

Multivariate statistical analysis of water chemistry in evaluating groundwater geochemical evolution and aquifer connectivity near a large coal mine, Anhui, China

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Abstract Major ion chemistry of groundwater from main aquifers near the Dingji Coal Mine (Anhui, China) was analyzed with a suite of statistical techniques, in an effort to understand aquifer connectivity and groundwater geochemical evolution. Fifty-seven groundwater samples were analyzed from four aquifers: the Cenozoic top, middle, bottom aquifers and a Permian coal strata aquifer. With increasing depth of the aquifers, groundwater became more mineralized showing greater hardness and salinity. The dissolutions of halite and sylvite, carbonate, sulfate, and silicate minerals were the primary processes controlling groundwater chemical compositions in the Cenozoic bottom and coal strata aquifers, while ($K^+ + Na^+$) and HCO_3^- originating from silicate mineral weathering were more enriched in the coal strata aquifer. Principal component analysis (PCA) identified two principal components, with the first component representing hardness variation and accounting for 57.5 % of total variance, and the second component (23.5 % of total variance) controlled primarily by salinity and sulfate reduction process. The Cenozoic bottom aquifer had greater hardness than other aquifers whereas the coal strata aquifer was characterized by higher salinity and larger influences of sulfate reduction. Cluster analysis revealed that the coal strata aquifer was largely isolated from the Cenozoic aquifers with possible infiltration at discrete locations, indicating that the high-yield,

thick Cenozoic aquifers may serve as a potential additional source for groundwater inrush into coal mines.

Keywords Dingji coal mine · Groundwater · Hydrochemical characteristics · Major ions water hardness · Water salinity · Sulfate reduction · Principal components analysis · Cluster analysis

Introduction

Coal has been the main energy source in China fueling the rapidly growing economy in recent years. In many exploited coal mines, groundwater system is complex, consisting of a number of aquifers with varied geochemical characteristics (Ganyaglo et al. 2011; Grasby et al. 2000; Stotler et al. 2009). From the viewpoint of both groundwater resource conservation and mining safety, it is important to understand processes controlling geochemical variability of aquifers in mining areas. Mining activities can contaminate groundwater, and the nature and extent of contamination can vary with geochemical characteristics of aquifer systems (Murkute 2014; Singh et al. 2010). Furthermore, catastrophic influx of groundwater into coal mines has always been a critical safety issue, especially with increasing depth, intensity, and scale of coal mining (Qiao et al. 2011; Yang et al. 2007). Hydrochemical parameters can provide information about recharge and discharge sources of aquifers (Koonce et al. 2006; Sun and Gui 2015; Vanderzalm et al. 2011; Villegas et al. 2013; Wu et al. 2014), and hence allow evaluation of aquifer connectivity and the sources of groundwater inrush (Chen et al. 2012; Sun 2014; Sun and Gui 2012).

Previous investigations assessing groundwater parameters range from simple comparison and contrasting of water

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chemistry variables to the application of multivariate statistical methods (Cloutier et al. 2008; Matiatos et al. 2014; Vasanthavigar et al. 2010). Principal component analysis (PCA) reduces an original set of variables into a smaller number of uncorrelated components without losing much information (Jolliffe 2002; Kim et al. 2005; Meglen 1992), and cluster analysis can measure the similarities among samples (Bu et al. 2010; Reghunath et al. 2002). Combining a suite of statistical techniques to analyze hydrochemical parameters has been shown useful in classifying groundwater of varied geochemical features and hence identifying primary processes regulating geochemical evolution and assessing hydraulic connectivity among aquifers (Fu et al. 2014; Huang et al. 2013; Usunoff and Guzmán-Guzmán 1989; Zumlot et al. 2013).

In the present study, we assessed hydrogeochemical variation among the four main aquifers in a coal mining area in Anhui, eastern China, using correlation analysis, PCA, and cluster analysis. Groundwater samples were collected in the vicinity of the Dingji Coal Mine, an underground mine with an area of ca. 100 km². This mine is part of PanXie coal mine area, which is one of the two main mining bases in the Huainan coalfields that have ca. 50 % of coal reserves in eastern China as one of the nation's five largest coal mines (Chen et al. 2014). The coalfields are near two cities (Huainan and Fuyang) where groundwater is an important source of water supply for local residents. However, geochemical characteristics of adjacent aquifers have not been well understood (Gui and Chen 2007; Lu et al. 2012; Sun 2014), hindering a reliable assessment of groundwater vulnerability to coal mining as well as the risk of groundwater inrush in coal mines. The present study aimed to fill this knowledge gap by establishing better understanding of water sources, geochemical evolution, and hydraulic connectivity among the aquifers in the study region.

Study site

The Dingji Coal Mine is located in the northwest of Huainan city, Anhui Province, China, under the alluvial plain of the middle Huaihe River (see Fig. 1a). The study area is influenced by semi-humid climate with evident seasonal monsoon patterns. From 1951 to 2013, the mean annual temperature is 15.1 °C, and the annual rainfall averages 926 mm, ranging from 472 mm (1966) to 1724 mm (1954). Precipitation is concentrated from June to August, accounting for around 40 % of annual precipitation.

