



Quality Evaluation of Water from Subsidence Area and Controlling Factor Analysis: Zhuxianzhuang Case Study

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ABSTRACT

Water in the subsidence area is considered to be a potential source for solving the shortage of water in the coal mining areas. In this study, forty-eight samples from four subsidence pools in the Zhuxianzhuang coal mine, Northern Anhui Province, China, were collected for analysing the quality for drinking and irrigation. The results suggest that the major ion concentrations in the water samples from different pools vary significantly and the samples can be classified to be Na-Mg-HCO₃, Na-HCO₃, Na-HCO₃ and Na-SO₄ types. Quality evaluation for drinking based on water quality index suggests that all of the samples are suitable for drinking (considering only the major ion concentrations). However, sodium adsorption ratio (SAR) and residual sodium carbonate (RSC) suggest that only the water from one pool can be used for irrigation directly, but others should be treated before irrigation. Relationships between major ions and statistical analysis suggest that different kinds and extents of water rock interactions are the main mechanisms controlling the chemical variations of water from different pools.

INTRODUCTION

Coal is the most important energy in China as more than 50% of the primary energy was contributed by coal during the recent years, and therefore, the production of coal is closely related to the development of the economy and society in China. However, coal mining was dominated by underground during the last decades (> 90% of the coal production comes from underground) (Yao et al. 2010), and a series of geological and environmental problems have been induced including not only the contamination of the environment (e.g. water, soil and air), but also the ground subsidence (Li et al. 2007), which have severely affected the ecological environment and the sustainable development of the mining area (Yang & Liu 2012).

Among the problems induced by underground coal mining, subsidence is a common environmental geologic hazard, which can not only destroy the construction and vegetation in the surface area, but also have an influence on the water systems in the surface and underground (Yin 1997). And now, it has been considered to be the most serious one among the environmental problems related to coal mining. In the last decade, the newly formed subsidence area is up to 130 km² every year and the subsidence area has raised up to 700,000 hm² by the end of 2006 (Meng et al. 2009).

Water shortage is a serious problem in the current world and China because of the natural conditions and the con-

tamination from human activities (e.g. agriculture and industry). This problem is also serious in coal mining areas. Previous studies suggested that more than 71% of the coal mining areas in China were lacking of water and 40% of them were serious (Gui et al. 2011). And therefore, water is important for the development of the economy in the coal mining areas, and a large number of studies have been carried out for solving the problem, such as studies related to underground water and discharged wastewater in the mining areas (Gui et al. 2009). However, the water from the subsidence has not been seriously considered before the year of 2000. In this century, more and more scientists realized that the large amount of water in the subsidence areas might be a good choice for solving the water lacking problem in the coal mining area, and a series of methods have been applied for the restoration of the water in the subsidence areas, such as the improvement of soil, vegetation, and applications of soil animals and microorganisms (Liu & Lu 2009).

However, the subsidence area is a multi-factors affected system, including natural and anthropogenic (e.g. water rock interaction, precipitation, evaporation, waste dispose). Therefore, before the application of the water in the subsidence area, the quality evaluation, as well as the source of the chemical constitutes in the water should be firstly processed. In this study, a total of forty-eight water samples have been collected from the subsidence water area in the

Zhuxianzhuang coal mine, a representative coal mine in the Northern Anhui Province, China, and their suitability for drinking and irrigation has been evaluated based on their major ion concentrations. Moreover, the main mechanisms controlling the chemistry of the water have also been discussed. The study can provide information about the usage of the water and the management of the subsidence area.

MATERIALS AND METHODS

Study area: There are five coal mines located in the region of Suzhou City: the Zhu Xianzhuang and Luling coal mines in the southeast, and Taoyuan-Qinan-Qidong coal mines in the south. The Zhuxianzhuang coal mine is located 13 km southeast to the Suzhou city (GPS: E117°05'37.6"-117°09'23", N33°33'31.4"-33°39'37.6") (Fig. 1). The annual production of coal is 1.2 million tons and has been increased up to 1.8 million tons since 2005. After more than 28 years of coal mining, there are more than 4 km² of subsidence areas been formed (Fig. 1). And now, this phenomenon has been identified and more than 1/3 of the subsidence areas have been changed to be farm land or park.

