2	370.56	–	169.81	169.81
Fe	μg·L^{-1}	120	960	420	–	90	90
Mn	μg·L^{-1}	937	1719	1,250.33	–	433	433
NH$_4^+$–N	mg·L^{-1}	0.14	1.29	0.55	–	0.04	0.04
SO$_4^{2-}$	mg·L^{-1}	1,547.76	1,962.44	1,694.76	–	1,756.46	1,756.46
Index	Units	III (*N* = 5)			IV (*N* = 41)		
		Min.	Max.	Mean	Min.	Max.	Mean
As(total)	μg·L^{-1}	5	84.2	45.08	5	887	62.51
Eh	mV	–160	194	14.8	–216	125	6.55
pH		7.8	8.5	8.12	7.4	9.5	8.2
HCO$_3^-$	mg·L^{-1}	85.51	149.04	120.45	78.18	342.05	133.82
Fe	μg·L^{-1}	20	60	40	20	620	56.90
Mn	μg·L^{-1}	50	441	218.6	0.29	1,095	119.53
NH$_4^+$–N	mg·L^{-1}	0.25	2.46	0.77	0.01	1.83	0.35
SO$_4^{2-}$	mg·L^{-1}	416.47	1,389.29	798.63	13.06	1,962.44	175.86

Statistical results show that SO_4^{2-} showed the highest concentration in the second group (Table 3). This could provide a sufficient source of SO_4^{2-} for desulfurization of groundwater. S^{2-} generated by desulfurization could easily form iron sulfide precipitates with Fe^{2+}, which could reduce the concentrations of Fe and Mn in groundwater. Although the concentration of Fe and Mn was higher in the first group, the influence of reducing conditions was more apparent in the flat downstream region. The data in Table 3 also support this result, indicating the increase in the redox related factors (including As and pH) in this group. In the third and fourth groups, the average value of Eh increased, indicating that the reducibility decreased, while oxidizability was enhanced. The concentrations of Fe and Mn also decreased accordingly. It indicates that geological surface processes (dissolution of minerals) have an important effect on the concentration of As in groundwater.

5.2. Control of redox conditions in high-arsenic groundwater

Notably, As is a redox sensitive element and its migration and transformation in groundwater are controlled by redox reactions. The first group of samples was mainly distributed in the middle and upper reaches. This area is characterized with terrain with a high slope, coarse formation of particles, generally high groundwater flow, fast circulation, and a relatively high permeability and hydraulic gradient. A high hydraulic gradient and electrical conductivity lead to massive replenishment of atmospheric precipitation and surface water, leading to enrichment of dissolved oxygen. Under the effect of hypoxic factors, the Eh value was low in this area, and the NH_4^+ concentration was high (Table 3).

NO_3^- has a strong buffering effect on the redox potential; therefore, As gets adsorbed on Fe minerals in the reducing environment, so that the reductive dissolution of Fe oxides is significantly inhibited. As free oxygen in the flow path is consumed, NO_3^- becomes the first electron acceptor in microbial oxidation of organic matter, resulting in a decrease in NO_3^- concentration and an increase in NH_4^+ concentration. With the flow of groundwater, the particle size in the middle and lower reaches changes from coarse to fine, resulting in an increase in the groundwater residence time. In general, the Eh value decreases with the increase in the groundwater retention time in the aquifer. At higher NH_4^+ concentrations, the Eh values in the first and second groups were lower (Table 3). The samples in the first and second groups (Fig. 1) were affected by lithology and reducibility factors, resulting in the reductive dissolution of Fe and Mn oxides. However, SO_4^{2-} decreased in the third and fourth groups, which might be due to the decrease in the reduction state of SO_4^{2-} accompanied by the formation of H_2S in groundwater. The third group of samples was mainly distributed in the middle and lower reaches of the study area. As the groundwater flowed, the consumption of SO_4^{2-} decreased continuously, forming a reducing environment. With the enhancement of the reducing environment, the concentration of As increased, and the concentrations of HCO_3^-, Mn, and NH_4^+ were expected to increase accordingly. However, as presented in Table 3, concentrations of HCO_3^-, Mn, and NH_4^+ in the third and fourth groups did not increase with the increase in the As concentration. This indicates that the accumulation of As in the groundwater in this area was not only related to the redox conditions and reduction of iron and manganese oxide minerals, but also affected by the combined action of SO_4^{2-} reduction and HCO_3^- competitive adsorption.