In the Dingji Coal Mine, the minefield has more than 20 coal-bearing layers, and most are distributed in Permian strata, which are overlaid by Cenozoic strata. The main minable, stable coal seams consist of six layers with an average thickness of 16.1 m, and from bottom to top, they

are numbered as 4-1, 4-2, 5-1, 8, 11-2, 13-1 (Fig. 1b). The formation strike of the mine has an overall east-titled monoclinic structure from north to south, with dip angles between 5° and 15° (Fig. 1b). Main faults include F27, F9, F40, F47, F66, F83, F84, and F87, and secondary folds and faults are unevenly developed (Fig. 1). Main aquifers in the study area include, from top to bottom, the Cenozoic loose sandy aquifer group, the Permian coal strata fractured sandstone aquifer (Permian fractured aquifer for short), the Carboniferous Taiyuan Formation fractured and karstified limestone aquifer, and the Ordovician fractured and karstified limestone aquifer. Present mining activities have been exploiting largely top coal seams (i.e., 13-1 and 11-2 in Fig. 1b) and are expected to have little influence on the Taiyuan limestone aquifer and Ordovician limestone aquifer below the Permian strata. Therefore, the present study focuses on the Cenozoic aquifer group and the Permian fractured aquifer.

The Cenozoic loose sandy aquifer group is a thick unconsolidated unit with thickness ranging between 326 and 573 m. The unit comprises mainly Tertiary to Quaternary sand and gravel layers composed primarily of clay minerals. This thick aquifer group is characterized by high porosity and includes the Cenozoic top aquifer, the Cenozoic middle aquifer, and the Cenozoic bottom aquifer. The top aquifer is the primary water source to local residents. The bottom aquifer is a confined aquifer with the bottom aquiclude composed of clay and siltstone, and has an unstable top aquiclude possibly allowing discrete connections to the top aquifer. The middle and bottom aquifers are considered not connected hydraulically because of a thick and stable aquiclude between the two aquifers (Liu 1997).

The Permian fractured aquifer is ca. 1000 m in thickness and composed mainly of medium- and fine-grained sandstone that consists primarily of quartz and feldspar with the presence of pyrite nodules. In minable seams and mudstone, fractures are prevalent and a number of unevenly developed apertures usually with calcium filling are observed. Fissure water in sandstones between coal seams is a potential source for coal mine inrush. The bottom aquiclude is 25–32 m and averages 30 m in thickness. It comprises mainly mudstone and siltstone with the local presence of fine sandstone. Because of this aquiclude, the Permian fractured aquifer is usually not hydraulically connected to the underlying Taiyuan limestone aquifer.

Materials and methods

Sampling

Sample collection, preservation, and analysis followed procedures outlined in the groundwater collection and

