Heavy metals in coal mine groundwater responding to mining activity: concentration, temporal variation and speciation

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Abstract

Six groundwater samples were collected from four aquifers in Renlou coal mine, northern Anhui Province, China, and concentration, temporal variation and speciation of five heavy metals (Cr, Cu, Ni, Pb and Zn) were analyzed. The results of physicochemical parameters and major ions showed that the selected groundwater were representative samples of Quaternary aquifer (QA), coal measure aquifer (CA), Taiyuan limestone aquifer (TA) and Ordovician limestone aquifer (OA). Cr, Ni and Zn increased in the four aquifers from 2002 to 2014, but Pb decreased from 2006 to 2014. Cu concentration increased in QA and TA, but decreased in CA and OA. Although all monitoring results met the standards recommended by WHO and GB5749-2006, Cr and Cu in some groundwater samples exceeded GB/T 14848-93, especially in CA. Soluble metallic hydroxides were the dominant species of heavy metals in QA, while free ions were the main species in TA and OA. Excepted Ni^{2+} and Zn^{2+}, $CuCO_3(aq)$ and $PbCO_3(aq)$ were the dominant species of Cu and Pb in CA, respectively, indicating more CO_2 had been flooded and dissolved in groundwater from ground atmospheric environment. The enhanced concentration and special dominant species of heavy metals revealed that the 'closed' characteristics of CA in Renlou coal mine might have been broken due to coal mining activity.

Key words: coal mine, groundwater, heavy metals, mining activity

INTRODUCTION

Ninety per cent of China's shallow groundwater is polluted, and an alarming 37% is so foul that it cannot be treated for use as drinking water (Qui 2011). In the mining areas, water pollution problems are also becoming a grave problem in water resources management and sustainable exploitation of water resources. Human exploitation of water resources in the mining regions is facing big challenges in terms of water quality and water quantity. Seventy-one per cent of 96 key state-owned mines are somewhat short of water, and 40% of them suffer from serious water shortages, because Chinese water resources are largely located in South China, while most coal lies in the north (Wang et al. 2013); moreover, the water quality of the mining areas is deteriorating, and excavation works have become a key factor in causing groundwater pollution. Thus, quality- and quantity-induced water shortage has come to be the prime factor, restricting the sustainable development of the coal mine areas.

Heavy metals (HMs) have drawn mounting concerns owing to their toxicity, persistence and bioaccumulative in the natural environment (Pekey et al. 2004). Contamination with heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) is a worldwide environmental problem (Muhammad et al. 2011), and has drawn mounting concerns in

recent decades. Besides natural processes (i.e. weathering, erosion of bed rocks, ore deposits and volcanic activities), HMs in water could also be derived from anthropogenic activities, (i.e. mining, smelting, industrial influx, wastewater irrigation and agriculture activities) (Demirak *et al.* 2006; Chanpiwat *et al.* 2010; Muhammad *et al.* 2010; Khan *et al.* 2013), and groundwater quality is increasingly threatened by anthropogenic activities through disposal of urban and agricultural chemicals and industrial wastes (Hu *et al.* 2015), where mining is an important source of trace metals (Cantor 1997). Investigation in terms of HMs in coal mine groundwater is essential to water quality monitoring and controlling, and it is very important to local residents who usually use groundwater as a direct drinking-water source.

In addition, to analyze the HMs in different aquifers might give a new approach to better understand the influencing mechanisms of coal mining activity to groundwater. In the Renlou coal mine, previous studies were conducted considering familiar hydrochemical indices, rare earth elements, trace elements, isotopes composing characteristics, and flow numerical simulation of groundwater in different aquifers, mainly to research water source discrimination (Sun & Gui 2012), chemical evolution (Gui & Chen 2007; Gui *et al.* 2007; Sun *et al.* 2011; Chen *et al.* 2011), and mining disturbance (Chen *et al.* 2008, 2012; Yin *et al.* 2013). However, to our knowledge, no study has been undertaken to understand the influence of coal mining activity, considering HMs and their species, in the Renlou coal mine or even other coal mines in the world. To address this critical knowledge gap, the present study was conducted with two objectives as follows: (1) to determine the HMs concentration (Cr, Cu, Ni, Pb and Zn) in groundwater collected from different aquifers, and to contrast them with water quality guidelines and our previously samplings results; and (2) to calculate HMs species through computation simulation, and try to analyze the distribution mechanisms in different aquifers and the influencing of coal mining activity to HMs in groundwater.

