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TECHNICAL ARTICLE

Hydrogeochemical Evolution of an Ordovician Limestone Aquifer Influenced by Coal Mining: A Case Study in the Hancheng Mining Area, China

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Abstract
Statistical analysis was used to study the hydrogeochemical evolution of an Ordovician limestone aquifer group in the Hancheng mining area. Before mining, the groundwater flowed from northwest to southeast, the water type was primarily SO_4–HCO_3, and was mainly controlled by the tectonic structure and the specific hydrogeological conditions. After 40 years of mining, two large groundwater depression cones had formed, centered on the Sangshuping and Xiangshan coal mines in the north and south zones, respectively. The groundwater dropped by ≈ 20 m in the center of the depression cones due to over-exploration and mine water inrush, which changed the groundwater flow field significantly. Both the total dissolved solids and the concentrations of major ions increased 2.3- to 4.7-fold, and the water type changed to SO_4–Cl. The saturation indices (SI) of the minerals along the two simulated paths both increased, indicating that the groundwater would dissolve minerals as it flowed, which verified the groundwater flow field. Groundwater quality deteriorated due to a mixture of old acidic pit water and hypersaline water intruding from the deep district. When studied vertically, the concentrations of major ions and SI of calcite and limestone increased, due to the limited cycling of water from shallow to deep. The coincidental Ca^{2+} and Mg^{2+} increases were caused by calcite-replacing dolomitization reactions. To summarize, long-term coal mining adversely affected the area's groundwater flow field and hydrogeochemical evolution, and effective action should be taken to prevent the Ordovician groundwater from continuing to deteriorate.

Keywords Coal mine · Statistical analysis · Flow field · Groundwater quality · Saturation index

Introduction

Coal mining can adversely impact on the natural groundwater environment (Younger 2004). With the mining depth increasing in China, the Ordovician groundwater environment has definitely been affected (Arkoc et al. 2016; Li et al. 2015; Yin et al. 2016). Mining-induced fissure conduct groundwater in the floor aquifer to the working face, which may cause mine water inrushes when the hydraulic pressure is high; fresh groundwater then typically becomes contaminated. In addition, groundwater quality can deteriorate due to intrusion of highly saline stagnant water as the groundwater table declines due to pumping (Galhardi et al. 2016; Gomo et al. 2016; Monaghan 2017; Qian et al. 2016; Sun 2014). The Chinese Academy for Environmental Planning (CAEP) issued the 'Water pollution control action plan' due to extensive concern about groundwater quality in mining areas in China (Liu et al. 2016; Sun et al. 2014, 2015). Safe drinking water must be guaranteed for local residents and guidance must be provided to prevent groundwater pollution.

The Hancheng mining area, an important coal production base in China's Shaanxi Province, has a long history of mining (Li 2016; Qian and Lin 2016; Zhang 2005). However, coal mining has polluted the groundwater with low-quality mine water and mine-waste leachates. Hence, the

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groundwater flow field and hydrogeochemical field of the Ordovician limestone aquifer in the Hancheng area became very complex after many decades of mining.

Many research methods, such as isotope technology, hydrogeochemical analysis, and cluster analysis, have been used to study the local hydrogeochemical evolution of the Ordovician limestone aquifer (Li et al. 2013a; Wu et al. 2014; Xue et al. 2014; Zhang and Gao 2013), but no one has studied the groundwater flow field change and hydrogeochemical evolution of the entire mining area, which is very meaningful for both drinking water security and groundwater protection. We attempted to analyze how this hydrogeochemical evolution affected the groundwater flow field, hydrogeochemical field, and the evolutionary process, with respect to time and space.

Geological Background

Geological Settings

The Hancheng mining area covers the northeastern part of the Weibei coalfield, which is in the southeastern part of the Ordos Basin. Loessic low mountains and hills are the general landform. The topography is high in the northwest (approximately 800 m) and low in the southeast, with a reduction in elevation of ≈ 400 m. The total coal-bearing area is 1100 km^2, covering 10 coal mines, two exploration areas, and one deep district (Fig. 1).

The Pennsylvanian Taiyuan and the Lower Permian Shanxi Formations are the major coal-bearing strata in