Analytical methods: A total of 48 water samples have been collected from the subsidence water areas in the Zhuxianzhuang coal mining area (14, 8, 14 and 12 samples from pools I, II, III and IV in the Fig. 1, respectively). Eight kinds of major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻ and CO₃²⁻) and total dissolved solids (TDS) have been analysed. The analytical methods are as follows: Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻ and SO₄²⁻ were analysed by ion chromatography, whereas HCO₃⁻ and CO₃²⁻ were analysed by acid-base titration in the Engineering and Technological Research Center of Coal Exploration, Anhui Province, China.

RESULTS AND DISCUSSION

Ion concentrations: The analytical results of the major ion concentrations are listed in Table 1 and shown in Fig. 2. As can be seen from the table, samples from the same subsidence pool have similar major ion concentrations, whereas the major ion concentrations of samples from different subsidence pools vary significantly.

Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ concentrations in samples from these four pools are 116-449, 1.59-7.71, 13.4-41.5, 19.0-31.5, 77.8-159, 0.1-254, 226-604 mg/L, respectively. The decreasing order of mean concentrations of major ions is HCO₃⁻ (417 mg/L) > Na⁺ (297 mg/L) > SO₄²⁻ (158 mg/L) > Cl⁻ (117 mg/L) > Mg²⁺ (26.2 mg/L) > Ca²⁺ (24.7 mg/L) > K⁺ (45.91 mg/L). The total dissolved solids (TDS) varied from 492 to 1140 mg/L (mean = 837 mg/L), and about 45.8% of the samples have TDS higher than the fresh water (< 1000 mg/L). However, samples from different

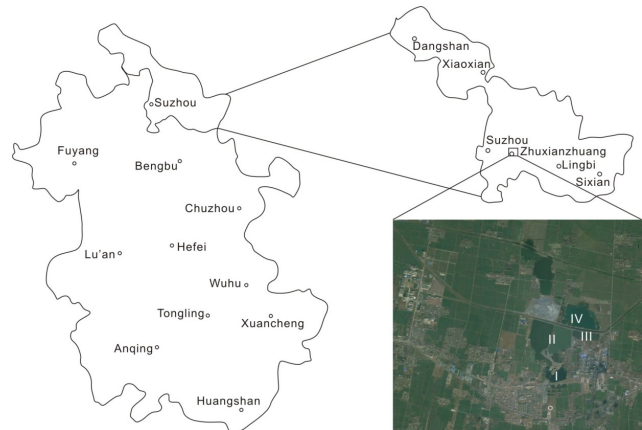


Fig. 1: Location of the study area (I, II, III and IV are sample locations in subsidence water areas around the Zhuxianzhuang coal mine).

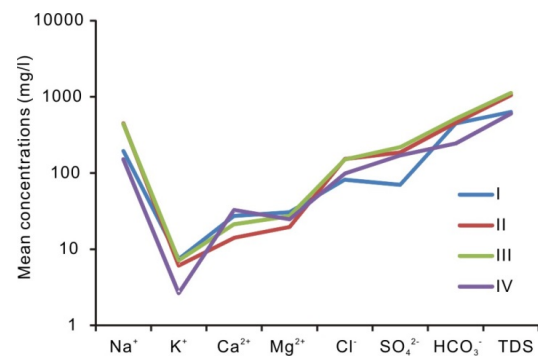


Fig. 2: Mean concentrations of major ions from different pools.

pools have different concentrations of major ions (Fig. 2).