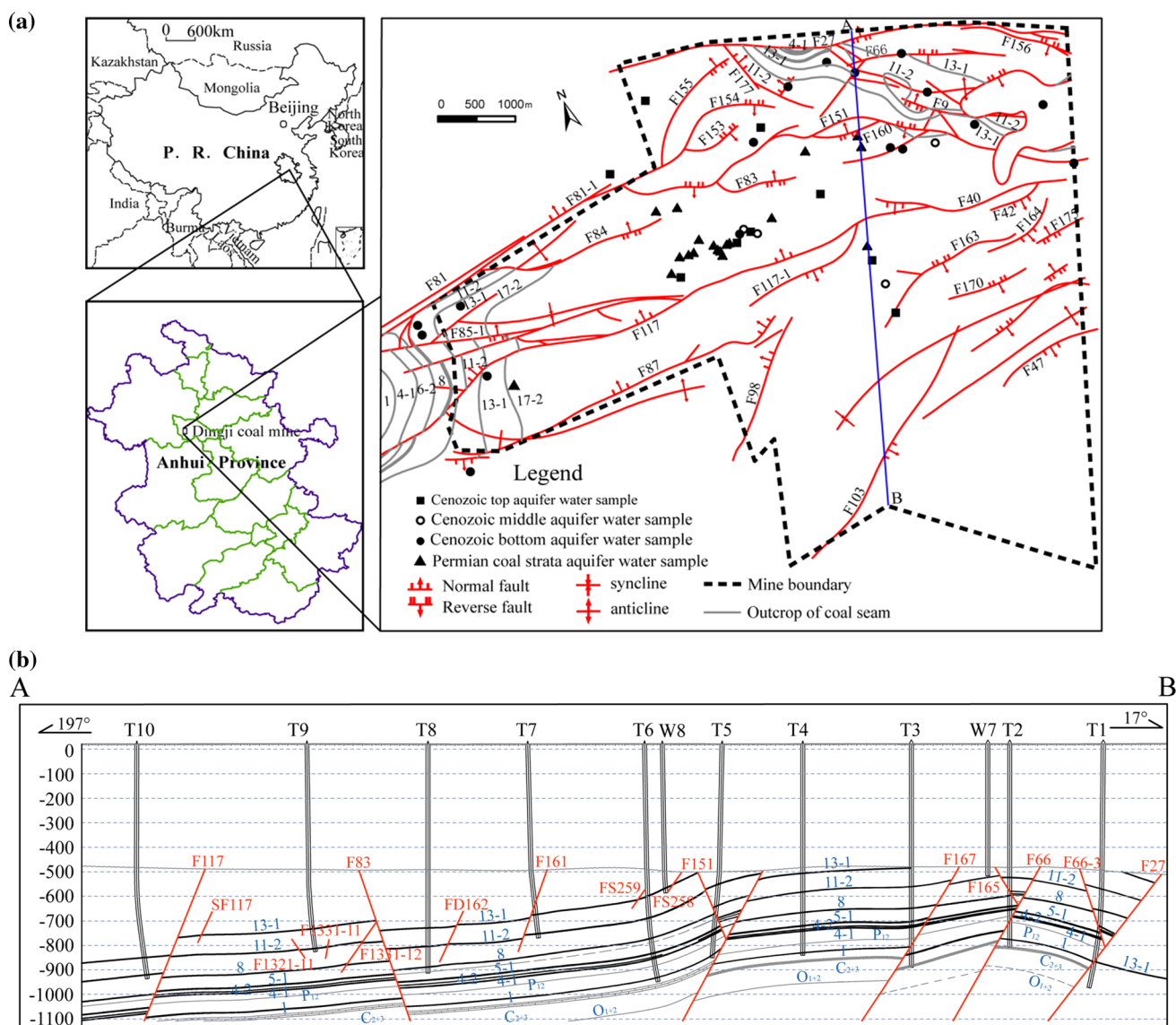


Fig. 1 **a** Map showing the location of the study area, with the distribution of faults, folds, and sampling sites within the Dingji coal mine; **b** Cross section of the Dingji coal mine along line A-B; T and W represent hydrogeological drill holes and observation wells, respectively

analysis manual published by the Ministry of Land and Resources of China (1993). A total of 57 groundwater samples were collected using hydrogeological boreholes or through underground water inrush, with 14 samples from the Cenozoic top aquifer, four samples from the Cenozoic middle aquifer, 17 samples from the Cenozoic bottom aquifer, and 22 samples from the Permian fractured aquifer (sampled mainly in coal strata 13-1 and 11-2, Fig. 1). Cenozoic samples were collected during the stage of mining exploration, while the Permian fractured aquifer samples were collected during periods of active coal mining. All samples were collected into acid-cleaned 500 ml polyethylene bottles and stored at 4 °C prior to laboratory analysis.

Cation and anion analysis

Samples were analyzed at the Water Quality Testing Center, Huainan Mining Industry (Group) Co., Ltd, Huainan, China for major ion concentrations within 24 h of collection. Concentrations of cations including calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), and potassium (K^{+}) were measured using an inductively coupled plasma atomic emission spectrometer (ICPS-1000 III C). Chloride (Cl^{-}) and sulfate (SO_4^{2-}) were measured using an ion chromatography (LC-10A), whereas bicarbonate (HCO_3^{-}) was analyzed through the titration method (Rowell 2014). Relative standard deviation of replicate measurements of all ions was within 5 %.

Statistical analysis

Statistical analysis was conducted using SPSS 18.0. The significance level (α) was set at 0.05. Pearson correlation was used to evaluate correlations between different variables. PCA was performed to identify main factors governing groundwater geochemistry, and the parameters included in PCA were $\text{Na}^+ + \text{K}^+$, Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- . Data normality was evaluated using Kolmogorov–Smirnov (K–S) test before the PCA analysis, and non-normally distributed data ($\text{K}^+ + \text{Na}^+$ in our data) were logarithmically transformed. Kaiser-Meyer-Olkin (KMO) test (>0.5) was conducted to evaluate sampling adequacy that indicates the proportion of common variance (Shrestha and Kazama 2007), and Bartlett's test of sphericity ($p < 0.05$) was performed to evaluate inter-correlation and extreme multicollinearity. Varimax rotation method was applied for maximizing the differences between the extracted components to provide ease for geochemical interpretations, and components with eigenvalue >1 were selected. Cluster analysis (Hierarchical agglomerative, HCA) was performed in the Q mode on the normalized dataset, following the Ward's method and measuring samples' similarity by Euclidean distances.

Results and discussion

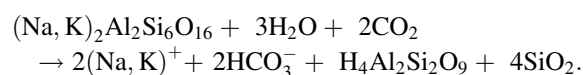
General hydrochemical characteristics

The groundwater samples were all slightly alkaline, showing a mean pH value >8 (Table 1). Relative to other aquifers, the Cenozoic top aquifer has a lower mean concentration of total ions (Table 1), which indicates lower levels of mineralization that can be attributed to dilution from precipitation and surface water due to the shallow burial depth (around 101–129 m). According to the Piper diagram (Fig. 2), the main chemical type of the top aquifer was $\text{Na} + \text{K} - \text{Ca} - \text{Mg} - \text{HCO}_3$. The Cenozoic middle and bottom aquifers showed similar main ion characteristics, and both were of $\text{Na} + \text{K} - \text{Cl}$ chemical type, while the bottom aquifer exhibited higher concentrations of Ca^{2+} , Mg^{2+} , and SO_4^{2-} . Samples from the coal strata aquifer were mostly $\text{Na} + \text{K} - \text{HCO}_3$ type, and relative to the three Cenozoic aquifers, they showed much higher mean values for $\text{Na}^+ + \text{K}^+$ and HCO_3^- but lower values for Ca^{2+} , Mg^{2+} , and SO_4^{2-} (Table 1).