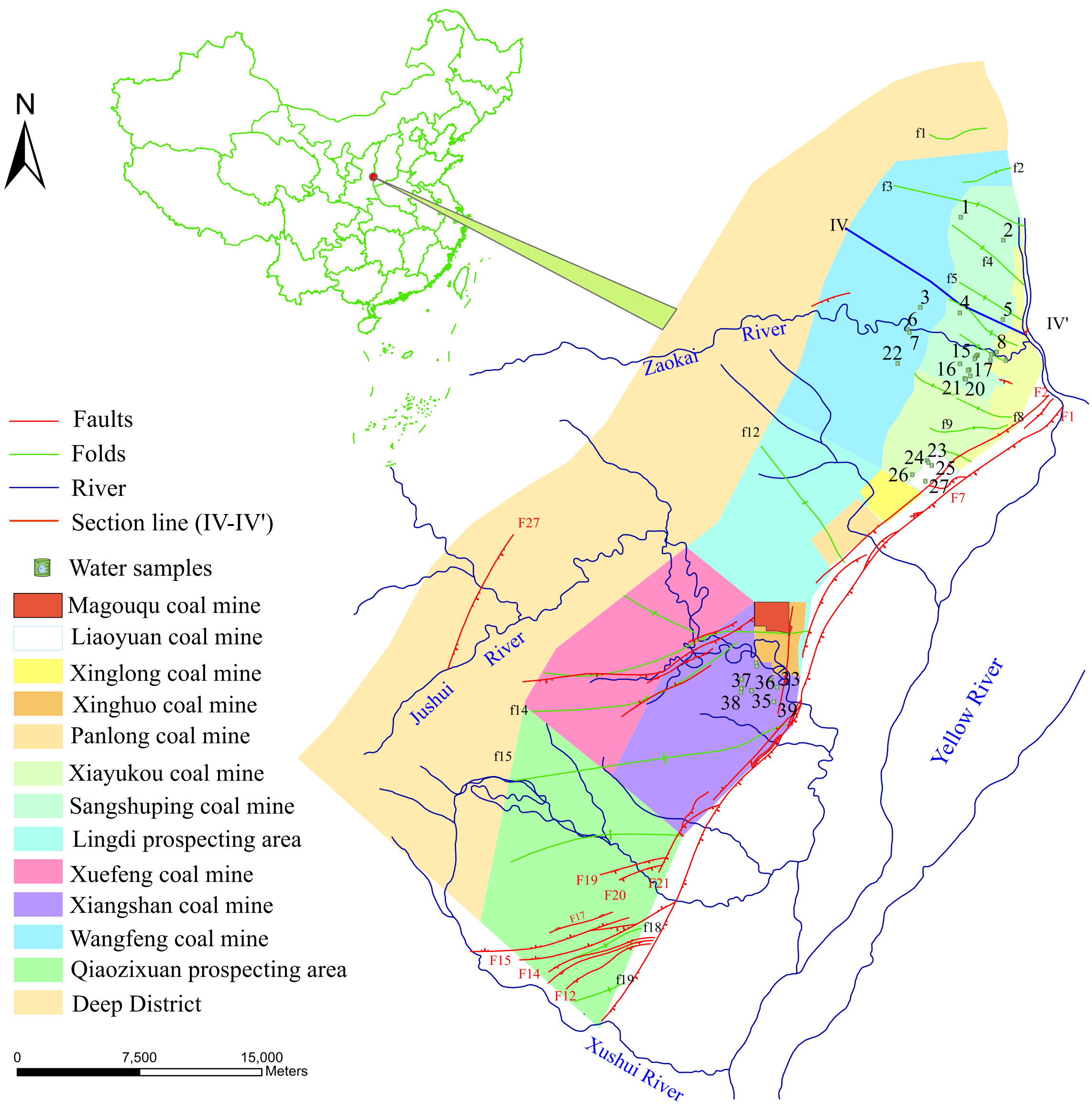


Fig. 1 Water sample location and tectonic distribution of the study area

the Hancheng mining area. The Ordovician strata consist of, in ascending order, the Yeli, Lower Majiagou, Upper Majiagou, and Fengfeng Formations.

Tectonically, the Hancheng mining area was a residual northwest flank of the overturned Hancheng anticline. It is located in the Tongchuan–Hancheng tectonic zone of the Ordos Basin, where Permian-Pennsylvanian coal-bearing strata dip gently towards the northwest at an angle of 5°–15°. The Permian coal-bearing strata underwent uplift and erosion during the Triassic Indosinian Orogeny but subsided and were reburied during the Jurassic to the Early Cretaceous. The latest tectonic movement involved faulting and folding during the Late Cretaceous Yanshanian Orogeny (Yao et al. 2009). In the study area, faults and folds are more intensive in the southeastern area, complex in the shallow areas, and simple in the deep areas. Slide structures caused by folds are mainly located in the north, whereas slide structures caused by faults are located in the south.

Generally, the Hancheng mining area is divided into north and south zones according to the coal-bearing characteristics. The no. 3 and no. 11 coal seams are distributed over the entire mining area, while the no. 2 coal seam can only be found in the north zone and the no. 5 coal seam can only be found in the south zone. The north zone includes the Sangshuping, Xiayukou, Liaoyuan, and Wangfeng mines, the northern parts of the deep district, and the Lingdi exploration area. The south zone includes the Magouqu, Xinghuo, Xiangshan, and Xuefeng mines, the southern parts of the deep district, the Lingdi exploration area, and the Qiaozixuan exploration area.

Ordovician Limestone Aquifer

The hydrogeological conditions, especially the groundwater flow field, are controlled by geologic structure and topography. The Ordovician limestone aquifer is mainly recharged from the limestone mountain to the northwest of the Hancheng mining area and precipitation that infiltrates through the limestone outcrops in the southeast. The groundwater generally flows from northwest to southeast.

The Ordovician limestone aquifer in the southeastern margin of the Hancheng mining area was originally uplifted by the overturned Hancheng anticline. It was cut by the Hancheng normal fault (F_1) in the Pliocene epoch, and outcrops in the shape of a band, covering an area of approximately 14.1 km^2 (Fig. 2). Affected by multi-phase tectonic movement, structural fractures are intensive in the southeastern margin. Karst fissure were well-developed by groundwater erosion. There are 3 formations, including 8 sections, in the Middle Ordovician aquifer, and the lithology of each section is detailed in Fig. 3. According to the drilling data, the Ordovician limestone aquifer is between 400 and 700 m thick, decreasing from northwest to southeast. The hydraulic conductivity is between 0.0008 and 9.14 m/day, and the drilling unit water inflow, which is an accepted index in China for evaluating the water yield of an aquifer (Qiao et al. 2017), is between 0.00015 and 7.38 L/(s m). The groundwater temperature is between 21 and 28 °C, TDS is between 404 and 4807 mg/L, and the hydrogeochemical type is very complex.