Hydrochemical facies: Classification of hydrochemical types of groundwater is important because of the dominant anion species of water change systematically from HCO₃⁻; SO₄²⁻ to Cl⁻, as groundwater flows from the recharge zone to the discharge zone (Toth 1999). However, it is also important for surface water because it can provide information to determine the main mechanism controlling the water chemistry, as evaporation controlling tends to obtain higher concentrations of SO₄²⁻ and Cl⁻ relative to HCO₃⁻.

Classification of water in this study is based on the concentration of cations and anions by using Aquachem and Piper diagram, and the result is shown in Fig. 3. The result indicates that all the water samples from the pool I, II and III are classified to be Na-Mg-HCO₃, Na-HCO₃ and Na-HCO₃ types, respectively, suggesting that the water samples collected from one pool are similar to each other. However, the water samples from the pool IV can be classified to be of three types, Na-SO₄ (2 samples), Na-HCO₃ (4 samples) and Na-Mg-HCO₃ (6 samples), indicating that the samples from

Table 1: Major ion concentrations of water from the subsidence areas (mg/L).

ID	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	TDS
I-1	197	7.71	30.5	27.0	82.8	0.10	453	0	572
I-2	197	7.42	30.4	26.9	82.3	77.9	491	0	667
I-3	198	7.51	30.3	26.6	81.6	78.3	453	0	649
I-4	196	7.42	30.3	26.7	81.3	77.7	468	0	654
I-5	196	7.53	30.4	26.8	81.5	77.9	423	0	632
I-6	196	7.46	30.2	26.4	81.9	78.0	453	0	646
I-7	196	7.48	30.4	26.9	81.3	77.3	423	0	631
I-8	195	7.48	30.5	27.0	81.7	76.3	453	0	644
I-9	191	7.28	30.9	27.8	81.5	73.3	423	0	623
I-10	181	7.35	30.2	31.6	79.9	65.7	438	0	614
I-11	184	7.31	31.5	28.8	80.3	67.9	438	0	619
I-12	194	7.32	30.5	27.2	81.8	75.9	468	0	651
I-13	193	7.24	30.5	27.3	81.0	75.3	423	0	626
I-14	196	7.35	30.5	25.8	81.4	77.9	408	0	623
II-1	447	5.99	20.0	15.6	155	185	483	0	1070
II-2	447	6.13	19.5	14.1	152	187	453	0	1052
II-3	446	6.12	19.6	14.1	151	187	438	0	1043
II-4	447	6.13	19.4	14.0	153	188	468	0	1060
II-5	447	6.14	19.4	14.0	151	186	408	0	1027
II-6	448	6.11	19.5	13.9	153	188	468	0	1062
II-7	440	6.12	19.0	13.8	149	181	468	0	1043
II-8	449	6.06	19.1	13.4	154	186	468	0	1061
III-1	441	7.15	27.3	21.2	150	215	513	0	1118
III-2	440	7.05	27.2	21.0	151	211	513	0	1114
III-3	440	7.15	27.2	20.6	153	222	491	0	1116
III-4	441	7.16	27.3	20.1	153	224	483	0	1114
III-5	445	7.30	27.4	18.6	159	233	491	0	1136
III-6	441	7.20	27.3	20.2	153	225	498	0	1123
III-7	442	7.23	27.3	20.3	153	223	483	0	1115
III-8	440	6.63	27.1	20.1	156	226	506	0	1128
III-9	440	7.13	27.2	20.3	151	220	483	0	1107
III-10	439	6.96	26.8	24.8	141	204	574	0	1129
III-11	439	6.97	26.9	24.9	139	201	604	0	1140
III-12	438	6.99	27.1	23.4	136	212	551	0	1118
III-13	441	7.18	27.2	20.8	150	222	506	0	1121
III-14	442	7.21	27.3	20.5	151	220	506	0	1121
IV-1	184	2.55	26.8	41.5	121	254	226	0	743
IV-2	186	2.43	26.6	41.3	120	251	226	0	741
IV-3	150	2.95	25.0	30.4	96.7	160	257	0	594
IV-4	150	3.00	25.0	30.4	97.5	162	242	0	589
IV-5	150	2.96	25.0	30.0	96.9	162	257	0	595
IV-6	151	2.94	25.1	30.5	97.5	162	287	0	612
IV-7	154	2.93	25.1	30.7	97.5	163	226	0	586
IV-8	135	2.28	22.1	33.6	90.4	143	242	0	547
IV-9	139	2.35	22.0	29.5	90.7	142	226	0	539
IV-10	116	1.59	22.0	33.6	77.8	113	257	0	492
IV-11	150	2.90	25.0	30.5	98.0	164	257	0	599
IV-12	150	2.92	25.0	30.5	96.5	162	226	0	581