MATERIALS AND METHODS

Geological backgrounds

The Renlou coal mine is located at the border of Suixi and Mengcheng counties in the southwest of Suzhou city, Anhui Province (Figure 1(a), 1(b) and 1(c)), belonging to the Linhua mining area. The coal mine lies adjacent to the Sutuan coal mine bounded by the Jiegou fault on the north and the Xutuan coal mine bounded by the fault F8 on the south (Figure 1(d)) (Guo *et al.* 2014). As an independent hydrogeological unit, the mine has simple geological structure and appears as a monoclonal structure, indicating it usually has weak hydraulic connection with surrounding coal mines (Duan 2004; Yin *et al.* 2013; Guo *et al.* 2014). Built in 1985 and operated in 1997 (Chen *et al.* 2013), the Renlou coal mine is 9.8–14 km long from north to south and 1.2–3.5 km wide with a total area of about 43 km^2 (Cai 2006; Sun *et al.* 2011; Gui & Sun 2011), where the average temperature is 14–15 °C, average annual rainfall is 750–900 mm, and annual evaporation is 800–1,300 mm.

The basement coal field is composed of Mesoproterozoic epimetamorphic rock series and deep metamorphic rock series of the Archaeozoic and early Proterozoic Era, which is a stable platform type, sedimentary from the floor to cover layer (upper Proterozoic to Permian), with 3,000 m total thickness, while the Middle-Upper Ordovician to Lower Carboniferous are lost. Dominated by the faults, the buried depth of bedrock surface increased from north to south in this mining area, by 200 m in the north and 280 m in the south (Sun *et al.* 2011). The Renlou coal mine is a completely concealed coalfield, and the coal-bearing stratum includes Shanxi formation and Shihezi formation, containing 10 coal seams (groups) totally, of which 3_1, 5_1, 7_2 and 8_2 were the main exploiting coal seams, with an average total thickness of 7.37 m (Duan 2004; Yan *et al.* 2004). The geological reserves in the Renlou coal mine are 2.74×10^8 tons, and the exploitable reserves are 1.29×10^8 tons.
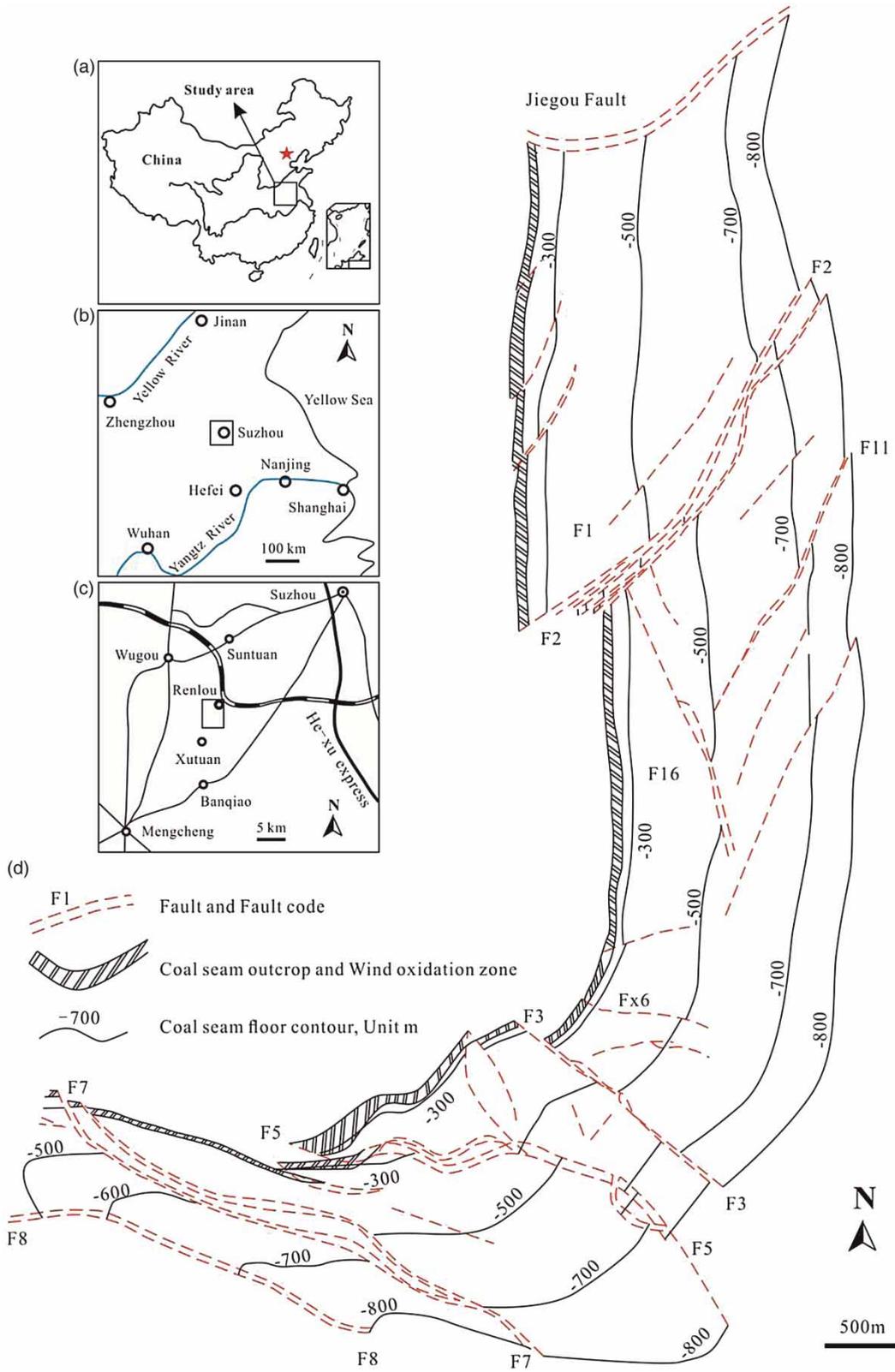
Figure 1 | Location and tectonic sketch of the Renlou coal mine.

