

Stable isotope and water quality analysis of coal bed methane produced water in the southern Qinshui Basin, China

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Abstract. China is one of the countries with the highest reserves of coal bed methane (CBM) in the world. Likewise, the CBM industry is significantly growing in China. However, activities related to CBM development have led to more environmental problems, which include serious environmental damage and pollution caused by CBM-produced water. In this paper, the detailed characteristics of CBM-produced water in the southern Qinshui Basin were investigated and analyzed and compared with local surface water and coal mine drainage. Most of CBM-produced water samples are contaminated by higher concentration of total dissolved solids (TDS), K (Potassium), Na (Sodium) and NH₄. The alkalinity of the water from coalmines and CBM production was higher than that of the local surface water. The concentrations of some trace elements such as P (Phosphorus), Ti (Titanium), V (Vanadium), Cr (Chromium), Ni (Nickel), Zn (Zinc), Ge (Germanium), As (Arsenic), Rb (Rubidium), and Pd (Palladium) in water from the coalmines and CBM production are higher than the acceptable standard limits. The δD and $\delta^{18}O$ values of the CBM-produced water are lower than those of the surface water. Similarly, the δD values of the CBM-produced water decreased with increasing drainage time.

Keywords: coal bed methane; produced water; stable isotope; geochemical characteristics; Qinshui Basin

1. Introduction

Coal bed methane (CBM) is a form of “clean” energy. The development and utilization of CBM has some positive effects such as the improvement of the energy structure, alleviation of energy shortage, reduction of environmental pollution, and the improvement of underground coal mine safety. CBM mainly occurs in coal reservoirs in the form of adsorption gas, free gas, or dissolved gas, which are in dynamic equilibrium in specific conditions. These three states of CBM change with the variations in the temperature and pressure conditions of the coal reservoir. The transformation from adsorption gas to free gas is the premise of CBM exploration, and step-down drainage is one of its effective development processes. During CBM exploration, a large quantity of groundwater from the coal reservoir must be discharged, which could be required for all stages of CBM exploration. In most areas in the world, such as the western USA, Canada, China and

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Australia, coal seams contain significant quantities of groundwater (Meng *et al.* 2011). The composition of CBM-produced water is relatively complex and is determined by several factors. For different geological tectonic backgrounds and different coal reservoirs, the physical and chemical characteristics of the CBM-produced water likewise differ, even among the different row stages from the same CBM well. CBM-produced water, with its high salinity, high mineralization, and high heavy-metal output, can cause environmental pollution and destruction when it is directly discharged into the soil, as reported by different research groups (McBeth *et al.* 2003, Rice 2003, Orem *et al.* 2007, Klein *et al.* 2008, Yan *et al.* 2008, Ahmadun *et al.* 2009, Cheung *et al.* 2009, Kinnon *et al.* 2010). Significant differences in the relative geochemical and isotopic compositions of CBM-produced water have been observed, which imply the various origins of solutes and the different water-rock interactions along multiple flow paths (Rice 2003, Rice *et al.* 2008). Based on the water and gas generated by CBM production in the Bowen Basin of Australia, Kinnon *et al.* (2010) used the same analytical method to determine the origins of the gas and water in a CBM production field. Their study was an effort to understand the water and gas flows over time in relation to the known geological compartmentalization of the reservoir. In the Powder River Basin of eastern Wyoming and southeastern Montana in the USA, the water that was produced from CBM wells has been typically discharged onto the land surface. The chemical components of the CBM-produced water can affect the surface water as well as the ground water in shallow aquifers (Patz *et al.* 2006, Jackson and Reddy 2007, Healy *et al.* 2008, Harris and Smith 2009, Healy *et al.* 2011).