Materials and Methods

A total of 61 samples were collected during coal mining (Fig. 1), of which 22 were collected from the Sangshuping coal mine (including two water inrush samples and two old pit waters samples; see Table 1), 21 from the Xiangshan coal mine, 5 from the Liaoyuan coal mine, 4 from the Wangfeng coal mine, 3 from the Xinghuo coal mine, one from the

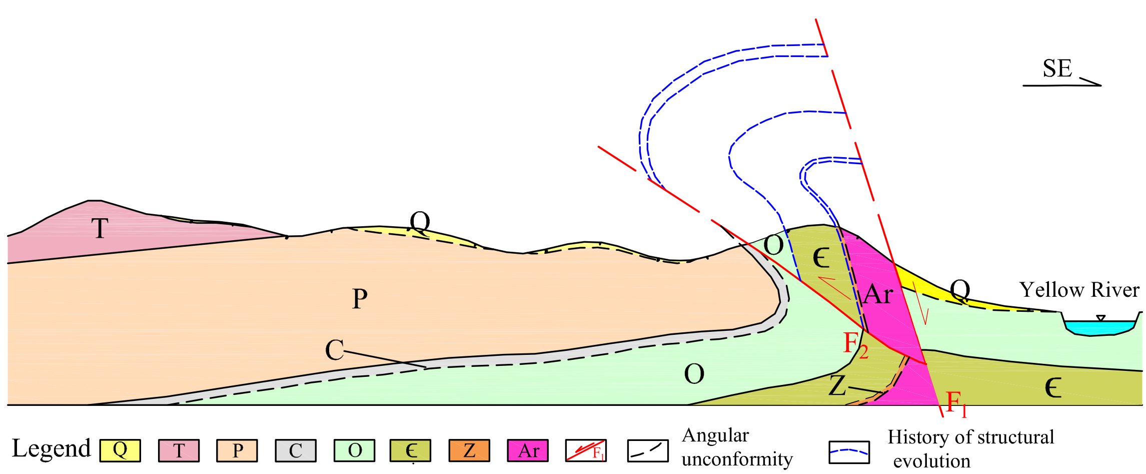
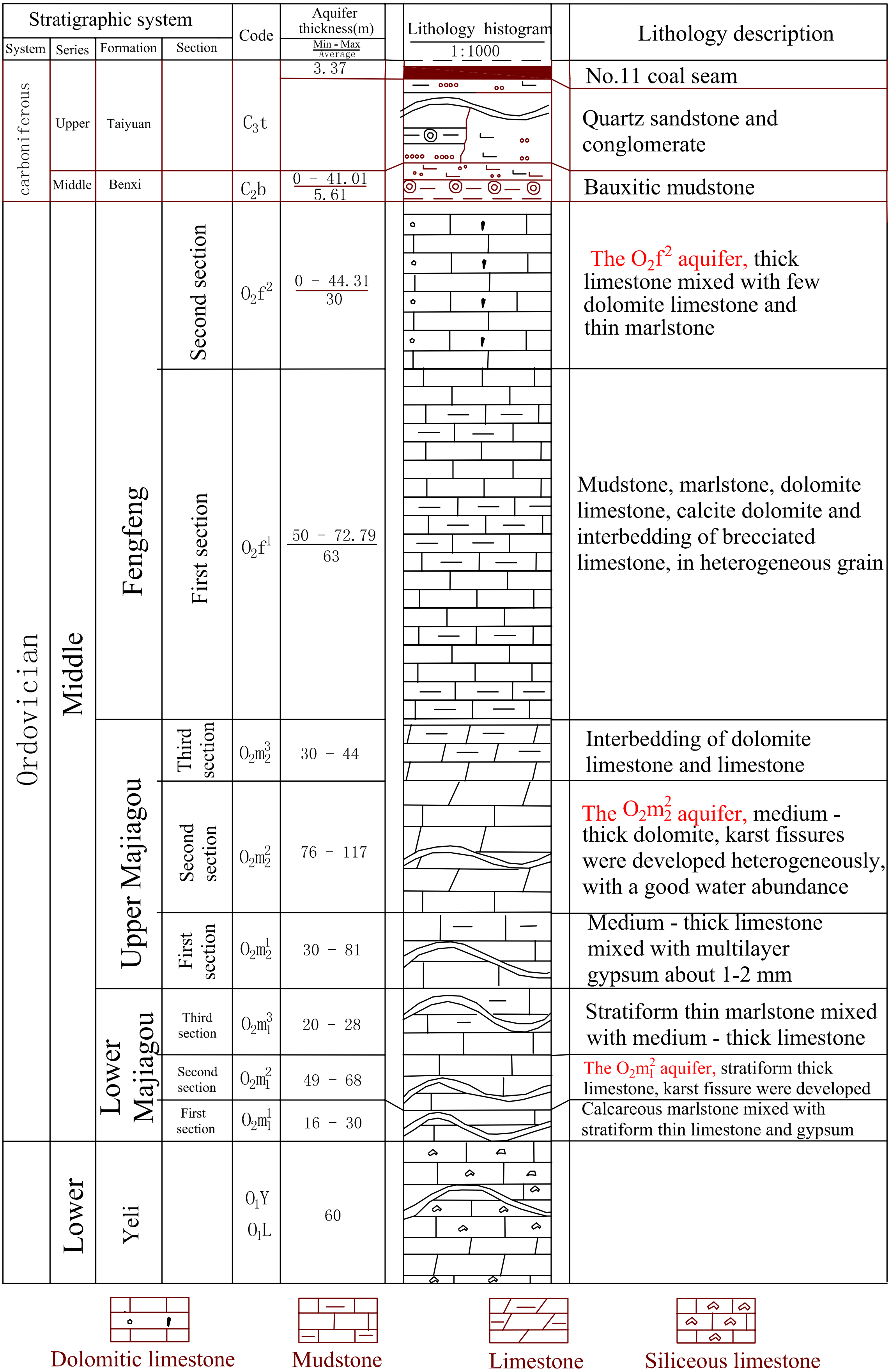