The hydrogeological condition of the coal mine was identified as a simple type at the beginning of mine constructing, but it shifted to an extremely complex type just after a serious water inrush occurred in 1996 (Cai 2006). According to hydro- and geological conditions, aquifers in the Renlou

coal mine subdivided into four parts, including QA or the 4th aquifer in unconsolidated formation (UF), CA, TA and OA (Yan *et al.* 2004; Cai 2006; Gui & Chen 2007; Gui & Sun 2011; Sun & Gui 2012), where the aquosity characteristics were weak ($q = 0.0094–0.028$ L/s m), poor ($q = 0.0087$ L/s m) moderate ($q = 0.1243–0.1558$ L/s m) and enrich ($q = 2.712$ L/s m), respectively.

Sampling collection

A total of six groundwater samples were collected from four aquifers in the study area on the 16 July 2014. The sampling numbers were 2, 2, 1 and 1 in UF, CA, TA and OA, respectively. The sampling information, including sampling aquifer, water level elevation and sampling location, is listed in Table 1. Unmixed and pure water samples were required in this study. The samples were selected under the coal mine preferentially, such as the water samples from CA (RL-3 and RL-4), and TA (RL-5) were sampled directly in the mine inflow points. When sampling under the coal mine was not convenient, a tailor-made sampler was used to collect groundwater samples from observation wells above ground, which were constructed for pumping test and groundwater regime observations of different aquifers, for example, the water sample numbered RL-2 in UF was collected by the above method. Moreover, water samples RL-1(UF) and RL-6 (OA) were collected directly from the water supply wells of Renlou coal mine.

Table 1 | Information of sampling sites in the Renlou coal mine

Sampling site	Aquifer	Water level elevation (m)	Location
RL-1	UF (2nd–3rd aquifer)	Unknown	14[#] water supply well
RL-2	QA or the 4th aquifer of UF	–93.5	1[#] observation well
RL-3	CA	–510	2014–2017 hole in transportation roadway (floor of 10th coal seam)
RL-4	CA	–538	II 5110 mechanical roadway (roof of 5th coal seam)
RL-5	TA	–843	–720 south roadway
RL-6	OA	Unknown	6[#] water supply well

Polyethylene bottles (2.5 L) were used to collect the groundwater samples and before collection all the polyethylene bottles were washed three times with double deionized water in the laboratory and the aimed water during field sampling, and the gas in the bottles was expelled by filling up. The water was then emptied over the source and refilled in the same manner. Two bottles of groundwater (5 L) were sampled in each sampling site, and one bottle for major ions examination, while the other one was used for trace elements detection. All the samples were transported to the laboratory within 24 h and stored in a refrigerator at 4 °C for further analyses.