China has the world's third-largest coal bed methane resources, behind only to Russia and Canada. The estimated coal bed methane reserve in China is about 36.8 trillion m³, located no deeper than 2000m below the surface (Meng *et al.* 2011). The Chinese CBM industry includes more than 5000 wells. In 2010, the CBM output reached 1.45 billion cubic meters, of which 1 billion cubic meters were produced in the southern Qinshui Basin. With the large-scale mining of CBM, the influence of CBM-produced water on the environment will become more prominent. Therefore, typical CBM wells were selected from key areas of CBM operations in the southern Qinshui Basin. The chemical composition and isotope characteristics of the CBM-produced water from these wells were studied in this paper, thereby providing a theoretical basis for the treatment and pollution control of CBM-produced water.

2. Geological and hydrogeological setting

The Qinshui Basin, which is located in the North China platform, is the largest structural coal-bearing basin in China. Likewise, this basin is one of the key areas of CBM exploration and development. The study area is located in the southern Qinshui Basin, and has a simple structure, stable thickness of its coal seam, and high CBM content. The Qinshui Basin formation belongs to the stratigraphic regionalization of north China, which is characterized by a lack of stratum from the Silurian, Devonian, and early Carboniferous periods. Moreover, the study area is located near the hold port of the southern synclinorium in the south-north direction. The strata distribution in this area has the typical characteristics of a syncline basin. The edge of the outcropped strata is old, with the newer strata within the basin outcrop. The lower Paleozoic strata are exposed to the surface around the basin, which is followed by the Upper Paleozoic and Mesozoic strata. Meanwhile, the Triassic strata remain largely exposed in the central region of the basin. The Taiyuan Formation (Upper Carboniferous) and the Shanxi Formation (Lower Permian) in this area

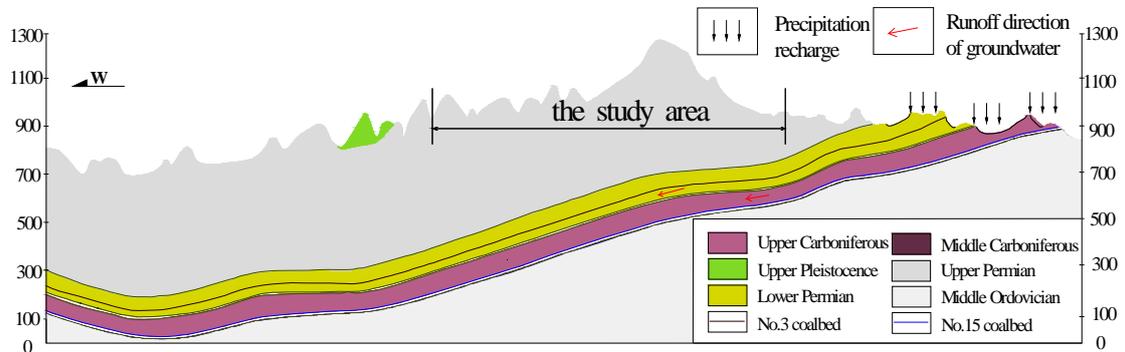


Fig. 1 Hydrogeological profile plot of the southern Qinshui Basin (Ye *et al.* 2001, revised)
1- Precipitation recharge; 2 - Runoff direction of groundwater

primarily contain coal, with an average thickness of 150 m. The Taiyuan Formation that was formed in the coastal plain contains a series of coal sedimentations from the ocean and the continent, which can be divided into three segments from bottom to top. One segment, which has an important floor section that contains the coal in the formation, is composed of gray-black mudstone, siltstone, quartz sandstone with fine particles, and around three to four layers of coal. The No. 3 coal seam can be mined and has a thickness of about 4 m to 7 m, with an average of 6 m. The general distribution shows that the coal bed thickness in the east of the formation is thicker than that in the west. The roof of the formation is mudstone with an average thickness of 2.1 m.