Fig. 2 Sketch map of the stratigraphic profile



Stratigraphic system
System
Series
Formation
Section
Code
Aquifer thickness(m)
Min - Max
Average
Lithology histogram
1:1000
Lithology description
3.37
No.11 coal seam
carboniferous
Upper
Taiyuan
C3t
Quartz sandstone and conglomerate
Middle
Benxi
C2b
0 - 41.01
5.61
Bauxitic mudstone
Ordovician
Middle
Fengfeng
Second section
O2f2
0 - 44.31
30
The O2f2 aquifer, thick limestone mixed with few dolomite limestone and thin marlstone
First section
O2f1
50 - 72.79
63
Mudstone, marlstone, dolomite limestone, calcite dolomite and interbedding of brecciated limestone, in heterogeneous grain
Upper Majiagou
Third section
O2m23
30 - 44
Interbedding of dolomite limestone and limestone
Second section
O2m22
76 - 117
The O2m22 aquifer, medium - thick dolomite, karst fissures were developed heterogeneously, with a good water abundance
First section
O2m21
30 - 81
Medium - thick limestone mixed with multilayer gypsum about 1-2 mm
Lower Majiagou
Third section
O2m13
20 - 28
Stratiform thin marlstone mixed with medium - thick limestone
Second section
O2m12
49 - 68
The O2m12 aquifer, stratiform thick limestone, karst fissure were developed
First section
O2m11
16 - 30
Calcareous marlstone mixed with stratiform thin limestone and gypsum
Lower
Yeli
O1Y
O1L
60
Dolomitic limestone
Mudstone
Limestone
Siliceous limestone

◂**Fig. 3** Ordovician strata histogram

Magouqu coal mine, one from the Xiayukou coal mine, one from the Yellow River, and 3 from a hydrogeological borehole at three different depths in the Ordovician limestone aquifer. Inrush water samples, old pit water samples, and Yellow River water samples were collected for comparison. All data were collected from the Hancheng Mining Bureaus, where the samples were labeled and analyzed for K^++Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, Cl^-, CO_3^{2-}, and TDS. K^+ and Na^+ were analyzed by atomic absorption spectrometry, and Ca^{2+} and Mg^{2+} were determined using the EDTA titrimetric method. Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-} were all measured by routine titrimetric methods. Total dissolved solids (TDS) were determined by drying and weighing. Duplicates were performed for quality assurance and quality control.

Results and Discussion

Groundwater Flow Field Evolution

After 40 years of mining and water exploration, two large groundwater depression cones centered on the Sangshuping and the Xiangshan coal mines formed in the north and south zones, respectively. Groundwater flowed into the cones of depression from all of the surrounding area, changing the original groundwater field.

There were 13 mine water inrush events from 1979 to 2010 in the Sangshuping coal mine; the water source was the Ordovician aquifer. The average value of the maximum mine water inflow was 1804 m^3/h, which is a tremendous quantity. The first cone of depression formed in the north zone.

There were 4 mine water inrush occurrences in the Xiangshan coal mine and 11 in the Xinghuo coal mine, and in both mines, the water source was the Ordovician aquifer. The average value of the maximum mine water inflow was 3.6 m^3/h (except once when the maximum water inrush rate was 12,000 m^3/h; the total inrush quantity was 38,715 m^3). In addition to mine water inrush, power plant water supply wells also extracted a large quantity of Ordovician groundwater. In 1979, the Xiangshan power plant, located in the Xiangshan coal mine, set up many water supply wells in the Ordovician limestone aquifer to provide water. Between 1979 and 1986, the total pumpage rate was 0.285 m^3/s; it increased to 0.423 m^3/s during 1987–2010, whereas the total recharge from the limestone outcrops has been steady, at 0.363 m^3/s. Therefore, between 1979 and 2010, the total output of the limestone aquifer was 25.87 billion tons, while the total recharge was 0.92 billion tons, totaling 16.68 billion tons of over-exploitation (Table 2), which led to a sharp groundwater table decline of approximately 20 m in the center of the cone of depression. This is how the second groundwater depression cone formed. The water supply wells were closed in 2010 to prevent the groundwater table from declining any more.

Groundwater head contour maps were established to analyze the groundwater field change during the past 40 years. From Fig. 4, we can see that in 1980, the groundwater table was approximately 390 m in the northwest and 380 m in the southeast, so that the groundwater generally flowed from northwest to southeast. There were also two abnormal points: one to the southeast of the Sangshuping mine, where the groundwater table was 395 m, and the other at the northeast corner of the Xiangshan mine, where the groundwater table was 399 m. Due to the intensive structure fissures in the southeast margin of the Hancheng mining area, the effect of groundwater erosion was strong, so that karst voids and collapse columns were well-developed along the Yellow River and at the estuary of the Zaokai and the Jushui rivers. It can be inferred that the abnormal groundwater points was probably caused by heterogeneous karst flow, though further study is needed.

By around 2010, the groundwater table was approximately 374 m high in the northeast and low in the northwest, approximately 370 m. The groundwater table declined approximately 15 m since 1980 with the two large cones of depression in the Sangshuping and the Xiangshan mines. It can be inferred that the groundwater flow field change was caused primarily by the groundwater table declining due to mine water inrush and groundwater over-exploitation by the Xiangshan power plant.