Sources of major ions

High concentration of sodium in groundwater is often associated with evaporite and silicate mineral weathering (Xu et al. 2010). Furthermore, the $\text{Na} - \text{Cl}$ relation can provide

information about the sources of Na^+ (Sami 1992). In our samples, we observed a general positive correlation between Cl^- vs. $\text{K}^+ + \text{Na}^+$ (Table 2; Fig. 3). In the Cenozoic aquifers, most samples plotted relatively near the 1:1 line, and $\text{Na}^+ + \text{K}^+$ showed positive correlations with SO_4^{2-} ($r = 0.553$, $p < 0.01$; Table 2), suggesting the dissolution of evaporate minerals such as halite, sylvite, and marabillite was the primary source of Na^+ and K^+ . By comparison, samples from the coal strata aquifer deviated more from the 1:1 line, showed higher concentrations of $\text{Na}^+ + \text{K}^+$ and HCO_3^- than the Cenozoic aquifers, and displayed a strong, positive correlation between $\text{Na}^+ + \text{K}^+$ vs. HCO_3^- ($r = 0.975$, $p < 0.01$; Table 2). These observations suggest that the weathering of potassium and sodium feldspar in sandstones may serve as another source of Na^+ and K^+ in the coal strata aquifer:



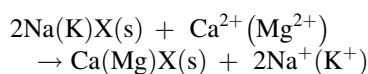
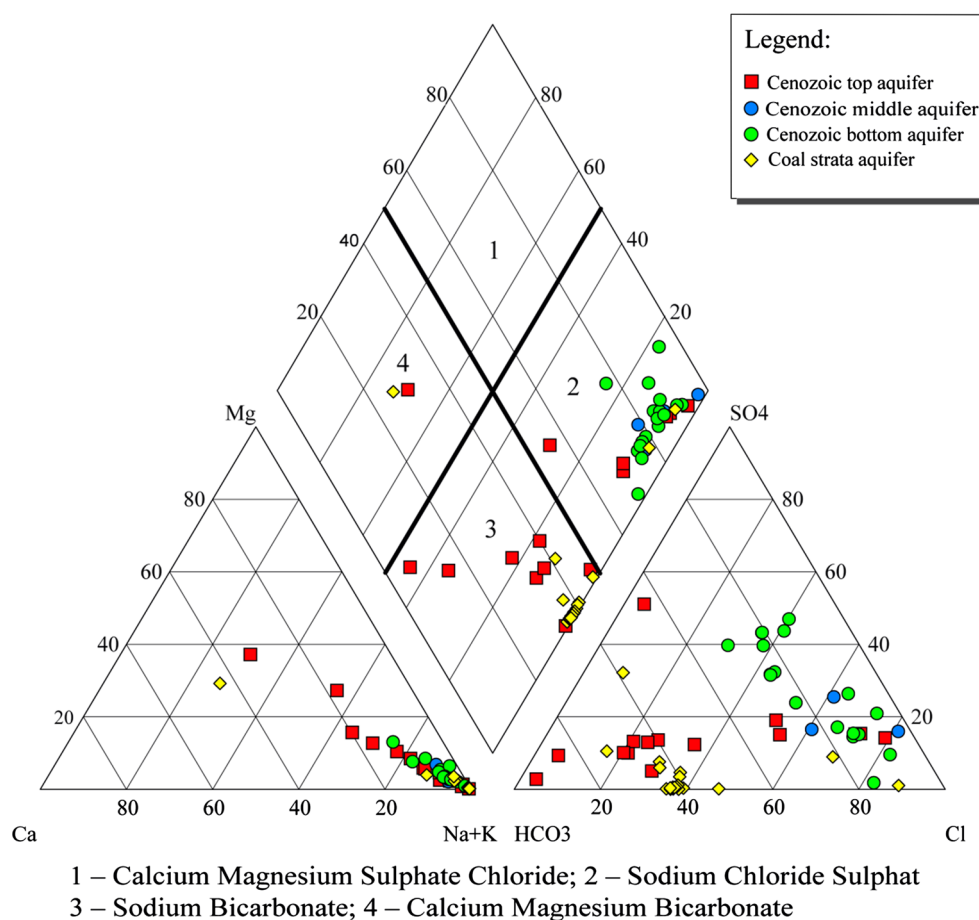
This process also yielded HCO_3^- , but it was not the only source of HCO_3^- on the basis that the values of HCO_3^- were higher than $\text{Na}^+ + \text{K}^+$ (Table 1). Carbonate mineral weathering also did not appear to be a significant source of HCO_3^- , based on the fact that the concentrations of Ca^{2+} and Mg^{2+} were low (Table 1) and that the correlations between Ca^{2+} vs. HCO_3^- ($r = -0.339$, $p > 0.05$) and Mg^{2+} vs. HCO_3^- ($r = -0.443$, $p > 0.05$) were weak (Table 2). Instead, sulfate reduction could be an additional source of HCO_3^- , as evidenced by much lower sulfate concentrations in the coal strata aquifer than in the Cenozoic aquifers.