In the southern Qinshui Basin, three major aquifer systems exist, namely, the Ordovician, the Permo-Carboniferous, and the Quaternary. The hydrogeological profile plot of the basin is shown in Fig. 1. These aquifer systems mainly include carbonate rocks, sandstone, and loose sediment layers. The aquitard is made up of almost argillaceous rock. Similarly, the compact carbonate rocks prevent water from entering specific layers of several sections. The Middle Ordovician system is the major aquifer of this area. The aquosity of the Permo-Carboniferous aquifer is usually weak, whereas that of the Quaternary loose sediments varies to a larger extent and its circle of influence is relatively confined. The major aquitards in the area include the Upper Carboniferous aquitard, the mudstone and sandstone aquitards of the Taiyuan and Shanxi formations, as well as the middle-bottom part of the aquitard group in the upper and lower Shihezi formations. The Upper Carboniferous aquitard mainly contains aluminum mudstones of the Benxi Formation and mudstones or coal layers of the Taiyuan Formation. The mudstone and sandy mudstone aquitards in the Taiyuan Formation and the Shanxi Formation resist water in the partial sections. The thickness of the middle-bottom part of the aquitard group in the Upper Shihezi Formation and the Lower Shihezi Formation, which are formed from mudstone and sandy mudstone, extends from dozens to around 200 meters, thereby showing the parallel composite structure along the vertical distribution in Gaoping. The waterproof layer is connected to the aquitard group at the top of the Shanxi Formation because the fracture was not developed well.

3. Sampling and methods

Water samples were collected from the southern Qinshui Basin to identify the components of

the CBM-produced water as well as to control the water quality and hydrogeological conditions in the study area. Batches of samples, which include the CBM-produced water samples, the coal mine drainage samples, and the surface water samples, were collected at specific intervals. Nine of these samples were used for water quality analyses, which were performed to determine general indicators as well as trace and rare-earth element concentrations. The general indicators such as pH, hardness, Ca^{2+} hardness, Mg^{2+} hardness, and total alkalinity, as well as HCO_3^- , CO_3^{2-} , Cl^- , NH_4^+ , and Cr^{6+} contents, were determined through conventional titration and spectrophotometric methods. In this study, trace elements were detected using an inductively coupled plasma mass spectrometer (Varian). Based on the *Groundwater Quality Inspection Methods DZ/T0064-93* and the *Inductively Coupled Plasma Mass Spectrometer Methods*, the amount of trace elements in the samples was determined, which include those of P, Ti, V, Cr, Ni, Zn, and Ga. These samples were analyzed for stable isotopes such as deuterium (^2H or D) and oxygen-18 (^{18}O) at the Institute of Geography of the Chinese Academy of Sciences to determine the composition of stable isotopes in the CBM-produced water.

4. Results and discussion

4.1 Hydrochemical characteristics

Table 1 presents the test results of the general indicators. As seen from the table, the water from the coalmines and CBM production is characterized by a high chloride content and high salinity. Several factors affect the water quality of the CBM-produced water. The water quality varies in different regions and even in different depths. The salinity generally increases with increasing CBM-well depth.

The CBM-produced water contained a variety of inorganic ions. The main cations were potassium and sodium, which account for over 85% of all the cations, whereas the calcium and magnesium concentrations were low. The major anions were chlorine and bicarbonate, which account for over 90% of all the anions and have a maximum value of 99% in a few samples. The sulfate concentration was always low. These results may be attributed to the drilling and fracturing fluid.

The water quality in the research area was generally slightly alkaline. The pH of the water from the coalmines and CBM production ranged from 7.5 to 9.0. These levels are within the allowed emission requirements of the Water Environment Quality Standard II, wherein the pH value should be between 6 and 9. In the study area, the total alkalinity had a significant positive correlation with the bicarbonate content, whereas carbonate had a minor effect on the total alkalinity because of its low concentration. As revealed by the experimental data (Table 1), the alkalinity of the water from coalmines and CBM production was higher than that of the local surface water. In the southern Qinshui Basin, the total hardness, calcium hardness, and magnesium hardness of the water were all low, and the hardness of water from the coalmines and CBM production meets the requirements of irrigation water quality standards. Water is typically associated with coal evolution. Sulfate reduction provides a more favorable environment to methanogens, and the bicarbonate concentration also increases. Bicarbonate is also produced through methane-fermentation processes that occur in deep seams. As the bicarbonate concentration increases, calcium and magnesium cations precipitate out of the water (Van Voast 2003).