The influence of water–rock interactions on groundwater hydrogeochemical characteristics is reflected by the extent of mineral dissolution and precipitation, which is in turn determined by the saturation index (SI; Li et al. 2013b). SI values less than zero indicate undersaturation, values of zero indicate saturation, while values greater than zero point to supersaturated (Al-Mashaikhi et al. 2012). Two simulated paths from the southeast to northwest were identified to identify the groundwater flow field in 2010: Path 1 was from point P10 to point P12; Path 2 was from point P34 to point P32 (Fig. 4). The SI of anhydrite, calcite, dolomite, gypsum, and halite were calculated using PHREEQC software. From Table 3, we can see that the groundwater tends to dissolve more minerals along the two simulated paths, which also proves that the groundwater flow field was realistic.

Hydrogeochemical Field Evolution

The Sangshuping Coal Mine

A hydrochemical Piper diagram was established to identify the water types using 22 groups of water samples that had been collected in 1975–1989 and 2010–2015 (Fig. 5). The

Table 1 Compositions of water samples collected in the Sangshuping coal mine in 2010

Number	Location	TDS (mg/L)	$Na^+ + K^+$ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	HCO_3^- (mg/L)	PH
1	O_2f^2	557.57	47.5	46.4	40.6	63.39	17	322.43	–
2	O_2f^2	1057.96	373.55	17.69	0.95	400.08	219.37	44.32	
3	O_2f^2	557.1	72.27	39.3	27.61	93.84	17.96	305.1	
4	O_2f^2	4775.5	464.16	526.16	202.89	3329.1	92.3	35.24	
5	O_2f^2	2339.95	510.54	249.95	18.65	685.3	582.18	289.43	7.4
6	O_2f^2	3477.78	833.1	299.59	81.3	812.65	1168.1	279.09	7.1
7	O_2f^2	851.03	126.1	99.08	34.87	215.47	118.58	246.8	7.3
8	O_2f^2	1845.86	363.96	129.09	54.16	670.19	168.25	453.32	7.3
9	O_2f^2	3632.46	770.58	271.12	109.2	1337.7	810.05	317.19	7.1
10	O_2f^2	1772.71	498.54	24.22	53.56	1015.2	115.97	30.14	7.3
11	O_2f^2	3092.88	671.57	301.21	47.18	817.85	945.68	306.34	7.3
12	O_2f^2	3098.88	680.21	295.15	46.2	834.48	958.65	281.44	7.3
13	O_2f^2	2727.26	484.96	181.57	107.58	1261.9	129.34	560.12	7.4
14	O_2f^2	2940.39	589.72	241.14	103.92	968.76	753.08	276.44	
15	O_2f^2	3024.52	808.71	55.98	22.34	379.3	108.27	1638.3	
16	O_2f^2	2826.52	140.18	559.63	82.82	1629.2	84.55	309.86	
17	O_2f^2	3216.4	336.06	579.5	73.755	1473.3	190.5	547.11	
18	O_2f^2	3240.04	223.5	653.34	78.28	1541.5	101.76	621.39	
19	A	1187.01	118.24	128.2	73.54	527.05	88	248.72	7.8
20	B	3318.62	397.44	428.49	158.48	1817.2	477.24	33.06	5.9
21	C	9396.32	59.87	462.76	194.02	7347.1	162.85	–	4.5
22	D	7653.78	26.91	481.32	156.84	6052.6	55.05	–	4.5

A refers to inrush water from the Ordovician aquifer; B refers to mine inrush water mixed with old pit water; C and D are old pit water

Table 2 Ordovician limestone groundwater exploration and recharge between 1979 and 2010 at the Xiangshan power plant

	Time	Pumping rate (m^3/s)	Total quantity (billion m^3)	Over exploration quantity (billion m^3)
Exploration	1979–1986	0.285	7.2	16.68
	1987–2010	0.423	18.68	
Recharge	1979–2010	0.363	0.92	

former time period was a HCO_3–SO_4–Ca–Na type, with an average TDS of 1252 mg/L, whereas the latter was a SO_4–Cl–Na–Ca type, with an average TDS of 2502 mg/L; both had high annual variability in hydrochemistry. Acidic, old pit water samples were the SO_4–Ca–Mg type, with an average TDS of 8525 mg/L and a pH of 4.5. Associated with the cone of depression in the Sangshuping mine, it can be inferred that the water type change was caused because SO_4–Cl–Na–Ca type water, with a TDS of 3017 mg/L in the deep district (Lyu et al. 2003), flowed towards the cone of depression and because old acidic pit water recharged the Ordovician aquifer via mining-induced fissures.

The Xiangshan Coal Mine

The over-exploration of the limestone aquifer groundwater jeopardized both the quantity and quality of the groundwater (Table 4). Between 1979 and 1986, the TDS, SO_4^{2-}, Cl^-, and Ca^{2+} in the groundwater remained consistent with that before 1979. However, when the pumping rate increased in 1987, the TDS, SO_4^{2-}, Cl^-, and Ca^{2+} also increased in the third quarter of 1989. The TDS, SO_4^{2-}, Cl^-, and Ca^{2+} had increased significantly by 2000.