Chemical analysis procedures

The main physicochemical parameters, including water temperature (T), total dissolved solids (TDS), pH and electrical conductivity (EC), were determined on the spot with a portable instrument (HM, COM-100). Major ions ($K^+ + Na^+$, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) were measured in the testing center of the Anhui province bureau of coal geology. Trace elements (Cr, Ni, Cu, Zn, Pb, etc.) were assayed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a) in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). Before trace elements analysis, each groundwater sample was filtered through 0.45 μm

filter paper and acidified with ultrapure HNO_3 (2 mL/L) to keep pH at <2. Deionized water (18 MΩ cm), super-pure chemical reagents (HNO_3 and HF) and multi-element standards (Claritas PPT, SPEX) were used during the analysis procedure, and one standard sample was inserted repeatedly after eight water samples had been finished for quality control.

Statistical analysis

Microsoft Excel 2010 and IBM SPSS Statistics 19 were used to perform statistical analysis. Corel-DRAW X7 and OriginPro 8 were applied for graphic processing and analysis. AquaChem software was used to analyze the hydrochemistry types, and Visual MINTEQ 3.1 software was used in order to estimate the HMs speciations, which are dominant in the ground water samples (Noorain *et al.* 2014). Hierarchical cluster analysis (HACA) was carried out to explain samples clustering.

RESULTS AND DISCUSSIONS

Physicochemical parameters

Physicochemical parameters values (T, pH, EC and TDS) of the groundwater samples collected from different aquifers are represented in Table 2.

Table 2 | Physicochemical parameters and major ions of the groundwater in the Renlou coal mine

Sampling site	RL-1	RL-2	RL-3	RL-4	RL-5	RL-6
T (℃)	25.7	26.2	24.4	24.2	25.4	27.9
pH	7.6	10.6	10	8.3	6.9	7.4
EC (μS)	2,060	2,600	980	2,980	4,780	3,270
TDS	1,460	1,910	677	2,200	3,690	2,443
$K^+ + Na^+$	217.21	279.92	702.87	569.94	426.7	304.87
Ca^{2+}	99.58	76.91	18.53	13.76	245.71	208.07
Mg^{2+}	85.67	12.76	15.63	6.87	146.55	87.39
Cl^-	264.25	490.75	811.09	643.47	957.62	549.09
SO_4^{2-}	352.33	15.64	30.46	23.87	527.26	442.47
HCO_3^-	407.12	0	441.78	394.4	300.22	374.05
CO_3^{2-}	0	62.57	62.42	27.53	0	0

Note: Apart from T, pH and EC, the unit of the other parameters was mg/L.

As shown in Table 2, temperature varied from 24.2 to 27.9 °C. In previous studies in this area (Duan 2004; Gui & Sun 2011), the temperature increased obviously with sampling depth as a whole, due to the geothermal gradient of the earth. However, the normal phenomenon was not well observed in this investigation, especially the water samples collected from UF, of which the temperature was even higher than CA and TA, and this was mainly because the sampling activity was conducted in the hottest time (July) in the study area. Under these conditions, shallow groundwater may be more affected by strong solar radiation than deep groundwater.

pH was varied from 6.9 to 10.6. Neutral to high alkaline pH (7.6 in RL-1 and 10.6 in RL-2), and moderate to high alkaline pH (8.3 in RL-4 and 10 in RL-3) were found in UF and CA, respectively, while pH values were all neutral in TA (6.9 in RL-5) and OA (7.4 in RL-6). Previous studies also showed that the pH value was alkaline, especially in QA and CA in the Renlou coal

mine (Gui & Sun 2011; Sun *et al.* 2011). In this study, the pH value of RL-2 and RL-3 had exceeded the guideline limit of 6.5–8.5 recommended by WHO (2011) and GB5749-2006 (MH & SAC 2006), and according to Quality Standards for Groundwater in China (GB/T 14848-93) (BQTS 1994), its water quality belonged to Class V (pH < 5 or pH > 9), indicating it was no longer suitable for drinking directly, or for using in industrial and agriculture activities without any treatment. Moreover, EC varied from 980 to 4,780 μS, and TDS ranged from 677 to 3,690 mg/L. Except for RL-3, TDS in all groundwater samples were all over the guideline value of 1,000 mg/L (MH & SAC 2006; WHO 2011). Negative correlations were observed between pH and TDS ($r = -0.646$, $p = 0.166$) (Figure 2), which was consistent with previous studies (Bi *et al.* 2012; Oyem *et al.* 2014).
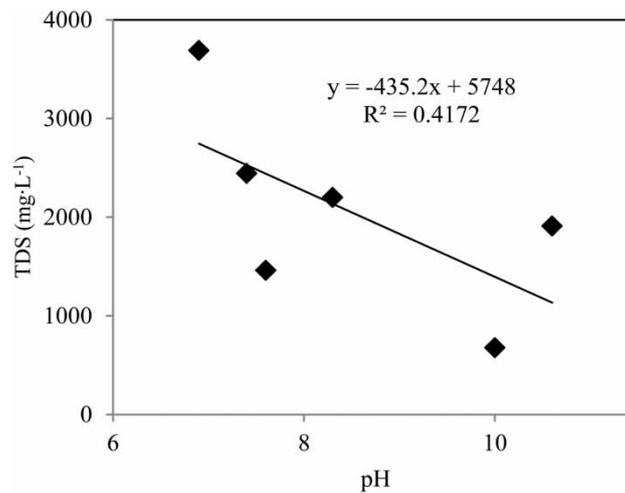