The chloride concentrations in the water from coalmines and CBM production were much higher than those in the surface water. The high chloride levels in CBM-produced water may be attributed to the components of drilling and fracturing fluids. Drilling fluids contain much Cl^- ions. Thus, the chloride concentration is elevated by the process of drilling and fracturing, which is introduced into the soil by the CBM-produced water during drainage and pump-down.

From Table 1, the quality of the CBM-produced water from CBM ZY-246, ZY-168, and TS-003 greatly changed over time. Some ion concentrations in the CBM-produced water decreased with increased drainage time, such as K^+ , Na^+ , and Cl^- . This effect may be related to the composition of drilling and fracturing fluids. Both fluids contain much K^+ , Na^+ , and Cl^- ions, which are carried into the strata and strands in the rock formations during drilling or fracturing. In the near wellbore areas, the concentrations of these ions may consequently rise. These ions are then carried into soil with drainage during initial mining. The concentrations of these ions gradually decreased with increasing drainage time. When the CBM-produced water is discharged, the groundwater circulation speeds up, which then leads to the decrease in the material composition. Simultaneously, the NH_4^+ concentration changes between the two sampling times. The NH_4^+ concentration in the water from ZY-246, ZY-168, and TS-003 was initially higher than the allowed national standard limits for drinking water ("Groundwater Quality Standard" GB/T 14848 93), thereby classifying these samples as inferior water. However, the NH_4^+ concentration was reduced within the standard limits during the second sampling.

A Piper diagram of the groundwater chemical composition can be used to analyze the genetic type, chemical type, and other characteristics of water (Piper 1994, Arumugam and Elangovan 2009). Fig. 2 illustrates a Piper diagram of the data from Table 1. The different water samples have different positions in the Piper diagram. The presence of the cations is particularly evident. The

Table 1 General components of the various water samples (mg/l)

Sample source	Collection date	pH	Total Hardness	Total dissolved solids	Total basicity	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
ZY-246	27 Sept 2010	8.13	499.1	2672	168.48	7.5	840	58.94	85.52	2.53	1446.7	112.92	205.45	0
ZY-246	7 Nov 2010	8.68	278.62	1939	204.01	3.5	655	31.24	48.75	< 0.02	1026.1	35.64	213.94	17.13
ZY-168	27 Sept 2010	8.54	162.93	1984	562.05	11	730	20.5	27.15	1.68	783.09	59.51	582.68	50.49
ZY-168	7 Nov 2010	8.73	121.65	1779	583.02	4.75	670	13.57	21.33	< 0.02	679.72	25.41	602.76	53.19
TS-003	27 Sept 2010	7.82	166.88	1594	721.03	3.75	565	20.9	27.87	2.58	452.2	60.95	879.24	0
TS-003	7 Nov 2010	7.79	130	1406	756.96	3.5	502.5	14.69	22.68	< 0.02	337.66	45.92	923.05	0
ZY01-IV	27 Sept 2010	8.91	34.98	811	634.31	4	320	6.31	4.67	0.25	60.65	22.19	596.17	87.18
No. 3 coal roof	27 Sept 2010	8.42	24.62	557	399.62	1.4	211	4.53	3.23	0.24	74.91	8.5	448.19	19.23
Surface water	27 Sept 2010	8.07	247.6	366	160.93	1.24	31.4	71.16	16.99	0.04	17.83	101.58	196.24	0