Waters collected in 1963–1982 and 2012–2014 were identified based on their chemical compositions (Fig. 5). The former time period (1963–1982) was of the SO_4–Cl(HCO_3)–Ca–Na type, with a TDS of 942 mg/L, whereas the latter was the SO_4–Cl–Na–Ca type, with a TDS of 2746 mg/L; again, both showed a high annual variability in hydrochemistry. From Fig. 5, we can see that around 2010, the groundwater table in the Xiangshan mine was 356 m, which was the lowest in the mining area, and the structural fissures were intensive here. Thus, as the cone of depression enlarged, deep hypersaline water would be

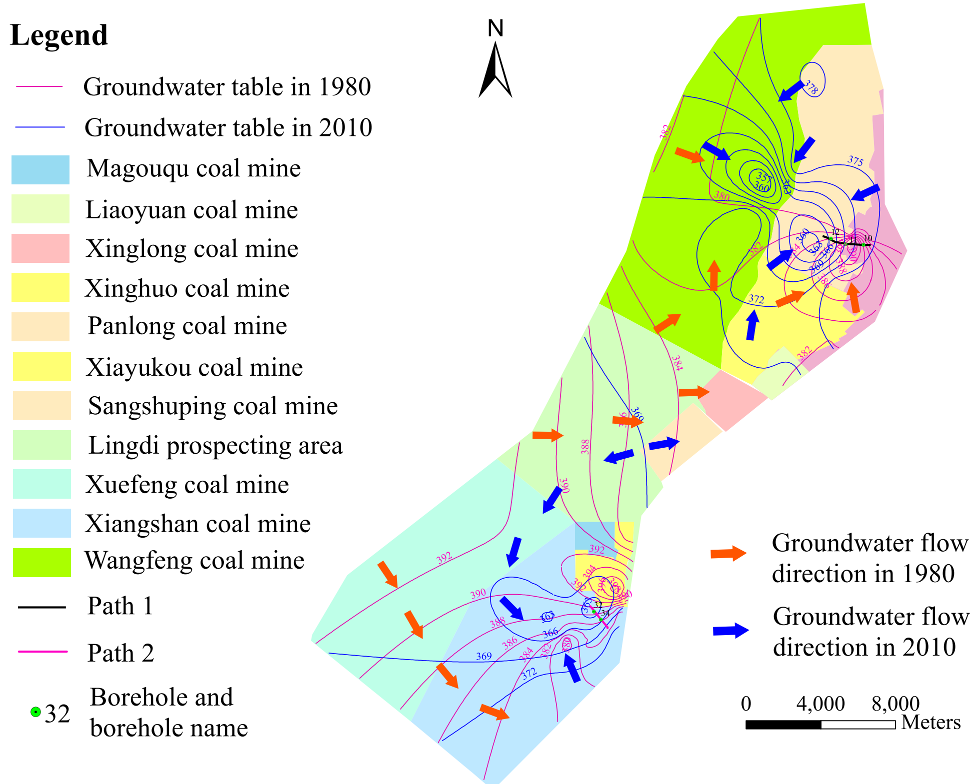


Fig. 4 Groundwater flow field in 1980 and 2010

Table 3 Saturation indices of anhydrite, calcite, dolomite, gypsum and halite along different paths

Phase	Saturation index							
	Path 1			Path 2		Different depth of Ordovician strata		
	10	11	12	34	32	O_2f^2	$O_2m_2^2$	$O_2m_1^2$
Anhydrite	− 1.5	− 1.09	− 0.68	− 1.67	− 1.45	− 2.02	− 0.74	− 0.31
Calcite	− 0.19	0.04	0.08	− 0.44	− 0.2	− 0.38	0.05	0.2
Dolomite	− 0.49	0.04	0.11	− 0.64	− 0.4	− 0.66	− 0.01	0.28
Gypsum	− 1.28	− 0.87	− 0.46	− 1.45	− 1.23	− 1.8	− 0.52	− 0.09
Halite	− 6.48	− 5.91	− 4.95	− 7.72	− 7.72	− 6.38	− 6.08	− 5.18

induced to flow into the Xiangshan mine, increasing TDS, SO_4^{2-}, and Cl^- significantly.

Other Coal Mines

13 water samples were collected for simple analysis, of which 5 were from the Liaoyuan coal mine in 2006, 4 from the Wangfeng coal mine in 2010, 3 from the Xinghuo coal mine in 2014, and 1 from the Yellow River in 2011 (Fig. 5). The Yellow River water was the HCO_3–Na–Ca type and the Ordovician groundwater from the Liaoyuan mine was the HCO_3–Na type. Groundwater from the Wangfeng mine was the SO_4–HCO_3–Na type, and groundwater from the Xinghuo mine was the Cl–SO_4–Na type. On a preliminary basis, it can be inferred that groundwater quality decreased from north to south and from east to west. As the northeast margin is next to the Yellow River, the groundwater frequently interacts with the Yellow River through the intensive fracture structures. The south margin is far from the Yellow River and the groundwater cycling is relatively slow.

Hydrogeochemical Evolution Process

The Ordovician karst water is the main water source that influences the no. 11 coal seam, which has a high total sulfur content (≈4.4%, twice the average organic S content; Shi and Luo 2000). Mining of the no. 11 seam will expose the original reducing sedimentary environment, and the sulfide will be oxidized. When the dissolved sulfate enters the Ordovician aquifer, the fresh karst water will be polluted.