Figure 2 | Linear relation between pH and TDS in groundwater of the Renlou coal mine.

Considering TDS in RL-3 (677 mg/L) was obviously lower than normal level 2,016–3,223 mg/L (Gui *et al.* 2007; Sun *et al.* 2011; Sun & Gui 2012), it was doubtful whether it was really a 'pure' water sample of CA. Performed and calculated with Ward's method and Euclidean distances after standardized using *z*-scores, HACA results for physicochemical parameters and major ions showed that RL-3 was obviously different from the other samples (Figure 3). As illustrated in Table 1, since
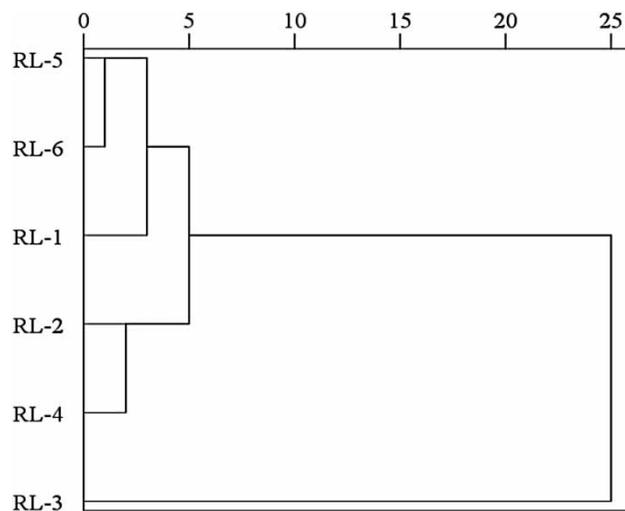

Figure 3 | Hierarchical dendrogram for cases obtained using Ward's method.

RL-3 was sampled from the floor of the 10th coal seam, together with the hydrological and geological condition of Renlou coal mine, RL-3 likely had been mixed by 'downstairs' groundwater from OA. Thus, the doubtful water sample RL-3 collected from CA was no longer considered for the comparison analysis of HMs in different aquifers.

Major ions hydrochemistry type

The concentration of major ions ($K^+ + Na^+$, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}) are also provided in Table 2. The relative error between anion and cation was calculated in each groundwater sample to examine its ion balance (Shen *et al*. 1993), and the results were all <5%, indicating the data were reliable. The hydrochemistry types of RL-1 and RL-2 in UF were Cl·SO$_4$–Na·Mg·Ca type and Cl–Na·Ca type, respectively. RL-3 and RL-4 were both Cl·HCO$_3$–Na type, while RL-5 and RL-6 all belonged to Cl·SO$_4$–Na·Mg·Ca type (Figure 4). Duan (2014) revealed that the hydrochemistry types of QA and CA were Cl·SO$_4$–Ca·Na type and Cl·HCO$_3$–K + Na type, respectively, while TA and OA were both Cl·SO$_4$–Na·Ca type, and the summaries were nearly all consistent with our observations in this study. So, as mentioned above, except RL-3, all the other groundwater samples had good representation in each aquifer in the Renlou coal mine.
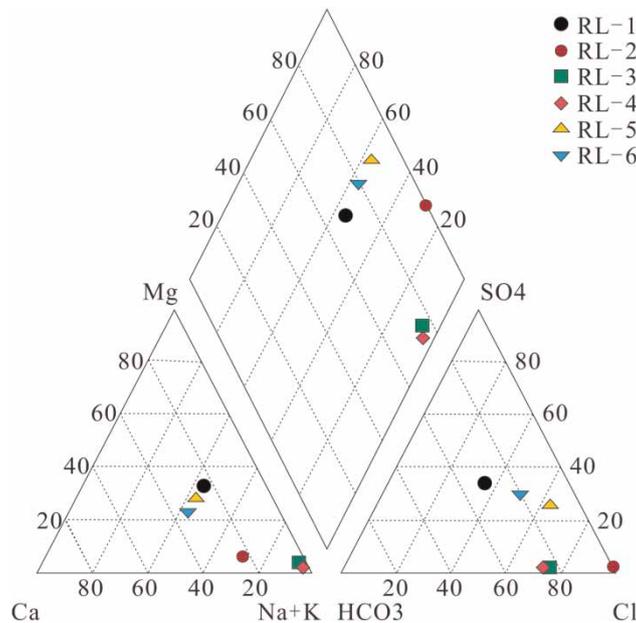

Figure 4 | Piper chart of groundwater samples in the Renlou coal mine.