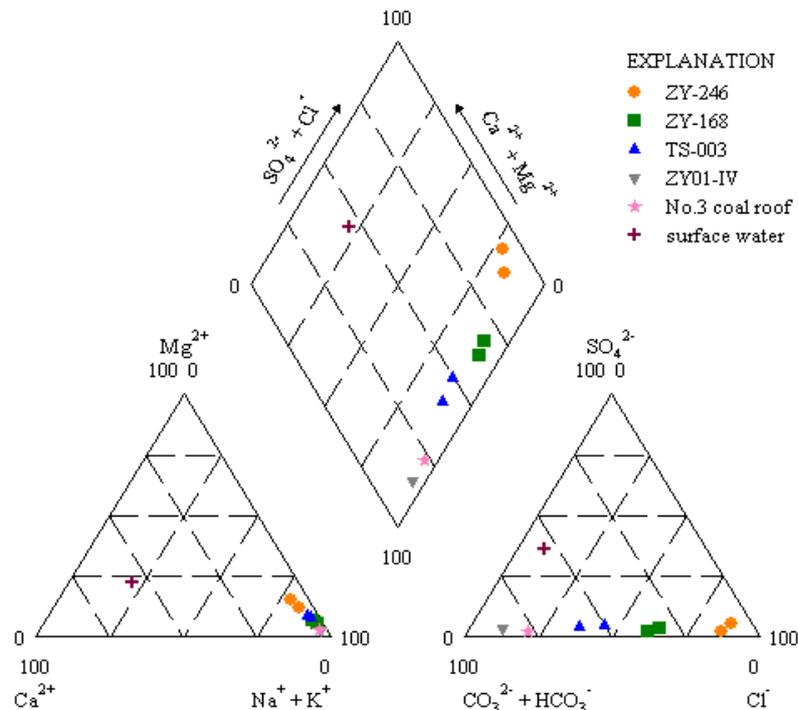


Fig. 2 Piper diagram of water quality data from the study area

water quality analysis results showed that surface water is a $\text{HCO}_3\text{-Ca}$ type of water, which is generally classified as river water and shallow groundwater. The water from ZY-246 is a Cl-Na type of water, which includes seawater, salt water, or hot water. The water from ZY-168 and TS-003 belong to the $\text{Cl-HCO}_3\text{-Na}$ and $\text{HCO}_3\text{-Cl-Na}$ types, respectively. Both of which are classified as deep groundwater. These results were affected by the composition of the fracturing fluid. The water from ZY01-IV and the roof of the No. 3 coal bed both belong to the $\text{HCO}_3\text{-Na}$ type, which is likewise considered to be deep groundwater. In the No. 3 coal bed roof, the sandstone is thoroughly distributed and contains a small amount of fissure water. A local abundant water section exists, which passes into the main coal bed. However, its fissure development is weak. Preliminary results showed that the produced water from ZY01-IV and the roof of the No. 3 coal bed comes from the sandstone aquifer. According to preliminary findings on the water chemical type and the characteristics of the water samples, the water from ZY-168, ZY-246, and TS-003 was initially believed to originate from the sandstone aquifer. Trace elements in water samples were determined and analyzed to establish comprehensive and reasonable countermeasures for CBM-produced water. Measurement results are listed in Table 2. As seen in Table 2, the concentrations of P, Ti, V, Cr, Ni, Zn, Ge, As, Rb, and Pd in water from the coalmines and CBM production as well as the surface water are higher than the acceptable standard limits. In particular, the Rb and Pd concentrations are much higher than what is allowed by the standards. These results showed that the surface water in the study area is polluted by these metals from the discharge of CBM-produced water. All of these are rare-earth metals; among which, as is a heavy metal element and Rb is a radioactive element.

Table 2 Concentrations of trace elements in the various water samples (ppb)