Note: I, II, III and IV are symbols of different pools.

the pool IV have been affected by multi factors. It is also noticed from Fig. 3 that the samples from the pools IV and II have higher concentrations of SO₄²⁻ relative to the samples from the other pools, implying that the water in these two pools might be affected by evaporation more significantly.

Quality evaluation for drinking: The water quality index (WQI) was calculated for evaluating the quality for drinking based on several key parameters of water chemistry, which has long been used for groundwater and surface water (Ramakrishnaiah et al. 2009, Vasanthavigar et al. 2010). To calculate the WQI, the weight has been assigned to the physico-chemical parameters according to the parameter's relative importance in the overall quality of water for drinking water purposes. The assigned weight ranges from 1 to 5. The maximum weight of 5 has been assigned for TDS, Cl⁻ and SO₄²⁻, 4 for Na⁺, 3 for Ca²⁺ and Mg²⁺ (Varol & Davraz 2015). The relative weight is computed from the following equation:

$$W_i = w_i / \sum_{i=1}^n w_i \quad \dots(1)$$

Where W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters.

$$Q_i = 100 \times C_i / S_i \quad \dots(2)$$

Where Q_i is the quality rating, C_i is the concentration of each chemical parameter (mg/L), and S_i is the World Health Organization standard (Na⁺ 200 mg/L, Ca²⁺ 300 mg/L, Mg²⁺ 30 mg/L, Cl⁻ 250 mg/L, SO₄²⁻ 250 mg/L, TDS 1500 mg/L) (WHO 2008).

$$WQI = \sum_{i=1}^n W_i \times Q_i \quad \dots(3)$$

Based on the results, the quality of the water for drinking can be classified to be of five classes (excellent < 50, good 50-100, poor 100-200, very poor 200-300 and unsuitable >300). The WQI for the water from the subsidence area in this study has WQI range from 41.2 to 93.8 (mean = 68.4), suggesting that these waters are excellent or good for drinking when considering only their major ion concentrations. However, the water from the four pools has different water qualities, the samples from pool I have the best quality, whereas, the samples from pool III have the worst quality, as the mean WQI values for samples from the pool I, II, III and IV are 49.3, 85.1, 91.4 and 52.7, respectively.

Quality evaluation for irrigation: There are several parameters been applied for quality evaluation of irrigation, including sodium adsorption ratio (SAR), percentage sodium (% Na) and permeability index (PI), residual sodium carbonate (RSC), Kelly's ratio and magnesium ratio. In this study, the most popular applied parameters (SAR and RSC) have been chosen for quality evaluation for irrigation.

The index used is the SAR that expresses the relative activity of sodium ions in the exchange reactions with the soil. This ratio measures the relative concentration of sodium to calcium and magnesium. SAR is an important parameter for determining the suitability of groundwater for irrigation. Excess sodium concentration can reduce the soil

Table 2: Results of factor analysis.

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS	Eigen value	% var
FA 1	0.73	-0.03	-0.32	-0.32	0.88	0.97	0.26	0.82	4.93	61.6
FA2	0.59	0.97	0.29	-0.68	0.30	-0.17	0.94	0.52	2.23	27.9

Table 3: Source compositions (mg/L).