Fig. 5 Piper diagram of all samples

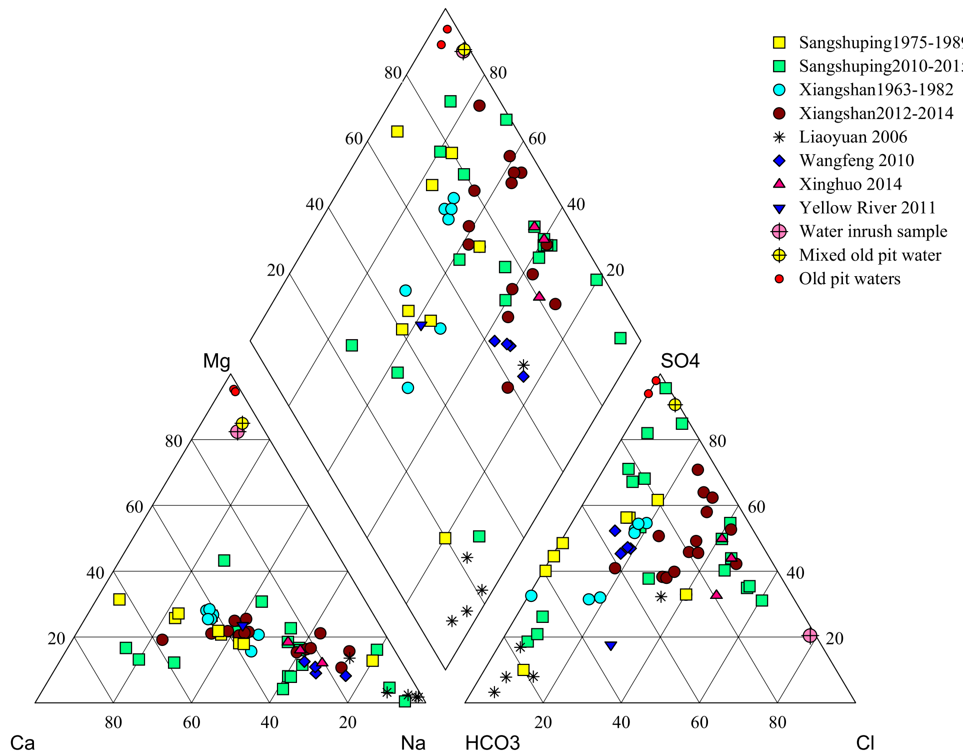


Table 4 Change in water compositions of the Ordovician limestone aquifer between 1979 and 2010 at the Xiangshan power plant

Time	Compositions (mg/L)			
	TDS	SO_4^{2-}	Cl^-	Ca^{2+}
Before 1986	776	312.06	88.622	99.83
In 1989	948	406.5	117.63	124.63
In 2000	1337	649.34	127.2	248.68

The Hancheng mining area has a long mining history. Over the past 40 years, many small coal mines operated irregularly, and coal mine water was discharged without purification, so a large quantity of old pit water entered the Ordovician limestone aquifer via mining-induced and structural fissures. Mixing with acidic, hypersaline, old pit water deteriorated the water quality. In addition, due to over-exploration and over-drainage, hypersaline groundwater flowed into the cone of depression, which also deteriorated the groundwater quality.

Evolution with Time

Coal mining can change both the quantity and quality of karst groundwater because of over-exploitation and over-drainage (Qiao et al. 2011). The arithmetic mean values of the concentrations of major ions in different years are listed in Table 5, which shows that from the late twentieth century to the early twenty-first century, the concentrations of major ions increased substantially, except for HCO_3^-, which decreased slightly. The TDS, SO_4^{2-}, and Cl^- increased by factors of ≈ 2.3, 3.1, and 4.7, respectively.

Vertical Evolution

The hydrogeochemical characteristics of the groundwater were the result of long-term water–rock interactions (Du et al. 2017; Li et al. 2014a, b, 2016a, b; Mu et al. 2016; Qian and Li 2011; Sun et al. 2017; Wu et al. 2015; Zhang et al. 2017). Hence, the groundwater chemistry was determined by the condition of the rocks, the minerals they contained, and their secondary changes. The aquifers of the O_2f^2, $O_2m_2^2$ and $O_2m_1^2$ Formations all have good water yield (Fig. 3). The O_2f^2 aquifer is comprised of pure limestone combined with a small amount of dolomite limestone and thin stratified marlstone. The $O_2m_2^2$

Table 5 Arithmetic mean values of the concentrations of major ions

Time	TDS (mg/L)	Compositions (mg/L)					
		$Na^+ + K^+$	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-
1963–1989	1098	141	135	44	295	78	333
2006–2015	2302	400	231	70	900	369	319

aquifer is a dolomitic limestone, with a total thickness of ≈ 100 m, and well-developed karst fissures. The $O_2m_1^2$ aquifer is a stratiform thick limestone bed, also with well-developed karst fissures. Several thin layers of gypsum, ≈ 1–2 mm thick, exist over and under the $O_2m_1^2$ aquifer.

Three water samples were collected from each aquifer using the same borehole; their main components are listed in Table 6. The TDS content and concentrations of major ions increased significantly from shallow to deep, whereas the pH and alkalinity slightly decreased. TDS can provide important information about the hydrodynamic process and reflect the regional hydrogeochemical features (Qiao et al. 2014). So, the significant increase of the TDS indicates poor water circulation in the deeper aquifer. With respect to the lithological condition of the $O_2m_1^2$ aquifer, the increase in SO_4^{2-} and Ca^{2+} concentration may be caused by gypsum dissolution. As more Ca^{2+} enters the groundwater, it caused oversaturation and precipitation of calcite, decreasing the HCO_3^- concentration and alkalinity. Finally, the water type changed from HCO_3–SO_4 to SO_4–Cl.

The SI values for calcite and dolomite, the main minerals of the O_2f^2 aquifer, are less than 0, which suggests well water circulation in the O_2f^2 aquifer (Table 3). The SI values for anhydrite and gypsum are much less than 0, since the O_2f^2 aquifer does not contain those minerals. In contrast, the $O_2m_2^2$ aquifer has an SI for calcite of 0.05, while dolomite is − 0.01, which indicates that the calcite is oversaturated and dolomite is nearly saturated. Since the $O_2m_2^2$ aquifer is mainly dolomite with a thin layer of gypsum underlying it, we infer that this is caused by calcite-replacing dolomitization reactions.

$$CaMg(CO3)_2 + Ca_2SO_4 \cdot 2H_2O = MgSO_4 + 2\ CaCO_3 \downarrow + 2\ H_2O$$

Gypsum dissolution increased the Ca^{2+} concentration, limiting the dissolution of Ca^{2+} from the dolomite, so while the $[Mg^{2+}]$ increased, the dolomite was replaced by calcite. This was verified by the fact that the corroded fissures had filled with calcite.