Sample source	Collection date	P31	Ti49	V51	Cr52	Ni60	Zn66	Ga71	Ge72	As75	Se78	Rb85	Pd105	Ag107	Hg202	Pb
Standard	None	1.5632	4.5363	0.7911	4.1349	0.5546	1.3671	0.0555	0.2684	2.8978	8.2899	0.0306	1.3682	0.0125	0.2782	0.0445
Surface water	27 Sept 2010	2.5261	3.4587	5.0074	7.8453	3.6476	9.5934	0.1221	1.5297	5.4037	32.7871	2.3046	598.2857	0.0032	0.1714	0.0241
ZY-168	27 Sept 2010	2.8021	2.9973	2.1843	10.6261	14.456	5.1148	0.1221	5.1792	4.8699	61.7418	51.4037	3784.402	0.0181	0.3615	0.0139
ZY-246	27 Sept 2010	1.9986	3.5919	0.8355	4.9408	2.2852	15.8619	0.0976	2.2788	11.3181	34.041	26.3252	5885.972	0.011	0.2022	0.0159
TS-003	27 Sept 2010	2.6456	2.2506	2.897	11.9746	3.4644	10.9908	0.1203	11.3666	7.0852	50.6491	31.5185	1776.507	0.0049	0.0707	0.0376
ZY01-IV	27 Sept 2010	3.0804	10.2027	4.8813	12.3269	1.8281	8.278	0.9663	2.9964	7.1168	37.5245	12.0467	367.7666	0.0063	0.1964	0.3309
No. 3 coal roof	27 Sept 2010	4.4149	2.2658	2.4877	10.0159	11.798	90.8559	0.6856	4.3416	27.3487	29.5406	11.9049	198.334	0.0092	0.0888	0.227
ZY-168	7 Nov 2010	2.2826	1.8503	2.01	8.2387	1.487	8.9849	0.1232	5.7216	7.7012	40.3788	54.377	1973.618	0.0057	0.2501	0.0227
ZY-246	7 Nov 2010	2.3367	2.3786	1.1239	6.1538	1.787	18.0026	0.0919	1.8592	10.6556	36.4404	23.0893	3970.704	0.0077	0.1617	0.02
TS-003	7 Nov 2010	2.5452	1.6388	2.4395	11.0297	3.5212	13.9329	0.2093	13.0829	7.221	32.8867	26.4841	1733.32	0.0051	0.0693	0.0796

Table 3 Statistical data of stable isotopes in the study area

Sample source	Collection date	Starting drainage date	δD (‰)	$\delta^{18}O$ (‰)
ZY-246	27 Sept 2010	2 Jul 2010	-80.04	-10.9
ZY-246	7 Nov 2010	2 Jul 2010	-80.5	-11.1
ZY-168	27 Sept 2010	15 Jun 2010	-77.8	-10.9
ZY-168	7 Nov 2010	15 Jun 2010	-78.5	-10.8
TS-003	27 Sept 2010	1 Jun 2010	-80.7	-11.3
TS-003	7 Nov 2010	1 Jun 2010	-81.9	-11.2
ZY01-IV	27 Sept 2010	1 Apr 2010	-79.3	-11
No. 3 coal roof	27 Sept 2010	None	-81.9	-11.2
Surface water	27 Sept 2010	None	-63.6	-8.9
TS-006	12 Aug 2010	31 May 2010	-81	-11.2
TS-192	12 Aug 2010	7 Jul 2010	-77.2	-10.9

4.2 Stable isotopic characteristics

The results showed that the hydrogen and oxygen isotopic composition from precipitation followed a strong trend. The δD values of the global meteoric water had an average of -22‰, and the $\delta^{18}O$ values of the global meteoric water had an average of -4‰. The δD and $\delta^{18}O$ values of the meteoric water are linearly related to each other. The national meteoric water equation is $\delta D = 7.9\delta^{18}O + 8.2$. According to the records from precipitation stations for the study area and its adjacent areas, the meteoric water equation specifically for the study area is $\delta D = 8.18\delta^{18}O + 10.5$. Table 2 lists the statistical data of the isotopic composition of the water samples. Fig. 3 shows a plot of the δD vs. $\delta^{18}O$ values of the water samples in Table 3.

As shown in Fig. 3, all the water samples from the study area were plotted slightly above the local meteoric water line, thereby indicating that each aquifer in the mining area has a unified water supply from the atmospheric precipitation. The influence of evaporation differed among different δD and $\delta^{18}O$ values. In addition, the isotopic composition of groundwater from different rock types and geological eras differed from each other, which reflected their different form experiences.

As shown in Table 3, the δD and $\delta^{18}O$ values of the CBM-produced water are lower than those of the surface water. Similarly, the δD values of the CBM-produced water decreased with increasing drainage time.