In our samples, the concentrations of Ca^{2+} and Mg^{2+} were positively correlated ($r = 0.865$, $p < 0.01$), indicating that the two ions were derived from the same source. The molar ratio of $[(\text{Ca}^{2+}) + (\text{Mg}^{2+})]$ to (HCO_3^-) is 0.5 when carbonate mineral dissolution is the only source for Ca^{2+} and Mg^{2+} (Chang and Wang 2010; Spears 1986). All samples from the Cenozoic groundwater showed ratios lower than 0.5 (ranging from 0.004 to 0.304) except for an outlier value of 0.15. Meanwhile, the values of the coal strata groundwater were mostly near zero, ranging from 0.002 to 0.081 and averaging 0.027. Both Ca^{2+} and Mg^{2+} were not significantly correlated with SO_4^{2-} in Cenozoic samples (Ca^{2+} vs. SO_4^{2-} : $r = 0.116$, $p > 0.05$; Mg^{2+} vs. SO_4^{2-} : $r = 0.282$, $p > 0.05$; Table 2), whereas coal strata samples showed moderate correlations (Ca^{2+} vs. SO_4^{2-} : $r = 0.466$, $p < 0.01$; Mg^{2+} vs. SO_4^{2-} : $r = 0.559$, $p < 0.01$; Table 2). This pattern demonstrates gypsum and epsomite dissolution occurred only in coal strata groundwater. Additional processes, however, were responsible for Ca^{2+} and Mg^{2+} variability in all aquifers. Given the similar source of Ca^{2+} and Mg^{2+} and an enrichment of Na^+/K^+ over Cl^- , cation exchange as follows could be responsible for low Ca^{2+} and Mg^{2+} contents in our samples:

Table 1 Summary statistics of hydrochemical parameters

Parameters	Cenozoic top aquifer (n = 14)			Cenozoic middle aquifer (n = 4)			Cenozoic bottom aquifer (n = 17)			Coal strata aquifer (n = 22)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Ca ²⁺	12.02	55.44	29.11	7.41	23.9	17.77	8.18	71.71	33.98	0.46	33.27	8.85
Mg ²⁺	3.16	38.31	15.48	3.77	19.85	10.78	4.96	33.88	20.15	0.34	15.55	3.7
K ⁺ + Na ⁺	58.88	1236	439.73	484.61	864.88	641.91	244.03	1098.29	865.81	23.26	2122.5	1336.94
HCO ₃ ⁻	131.8	1513.3	501.62	64.68	344.76	222.88	118.84	648.4	379.27	5.55	3295.08	2084.91
Cl ⁻	13.55	1051.8	336.96	279.89	1053.3	639.83	150.4	1065.67	764.77	4.89	1084.42	734.95
SO ₄ ²⁻	13.99	374.63	148.2	197.57	486.29	330.77	29.96	1060.7	477.47	0.45	214.65	59.32
pH	7.6	8.96	8.13	8	8.44	8.22	7.56	10.5	8.35	7.79	9.23	8.46

All units are in mg/L except for pH

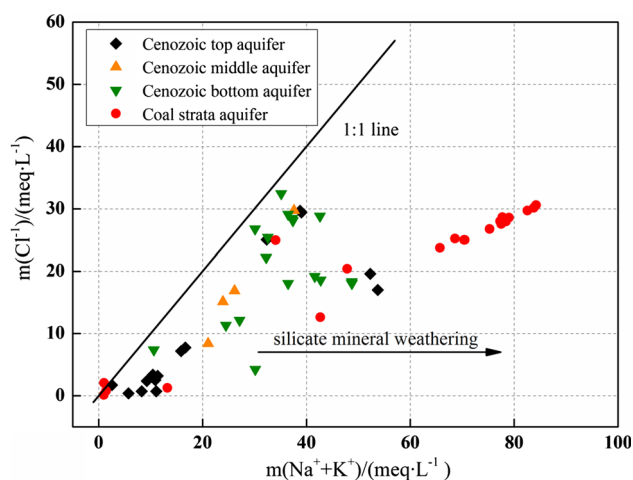
Fig. 2 Piper trilinear diagram of the chemical type of groundwater samples in the four study aquifers

where dissolved Ca²⁺ and/or Mg²⁺ released Na⁺ and/or K⁺ in the Cenozoic sediments and rocks represented by X(s). The importance of cation exchange processes is further confirmed by the positive correlation between the

[HCO₃⁻ + SO₄²⁻ - (Ca²⁺ + Mg²⁺)] vs. (Na⁺ + K⁺ - Cl⁻) (Fig. 4). The correlation line has a slope near 1 when ion exchange between groundwater and the hosting rocks is an important process controlling groundwater geochemistry [Carol et al. 2009; Moussa et al. 2010]. All samples showed positive values near the 1:1 line, showing that cation exchange is an important process in all the aquifers.