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	TDS
Source 1	96.1	3.81	15.0	12.9	38.1	27.3	227	307
Source 2	7.71	-0.105	3.46	6.27	14.2	34.2	11.7	71.5
Source 3	193	2.22	7.72	5.55	64.7	96.6	178	459

permeability and soil structure (Todd 1995). Irrigation using water with a high sodium adsorption ratio may require soil amendments to prevent long-term damage to the soil (Michael et al. 2008). SAR is a measure estimated by $Na^+ / [(Ca^{2+} + Mg^{2+})/2]^{1/2}$ (concentrations in meq/L). The calculated value of SAR in this area ranges from 2.89 to 17.4 (mean = 8.37). And the samples from pool I and IV can meet the requirement for irrigation (SAR < 10), which accounts for 54% of the total samples. However, all the samples from the pools II and III have high SAR values (> 10).

RSC exists in irrigation water when the carbonate (CO₃) plus bicarbonate (HCO₃) content exceeds the calcium (Ca²⁺) plus magnesium (Mg²⁺) content of the water. An excess value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton 1950). The results of this include direct toxicity to crops, excess soil salinity (EC) and associated poor plant performance, and where appreciable clay or silt is present in the soil, loss of soil structure and associated decrease in soil permeability. RSC is a measure employed by calculating $(CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$ (Ragunath 1987). RSC value < 1.25 meq/L indicates good water quality. If the value of RSC is between 1.25 and 2.5 meq/L, the water is slightly suitable while a value > 2.5 the water is considered as unsuitable for irrigation. RSC values in this study range from -0.57 to 6.44 (mean = 3.44), and 12 samples from the pool IV can be used for irrigation directly (RSC < 1.25 meq/L), which accounts for 25% of the total samples.

If considering SAR and RSC simultaneously, only the samples from the pool IV can be used for irrigation directly. Samples from the pool I can meet the requirement of SAR but cannot meet the requirement of RSC, whereas, samples from the pool II and III cannot meet the requirement of both SAR and RSC. This should be due to the lack of Ca²⁺ and Mg²⁺ relative to Na⁺ or HCO₃⁻ concentrations. And therefore, Ca²⁺ and Mg²⁺ should be added before the application of the water for irrigation, because it can balance additional

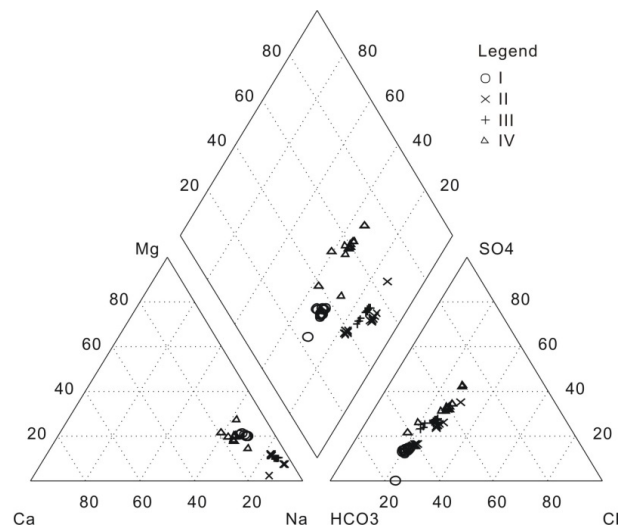


Fig. 3: Piper diagram .

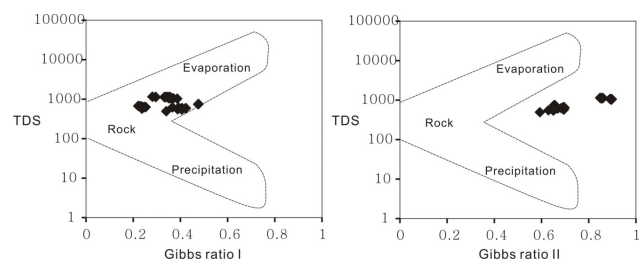


Fig. 4: Gibbs diagrams.