With respect to the $O_2m_1^2$ aquifer, both the calcite and dolomite were oversaturated, which implies slow water circulation. The gypsum is also nearly saturated, due to gypsum dissolution. All of the results inferred by the hydrogeochemical analysis are in accordance with the drilling records.

Horizontal Evolution

The Sangshuping mine is 0–4 km from the Yellow River, and the Xiayukou and Liaoyuan mines are about 5 km from the Yellow River. The mines in the south zone are about 10 km from the Yellow River. The water sample collected in the Wangfeng coal mine is approximately 5 km from the deep district and 10 km from the Yellow River. Table 7 lists the groundwater types of each coal mine, from which we can see the water in the mines close to the Yellow River are similar to the water in the Yellow River, while the water types of the mines in the south are different. The water of the Wangfeng mine is the SO_4–Cl(HCO_3)–Na type due to poor groundwater circulation. After 40 years of mining and mine water intrusion, the water of the Sangshuping mine is the same, while that of the Xiangshan mine is the SO_4–Cl–Na–Ca type.

Therefore, the groundwater in the northeast shallow area was, and is, influenced by the Yellow River along with water table variation. Generally speaking, the TDS is low in the northeast and high in the southwest. After 40 years of mining, such horizontal evolution features reflect the effects of

Table 7 Groundwater types of each coal mine

Location	Water type	Time
Yellow river	HCO_3–Na–Ca	2011
Sangshuping coal mine	HCO_3–SO_4–Ca–Na	1975–1989
	SO_4–Cl–Na–Ca	2010–2015
Wangfeng coal mine	SO_4–Cl(HCO_3)–Na	1984
	SO_4–HCO_3–Na	2010
Xiayukou coal mine	HCO_3–SO_4–Na	–
Liaoyuan coal mine	HCO_3–Na	2006
Magouqu coal mine	SO_4–HCO_3–Ca–Na	–
Xinghuo coal mine	Cl–SO_4–Na	2014
Xiangshan coal mine	SO_4–Cl(HCO_3)–Ca Na	1963–1982
	SO_4–Cl–Na–Ca	2012–2014

Table 6 Ordovician limestone groundwater compositions in aquifers at different depth

Aquifer	Compositions (mg/L)								Alkalinity (meq/L)	Temp (°C)	Water type
	TDS	Na^++K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	PH			
O_2f^2	684	191	39	22	139	97	382	8.0	6.45	20	HCO_3–Na SO_4–HCO_3–Na(Ca Mg) HCO_3–SO_4–Na(Ca Mg)
$O_2m_2^2$	2293	402	243	88	1008	105	276	7.5	4.898	22	SO_4–Cl–Na Ca
$O_2m_1^2$	4186	526	547	191	2007	716	234	7.3	3.837	25.3	SO_4–Cl–Ca Na

coal mining at least as much as it does the region's original tectonic and topographic characteristics.

Uncertainty Analysis

The limited number of interpolating points of groundwater table potentially introduces uncertainty to the groundwater flow field, but the water balance calculation in the Xiangshan coal mine can explain the flow field change. The increasing SI values of anhydrite, calcite, dolomite, gypsum, and halite in flow paths one and two indicates that groundwater should dissolve minerals along both flow paths, and corresponds to observations. The uncertainty of the volume of water draining from small illegal coal mines also affects the groundwater flow field, but since the mining depth of such mines are usually limited, they have little effect on the groundwater flow field of the Ordovician limestone aquifer.

The uncertainty of the hydrogeochemical evolutionary process in this study were affected by both the precision of data used and the uncertainties that affect each variable, along with the potential of human error in sampling, handling, and analysis. The chemical reactions, such as the calcite-replacing reactions, were inferred by the SI values of anhydrite, calcite, dolomite, gypsum, and halite at three different depths and the results inferred by the hydrogeochemical analysis can be verified by the corroded fissures filled with calcite. Therefore, the results of this study were judged to be tenable.

Conclusions

Before mining, the Ordovician limestone water was fresh in the shallow northeast area of the Hancheng mining area and hypersaline in its southwest and deep district, reflecting the tectonic structure. During mining, the groundwater flow field changed its hydrogeochemical character and the groundwater quality deteriorated. The cones of depression that formed caused groundwater to flow from the surrounding areas, including hypersaline water from the deep district. In addition, old, acidic pit waters were induced to flow into the limestone aquifer via mining-induced fissures and structural fissures. Measures should be taken as soon as possible to prevent continued deterioration of the Ordovician groundwater.

Vertically, the variation in the water of the O_2f^2, $O_2m_2^2$, and $O_2m_1^2$ aquifers indicates that water circulation in $O_2m_1^2$ was poorer than in O_2f^2 and $O_2m_2^2$. The SI of gypsum approaches saturation in the deeper water due to the dissolution of thin layers of gypsum that sandwich the $O_2m_1^2$ aquifer. The parallel Ca^{2+} and Mg^{2+} increases were caused by calcite-replacing dolomite reactions.

Other regions with similar hydrogeological conditions can use these results as a reference. The potential deleterious impacts of mining on the groundwater quantity and quality should be evaluated before mining, and relevant precautionary measures should be taken.

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