Heavy metals concentrations

The HMs contents of groundwater are shown in Table 3, and water quality guidelines and our historical data (2002–2011) are also presented for comparative analyses. The historical HMs contents in our previous studies were all measured with ICP-MS in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). As mentioned above under section Geological backgrounds, four main aquifers (QA, CA, TA and OA) were found in the Renlou coal field. To compare the temporal variation of HMs in these four aquifers, RL-1 sampled from the 2nd–3rd aquifer of UF was not selected for comparative analyses. In other words, only RL-2, RL-4, RL-5 and RL-6 were, respectively, chosen as representative samples in QA, CA, TA and OA in this section.

Table 3 | HMs concentrations in groundwater of the Renlou coal mine (µg/L)

Aquifers	Sampling time	n[a]	Cr	Ni	Cu	Zn	Pb
QA	2002.10	1	1.06	1.10	0.26	–[b]	nd[c]
	2006.8	4	4.20	1.94	17.88	27.36	0.39
	2014.7	1	3.28	1.73	1.89	49.38	0.07
CA	2006.8	3	8.57	0.55	43.23	2.70	0.15
	2009.11	7	3.27	1.30	8.03	0.61	0.11
	2011.4	4	3.16	1.18	21.73	2.42	0.43
	2014.7	1	10.81	0.93	3.11	10.02	0.10
TA	2002.10	1	7.66	2.19	0.08	0.72	nd
	2006.8	5	5.76	3.52	21.35	6.10	0.17
	2009.11	4	1.18	0.64	4.78	1.08	0.02
	2011.5	1	1.9	0.46	18.9	2.39	1.53
	2014.7	1	8.56	3.54	2.83	11.82	0.05
OA	2002.10	1	1.77	–	–	–	nd
	2006.8	1	1.60	0.87	2.17	4.76	0.85
	2014.7	1	5.78	2.86	2.03	7.04	0.04
WHO (2011)			50	20	1,000	1,000	10
GB5749-2006			50	20	1,000	1,000	10
GB/T 14848-93	Class I ≤		5	5	10	50	5
	Class II ≤		10	10	50	500	10
	Class III ≤		50	50	1,000	1,000	50

[a]Sampling number.
[b]Below detection limit.
[c]No determination data.

In general, Cr, Ni and Zn all increased in the four aquifers from 2002 to 2014. Cr increased from 1.06 to 3.28 µg/L in QA, 8.57–10.81 µg/L in CA (from 2006 to 2014), 7.66–8.56 µg/L in TA and 1.77–5.78 µg/L in OA, respectively. Ni increased from 1.10 to 1.73 µg/L in QA, 0.55–0.93 µg/L in CA (from 2006 to 2014), 2.19–3.54 µg/L in TA and 0.87–2.86 µg/L in OA, respectively. Zn increased from 27.36 to 49.38 µg/L in QA (from 2006 to 2014), 2.70–10.02 µg/L in CA (from 2006 to 2014), 0.72–11.82 µg/L in TA and 4.76–7.04 µg/L in OA (from 2006 to 2014), respectively. However, the variation tendency of Pb decreased from 2006 to 2014, from 0.39 to 0.07 µg/L, 0.15–0.10 µg/L, 0.17–0.05 µg/L and 0.85–0.04 µg/L in QA, CA, TA and OA, respectively. Cu concentration increased in QA and TA, while it decreased in CA and OA. All the monitoring results met the standards recommended by WHO and GB5749-2006 (MH & SAC 2006; WHO 2011), however, Cr and Cu in some groundwater samples had exceeded Class I and Class II of GB/T 14848-93, especially in CA, where the maximum value of Cr (10.81 µg/L) and Cu (43.23 µg/L) were obtained. Moreover, in 2014, the peak values of Cr (10.81 µg/L), Cu (3.11 µg/L) and Pb (0.10 µg/L) were also obtained in CA.