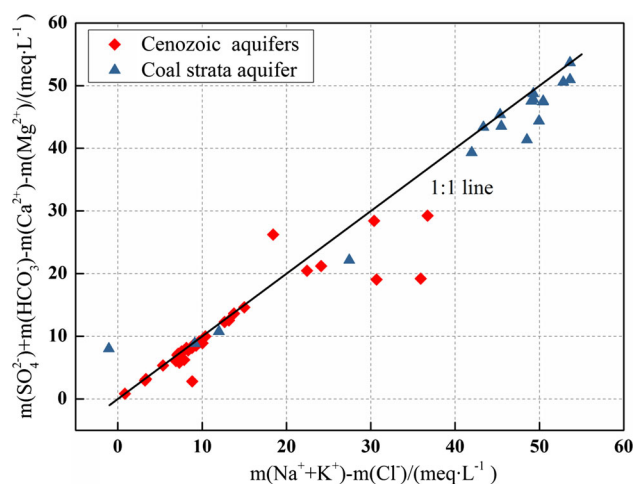
Table 2 Pearson correlation coefficients (r) among various ions

	Ca^{2+}	Mg^{2+}	$\text{Na}^+ + \text{K}^+$	HCO_3^-	Cl^-	SO_4^{2-}
Cenozoic aquifers						
Ca^{2+}	1					
Mg^{2+}	0.767**	1				
$\text{Na}^+ + \text{K}^+$	-0.276	-0.315	1			
HCO_3^-	-0.210	-0.184	0.378*	1		
Cl^-	-0.063	-0.167	0.656**	-0.069	1	
SO_4^{2-}	0.116	0.282	0.553**	-0.006	0.295	1
Coal strata aquifer						
Ca^{2+}	1					
Mg^{2+}	0.799**	1				
$\text{Na}^+ + \text{K}^+$	-0.408	-0.404	1			
HCO_3^-	-0.339	-0.443	0.975**	1		
Cl^-	-0.349	-0.215	0.959**	0.894**	1	
SO_4^{2-}	0.464	0.559**	-0.237	-0.481	-0.199	1

* $p < 0.05$ ** $p < 0.01$ **Fig. 3** Cross plot of Cl^- concentration vs. $(\text{Na}^+ - \text{Cl}^-)$ concentration in groundwater samples from the study aquifers; the solid line denotes 1:1 line

Principal component analysis

PCA selected two components, accounting for 81 % of total variance (see Table 3). Principal component 1 (PC1) explained 57.5 % of the total variance, and it was characterized by high positive loadings for Ca^{2+} , Mg^{2+} , and SO_4^{2-} (Table 3; Fig. 5a). High PC1 scores corresponded to greater groundwater hardness due to the dissolution of carbonate minerals (e.g., calcite, dolomite). Principal component 2 (PC2) explained 23.5 % of the total variance, and it had high positive loadings for $\text{K}^+ + \text{Na}^+$ and Cl^- (Table 3; Fig. 5a) and thus represented salinity related to halite/sylvite

**Fig. 4** Cross plot of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $(\text{Na}^+ - \text{Cl}^-)$ in groundwater samples from the study aquifers; the solid line denotes 1:1 line

dissolution. Both components were also influenced by sulfate reduction, according to the positive loading for SO_4^{2-} on PC1, the positive loading for HCO_3^- on PC2, as well a negative correlation between the two ions ($r = -0.42$, $p = 0.01$).

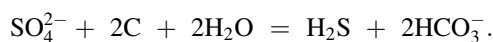
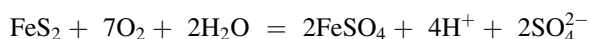
Samples from the Cenozoic top aquifer fell mainly in the third quadrant (Fig. 5b), showing low hardness, low salinity, and little influence of sulfate reduction, agreeing with our interpretation that it was recharged by atmospheric precipitation and surface water with incomplete water-rock interaction. By comparison, the samples from the Cenozoic middle and bottom aquifers were mostly in the first quadrant indicative of greater hardness and salinity

Table 3 Loadings of different parameters for the two principal components following varimax rotation

Parameter	Component 1	Component 2
Ca ²⁺	0.826	−0.319
Mg ²⁺	0.864	−0.301
Log (K ⁺ + Na ⁺)	−0.290	0.938
HCO ₃ [−]	−0.565	0.676
Cl [−]	0.063	0.897
SO ₄ ^{2−}	0.820	0.128
Eigenvalue	3.448	1.411
% of variance explained	57.46	23.51
% of cumulative variance	57.46	80.97

High loading values are highlighted in bold

than the top aquifer. Samples from the coal strata aquifer were found mainly in the second quadrant, corresponding to relative low hardness but high salinity, and they were influenced by sulfate reduction to a greater extent than the Cenozoic aquifer group. This could be attributed to FeS₂ present in coal strata, which could consume oxygen and facilitate sulfate reaction as follows:



Notably, a few samples from the coal strata aquifer had low PC2 scores and were similar to the Cenozoic aquifer samples (Fig. 5b). This observation may indicate sporadic penetration of the Cenozoic aquifers to the Permian fractured aquifer through fractures caused by mining activities. With high porosity and water yields, the thick Cenozoic aquifers could serve as a potential source for coal mine inrush in addition to Permian aquifer water.