CO₃²⁻ and HCO₃⁻, and also, reducing the relative concentrations of Na⁺ in the water.

Mechanism controlling water chemistry: Gibbs (1970) proposed a diagram to understand the relationship of the chemical components of water from their respective aquifer lithology. Various factors controlling groundwater chemistry are analysed by the diagram. Gibbs diagram consists of three distinct fields, namely precipitation dominance, evapo-

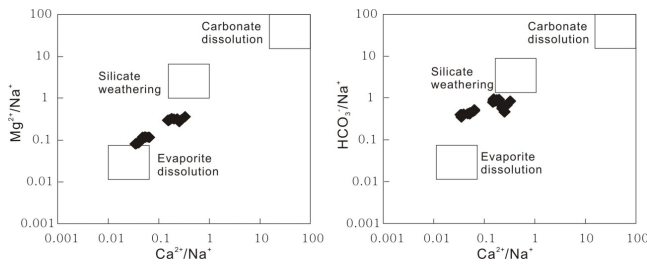


Fig. 5: Na⁺ normalized Ca²⁺-HCO₃⁻ and Ca²⁺-Mg²⁺ plots.

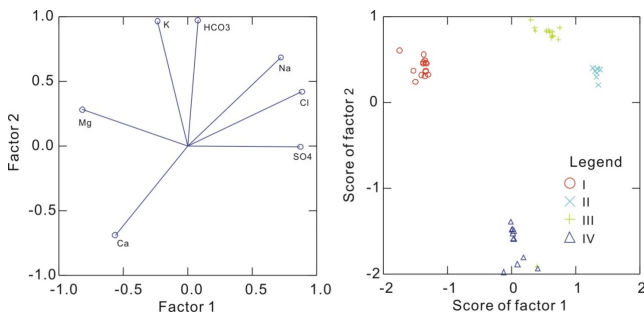


Fig. 6: Results of factor analysis.

ration dominance and rock dominance. Further, the Gibbs ratios are calculated by: Gibbs ratio I = $Cl/(Cl+HCO_3^-)$ and Gibbs ratio II = $(Na^++K^+)/(Na^++K^++Ca^{2+})$ (in meq/L). In the present study, Gibbs ratio I values varied from 0.22 to 0.48 and Gibbs ratio II values varied from 0.59 to 0.90. From Fig. 4, it is clear that all the samples fell between rock and evaporation dominance area with Gibbs ratio I, whereas, the samples plotted outside the evaporation-rock-precipitation area according to Gibbs ratio II. The former indicates that water-rock interaction, as well as evaporation and/or dissolution of evaporates play important roles in controlling the water chemistry in this study, whereas, the later might be affected by the lower concentrations of Ca²⁺ and Mg²⁺ relative to Na⁺.

Moreover, it can also be obtained from Fig. 5 that the water samples in this study have Ca²⁺/Na⁺ and Mg²⁺/Na⁺ ratios range from 0.03 to 0.33 and 0.08 to 0.36, respectively, and suggest that dissolution of evaporate minerals cannot be ruled out, whereas, weathering of silicate minerals and/or dissolution of carbonate minerals might also have occurred in the pools. It is also supported by the correlation between Ca²⁺/Na⁺ and HCO₃⁻/Na⁺ (0.34-0.94) (Fig. 5).