In our previous studies, compared to the other aquifers, the worst water quality was observed in CA, which might result from the mining activities (Lin et al. 2014a), and Cr was also found as the primary control target for environmental health risk management in this study area (Lin et al. 2014b). Although the contents of selected HMs were not very high in the Renlou coal mine, their concentration tended to increase as a whole. Hao et al. (2015) also pointed out that HMs (Hg, Fe, Zn, Cr and Mn) contents in karst groundwater increased distinctly during the nearly 30 years mining activities in the Fengfeng coal mining area. Coal mining activities can not only destroy the aquifer structure, it can decrease the water level, change the flow field or even influence the whole groundwater system (Liu 2005, 2009; Yin et al. 2013), but it can also affect groundwater quality in the local areas (Wang

2011; Xie 2012). Previous studies in the Renlou coal mine revealed that the groundwater flow and environment evolution in QA and CA had been influenced by coal mining activity from the perspectives of numerical simulations (Yin *et al.* 2013), hydrochemical (Gui *et al.* 2007; Chen *et al.* 2012) and isotopes composing characteristics (Chen *et al.* 2008, 2013). CA is a relatively 'closed' aquifer in the Renlou coal mine area, where groundwater has weak hydraulic connections with meteoric waters (Chen *et al.* 2008, 2013). The enhanced concentration of HMs in groundwater of CA and their increased temporal variation overall indicated the groundwater quality had been possibly influenced by coal mining activities, and this conclusion was confirmed with the previous studies.

Heavy metals speciation

HMs toxicity and biotransformation are certainly controlled by species distribution in aqueous solution, which is affected by the oxidation and reduction process (Noorain *et al.* 2014). To well understand the HMs species distribution and their concentration change mechanism of groundwater in different aquifers responding to mining activity, Visual MINTEQ 3.1 was applied to calculate the HMs speciation in the Renlou coal mine. Although chemical species are usually explained including valence state, compound state, combined state and structure state (Tang 1985), however, the valence state of the HMs was not considered because Cr^{6+}, Ni^{2+}, Zn^{2+} and Pb^{2+} were selected as the dominant valence state of the selected HMs in natural waters.

RL-1 was sampled from the 2nd–3rd aquifer of UF, which was 'upstairs' of the 4th aquifer of UF, not very close to CA and may easily disturbed by complex humans activities. So, only RL-2 collected from QA was chosen to compare with RL-4 (CA), RL-5 (TA) and RL-6 (OA). The analysis results showed that Cr^{6+} mainly existed in the form of CrO_4^{2-} (about 100%) in the four groundwater samples. The
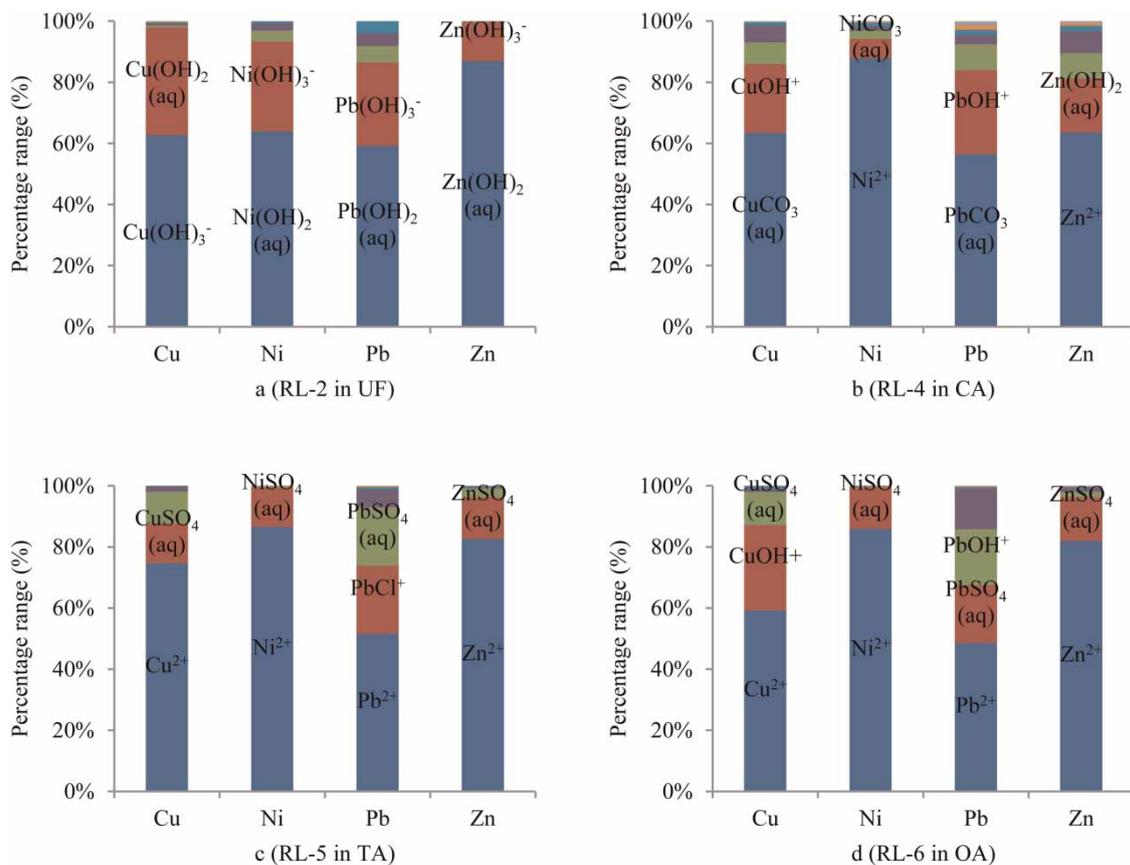