Cluster analysis

Cluster analysis yielded results given as a dendrogram in Fig. 6. The position of the phenon line of 2.5 divided the samples into five clusters (G1–G5). G1 and G2 consisted of various types of samples, and they were grouped together. The concentrations of Na⁺ + K⁺ and Cl[−] increased from G1 to G2, demonstrating increasing salinity in groundwater due to halite solution. G3 and G4, comprising mostly samples from the Cenozoic bottom aquifer and the Cenozoic top aquifer, respectively, were further grouped together, agreeing with the previous observation that the bottom aquifer connects to the top aquifer at localities with thinning or “pinching out” of the top aquiclude (Ma et al. 2013). Relative to other groups, G5 showed lower concentrations of Ca²⁺ and Mg²⁺ but overall higher concentrations of Na⁺ + K⁺ and HCO₃[−], indicating water became softer and more influenced by sulfate reduction. Most samples from the coal strata aquifer fell in G5, indicating

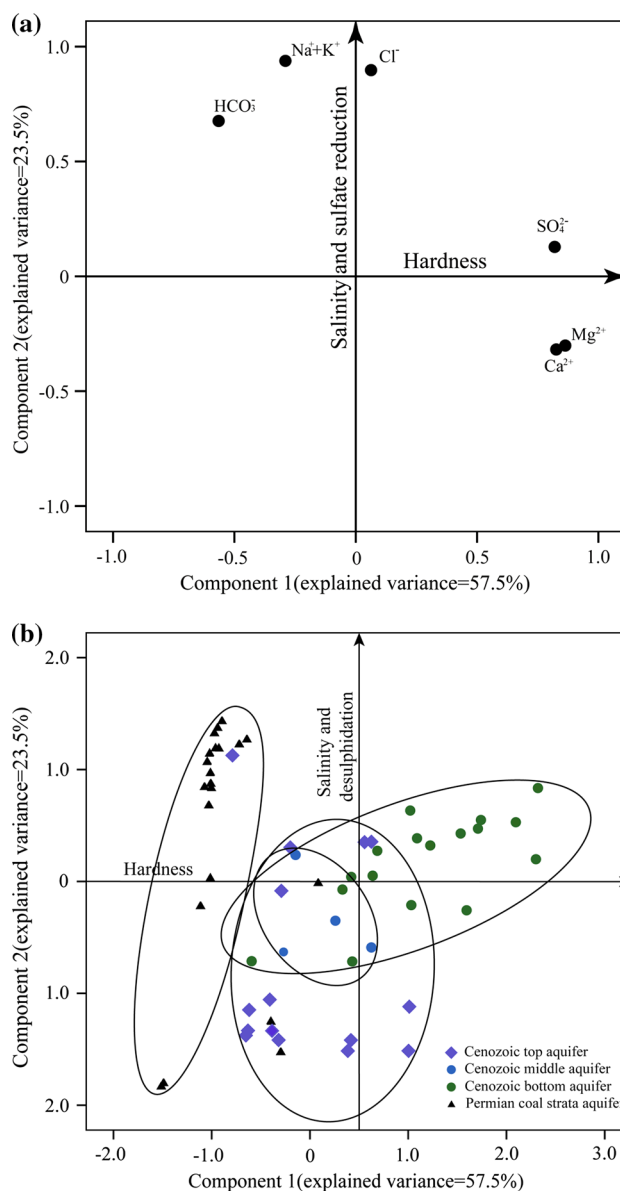


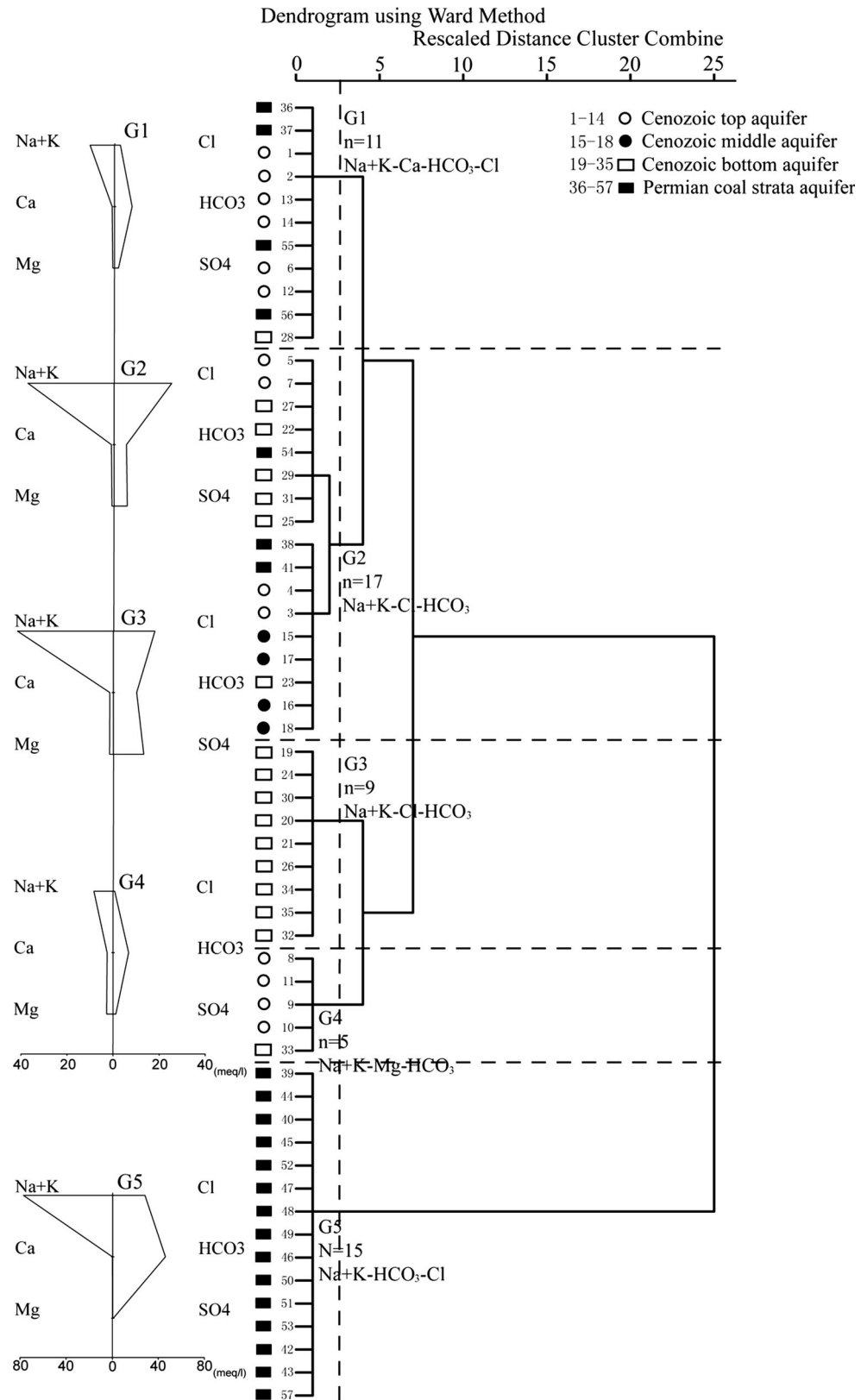
Fig. 5 Principal component analysis plots: **a** variable loadings for the first two components with varimax rotation; and **b** PCA scores for the groundwater samples from different aquifers

that this aquifer was relatively isolated with stable geochemical characteristics, while a few samples falling in other groups (i.e., 36, 37, 38, 41, 54, 55) was possibly due to local infiltrations from the Cenozoic aquifers.

Conclusions

This paper presents geochemical variation in groundwater from main aquifers near a large coal mine in Anhui Province, eastern China. Using a suite of statistical techniques, we found:

Fig. 6 Dendrogram for the major ions in the groundwater of the four study aquifers and corresponding Stiff diagrams based on the arithmetic averages of the concentrations of major ions in meq/L



1. The weathering of evaporite, carbonate, sulfate, and silicate minerals played a primary role in governing the chemical composition of groundwater, while the

processes of cation exchange and sulfate reduction also influenced geochemical variability among the aquifers.

2. With increasing depth of burial, the level of mineralization increased in groundwater. Relative to the Cenozoic top aquifer, the middle and bottom aquifers had higher concentrations of Ca^+ , Mg^{2+} , and SO_4^{2-} , due to greater influences of dissolution of carbonate and sulfate minerals.
3. Both PCA and cluster analysis show that the coal strata aquifer had geochemical characteristics distinct from the Cenozoic aquifer group; it had lower hardness, higher salinity and was influenced more by sulfate reduction facilitated by pyrite in coal strata. A few samples showed characteristics more similar to the Cenozoic samples. These data indicate that the coal strata aquifer was overall isolated from the Cenozoic aquifers while infiltration from the Cenozoic aquifers had occurred locally, suggesting that the thick, high-yield Cenozoic aquifers may serve as a potential, additional source for groundwater inrush into coal mines.

Collectively, our data demonstrate that combining simple cation and anion analyses of groundwater with multivariate statistical methods provides a rapid, inexpensive means to understand not only groundwater geochemical evolutions but also aquifer connectivity, thereby allowing assessment of the risk of groundwater inrush to underground coal mines.

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