For getting more information about the source of major ions in the water, statistical analysis, including factor analysis and EPA Unmix model have been applied, which have long been used for quantifying the source of major ions in the groundwater (Sun 2015). With eigen value higher than one after varimax rotation, two factors have been obtained

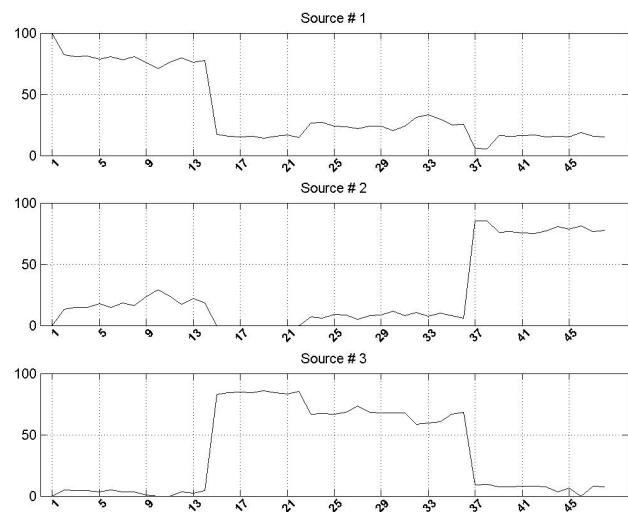


Fig. 7: Source contributions (samples 1-14, 15-22, 23-36 and 37-48 are samples from pools I, II, III and IV, respectively).

(Table 2 and Fig. 6). As can be seen from the table, factor one has high positive loadings of Na⁺, Cl⁻, SO₄²⁻ and TDS, which accounts for 61.6% of the total variance, whereas, factor two has high loadings of K⁺ and HCO₃⁻, to a lesser extent, Na⁺ and TDS, which accounts for 27.9% of the total variance. According to the discussion above, as well as the relationships between major ions during dissolution or weathering of minerals, factor one and two can be explained to be evaporate and silicate factors. Moreover, factor one has highest contributions for the samples from the pool II, whereas, samples from the pool IV have the lowest contributions from factor two (Fig. 6).

As to the analysis of Unmix model, three sources have been identified (Table 3), with Min Rsq = 1.00 (> 0.8) and Min Sig/Noise = 5.00 (> 2), which suggest that 100% of the information can be modelled by Unmix and the results are reliable (Ai et al. 2014). As can be seen from Table 3, source 3 has the lowest ratios of Ca²⁺/Na⁺ (0.03) and Mg²⁺/Na⁺ (0.08), whereas, source 2 has the highest ratios (0.93 and 0.85, respectively), and these ratios of source 1 are in the medium. And therefore, source 1, 2 and 3 can be explained to be silicate, carbonate and evaporate sources. In consideration with their contributions for each sample (Fig. 7), samples from the pool IV have the highest contributions from the carbonate source (near 80%), which is consistent with the truth that there is a large coal gauge hill (carbonate is the main minerals) located in the west of the pool, and dissolution of carbonate minerals might be flowed into the pool. However, samples from the pool II and III have the highest loadings of the evaporate source (60-80%), it is consistent with the truth that the pools are shallow and evaporation

might be dominant. Moreover, the samples from the pool I have the highest contributions from the silicate source (near 80%), which is consistent with the truth that the pool I has the deepest water and the water amount in the pool is enough for the dissolution of silicate.

CONCLUSIONS

Based on the major ion concentrations of water samples from the subsidence area in the Zhuxianzhuang coal mine, Northern Anhui Province, China, the following conclusions have been obtained:

1. Water samples from different subsidence pools have different concentrations of major ions, and they can be classified to be Na-Mg-HCO₃, Na-HCO₃, Na-HCO₃ and Na-SO₄ types.
2. All of the samples have WQI range from 41.2 to 93.8 (mean = 68.4), suggesting that they are excellent for drinking when considering about only their major ion concentrations.
3. SAR and RSC values for the samples are 2.89 to 17.4 (mean = 8.37) and -0.57 to 6.44 (mean = 3.44), respectively, and only the water from the pool IV can be used for drinking and irrigation simultaneously.
4. Relationships between major ions and statistical analysis suggest that different kinds and extents of water rock interactions are the main mechanisms controlling the chemical variations of water from different pools, which is consistent with their natural conditions.

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