The δD and $\delta^{18}O$ values of the water from ZY-246 and ZY01-IV are very similar to those of the No. 3 coal roof, thereby indicating that ZY-246 and ZY01-IV received water from the said roof. The δD and $\delta^{18}O$ values of the water from TS-006 are close to those of the water from TS-003, whereas the δD and $\delta^{18}O$ values of the water from TS-192 are close to those of the water from ZY-246. These trends indicate that the two groups of wells have unified sources. Compared with the latter group, the δD values of the former group all decreased, which suggested that the buried depth of the water from TS-006 and TS-003 is greater than that of the water from TS-192 and ZY-246. The value of δD tends to decrease with increasing buried depth.

According to the stratum situation in the study area and in the drainage data, the CBM-produced water has the characteristics of a sandstone aquifer as supported by the results of

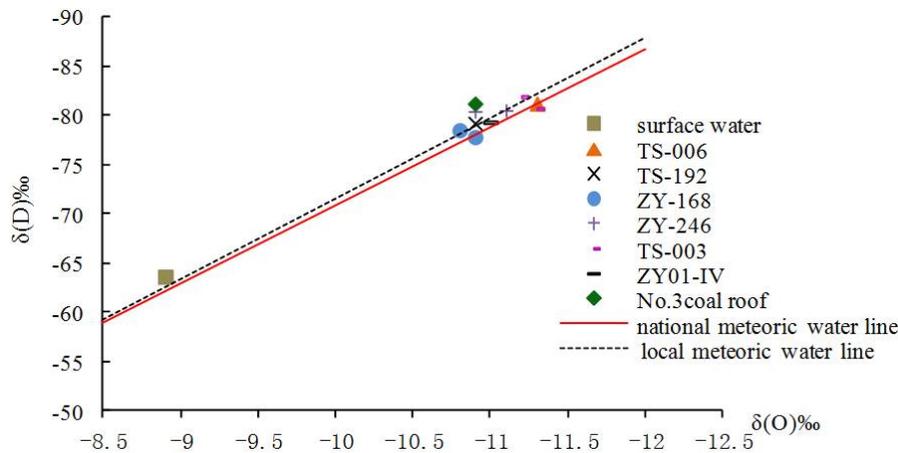


Fig. 3 δD vs. $\delta^{18}\text{O}$ values for groundwater of the study area

the water chemistry and environmental isotope tests. The CBM-produced water is hypothesized to receive its supply from the sandstone aquifer of the No. 3 coal seam roof, whose supply aquifers are mostly in the Shihezi Formation of the Permian layer and the confined water aquifers of Shanxi Formation sandstone. At one point in time, the water from TS-006 and TS-003 may have been supplied as mixed water from the No. 3 coal seam roof sandstone aquifer and the No. 15 coal seam. Thus, its supply aquifers are mostly in the Shihezi Formation of the Permian layer, the confined water sandstone aquifers of the Shanxi Formation, the limestone aquifers in the Taiyuan Formation of the upper Carboniferous layer, and the confined water aquifers of the sandstone karat fractures.

5. Conclusions

Based on a comparative analysis of water samples from the coalmines and the surface water in the southern Qinshui Basin, the CBM-produced water in the southern Qinshui Basin is characterized by high salinity. However, its pH value and hardness generally do not exceed the national standards. The concentrations of particular ions such as SO_4^{2-} meet the farmland irrigation water quality standards. Other compounds such as NH_4^+ go beyond the allowed limits of these water quality standards in the early stages of mining, but can meet the national standards during the mining process. These concentrations may be attributed to drilling and fracturing fluids. Several trace elements and heavy metal elements also exceed the emissions standards.

The stable isotope analysis and water quality tests were conducted for samples collected from the southern Qinshui Basin in an effort to study the geochemical characteristics of the water and to provide the preliminary identification of groundwater sources and flow pathways. The relationship between the environmental isotopes D and ^{18}O suggests that each aquifer has unified supply water that is replenished by atmospheric precipitation. The CBM-produced water in the study area receives water from the sandstone aquifer of the No. 3 coal seam roof. The TS-006 and TS-003 wells probably receive a mixed water supply from the sandstone aquifer of the No. 3 coal seam roof and the No.15 coal seam.

Acknowledgements

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