5.3. Source analysis of arsenic in groundwater

Notably, As in groundwater can originate from both natural and human activities, and the release of As may get affected by human activities. The application of As-containing pesticides and irrigation using As-containing water might cause changes in the concentration of As in groundwater through leaching. Studies have shown that the concentration of As can be limited by introducing NO_3^- from the surface. However, the correlation between As and NH_4^+ was not significant (Fig. 2e) and the sampling points in this study area showed that high-As groundwater was mainly in deep aquifers (well depth greater than 80 m), thus less affected by human activities. Results from FA showed that the first principal component was highly positively correlated with the concentrations of HCO_3^-, Fe, Mn, and SO_4^{2-} (Table 2), indicating that the dominant factor controlling As concentration was geological lithology (iron and manganese minerals). Moreover, the results of the cluster analysis showed that the concentration of As in the fourth group was the highest and was the lowest in the first group. High As concentration corresponded to a strong reducing environment, and low As concentration corresponded to a high concentration of SO_4^{2-}, indicating that the migration of As in the study area was significantly affected by redox factors. The study area is rich in mineral resources, including coal, iron, copper, and gold. The coal seam contains a large amount of As. Hongli [44] and other researchers showed that the As content in these deposits is between 10% and 39%, and the As content in the surface oxidation zone is 2.4% to 4.5%. Moreover, the rocks, such as mudstone, shale, granite, and so on, are also rich in As element. The As content in mudstone and shale can reach 10 $mg{\cdot}kg^{-1}$, and the granite content is 1.5–2 $mg{\cdot}kg^{-1}$. Moreover, the distribution of siderite, calcium arsenate, ferromanganese ore, manganese arsenate, and other minerals in the surrounding mountains also provide a material source for As content exceeding the standard. Furthermore, the area has a dry climate, a long sunshine time, and a strong evaporation and concentration effect, which further lead to the increase in the concentration of As in the groundwater. Therefore, As in groundwater of this area mainly comes from nature.

5.4. groundwater safety issues

In the upper reaches of the Kuitun River Basin, the concentration of As in the ground was low. In the upper reaches, groundwater was mainly affected by surface water leakage and subsurface flow in mountain valleys, large gravel particles, strong oxidizability, and weak reduction. However, in the third group (the middle and lower reaches of the river), the concentration of NH_4^+ was relatively high. Moreover, the average concentrations of As in all the groups were more than the value indicated as safe in the World Health Organization Drinking Water Guidelines

(Table 2); therefore, the groundwater in this area is not suitable for drinking; however, this groundwater was used for agricultural irrigation. Studies have shown that As can be introduced into the food chain through high-As groundwater irrigation, which is one of the major routes of As exposure. Tong et al. [45] and Neidhardt et al. [46] found that irrigation carried out using high-As groundwater led to the increase of As concentrations in wheat, corn, and sunflower. These crops irrigated with high-As groundwater pose a potential threat to the health of local residents. Therefore, there is an urgent need to find an effective and economical method to predict the safety of groundwater.

6. Conclusions

Multivariate statistical methods (FA and HCA) indicated that the main factors controlling the concentrations of As and other physical and chemical parameters affecting groundwater composition include geological factors, reducing factors, and competitive ion adsorption factors. Among them, geological action is the dominant factor of high-arsenic groundwater, which provides the source of arsenic for high-arsenic groundwater and leads to the release of arsenic to groundwater under reduced conditions.

The relative importance under diverse conditions is different. According to HCA, among the four clusters, the influence of reducing factors was greater in cluster 1 and cluster 2. As the reducing environment caused the dissolution of Fe–Mn minerals, arsenic activity got enhanced and it was released to groundwater. In cluster 3, the influence of NH_4^+–N was greater. In the runoff process, as solutes migrated, oxygen consumption decreased until the reducing environment was formed that led to the desorption of As. In the fourth cluster, pH was the most important factor. Under weakly alkaline reducing conditions, As desorbed from the surface of hydrates and clay minerals such as iron and manganese oxides or hydroxide; and part of the iron and manganese oxides could be reduced to soluble iron and manganese with low valence states, allowing As to combine with it and be released into groundwater, thus leading to the increase in the mass concentration of As in groundwater.

Currently, statistical methods (FA and HCA) are applied in the field of hydrology. Models based on FA and HCA methods can improve the understanding of arsenic sources and enrichment by intrinsic factors such as land use patterns, aquifer lithology, and water depth, and explain the impact of topography and geomorphology on arsenic migration in aquifers. However, some limitations also exist, for example: (1) FA lacks a comprehensive consideration of the combined influence of multiple factors, and in case of limited samples, it is difficult to acquire an ideal result; (2) the enrichment of As in an aquifer is a long-term process, and the use of these two statistical methods could not accurately describe the interactions of the paleogeographic environment, surface water, and groundwater on As; (3) the migration and transformation of arsenic in aquifer is a very complex process that needs to be verified from the aspect of organic matter, in which two statistical methods could not be simply applied and organic matter such as microorganism plays a significant role. Reductive dissolution of iron ore is a prerequisite for As release, As may come from geological and climatic sources or from anthropogenic sources. Further studies can be used to evaluate geochemical processes that control the occurrence and migration of As groundwater, and may also be related to the driving effect of groundwater level, local specific recharge, discharge effects.

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