Figure 5 | Percentage of HMs species distribution in the groundwater of the Renlou coal mine.

dominant species of Cu, Ni, Pb and Zn were all soluble metallic hydroxides in QA (Figure 5(a)), where the percentages of $Cu(OH)_3^-$, $Ni(OH)_2(aq)$, $Pb(OH)_2(aq)$ and $Zn(OH)_2(aq)$ were 62.68%, 63.93%, 59.24% and 86.96%, respectively. This was mainly due to the high pH value 10.6 in RL-2. In CA (Figure 5(b)), free ions Ni^{2+} and Zn^{2+} were the main species of Ni and Zn, accounting for 87.83 and 63.53%, while Cu and Pb existed in the form of solubility carbonate combined state $CuCO_3(aq)$ (63.46%) and $PbCO_3(aq)$ (56.39%). However, overall, free ions were the dominant species of Cu, Ni, Pb and Zn in TA (Figure 5(c)) and OA (Figure 5(d)).

Carbonate and bicarbonate ions were mainly the dissolved product of carbonate minerals in groundwater, and carbonate rock weathering is very sensitive to soil CO_2 change (Li et al. 2010). Previous studies had revealed that because of coal mining activities, including coal exploiting and excavation works, the 'closed' characteristics of CA had been certainly broken in the Renlou coal mine, and thus CO_2 flooded in and dissolved in the groundwater, which made the carbonate ion and bicarbonate ion increase (Gui et al. 2007). The mechanism is described using the following formula:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \qquad (1)$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad (2)$$

When the concentration of dissolved CO_2 enhanced, according to Equations (1) and (2), the chemical reactions tended to the right, which made carbonate and bicarbonate ions increase, which then had more chance to combine with other cations, including the free ions of HMs. Activity of pH/Eh affects the solubility and mobility of HMs (Hitchon 2006; Noorain et al. 2014), weak oxidative properties were both observed in QA (Eh between 56 and 78 mV) and CA (Eh between 45 and 57 mV), while reduction property was obtained in TA (Eh between –60 and –300 mV) in the Renlou coal mine (Gui & Sun 2011). Moreover, since QA was nearly an 'open' system, CA was a relatively 'closed' system, while TA and OA were 'closed system' (Gui & Sun 2011; Sun et al. 2011; Sun & Gui 2012) in the Renlou coal mine. The reasons why free ions were both the dominant species of the selected HMs in TA and OA were mainly because of their common oxidation and deoxidization status.

CONCLUSIONS

In previous studies, familiar hydrochemical indices, isotopes composing characteristics and numerical simulation were employed to analyze the influence of coal mining activity to groundwater in the Renlou coal mine. However, the HMs (Cr, Ni, Cu, Zn and Pb) in different aquifers were firstly selected to explain whether the groundwater samples had been affected by coal mining activity in our study, from the perspectives of temporal variation and species distribution. Based on the analysis of geological background, physicochemical parameters and major ions, groundwater samples named RL-2, RL-4, RL-5 and RL-6 were firstly identified to represent the groundwater samples in QA, CA, TA and OA as the 'pure' samples, respectively.

Except for Pb, HMs (Cr, Ni, Cu and Zn) contents were enhanced and increased overall from 2002 to 2014, especially in CA, indicating water quality might have been affected by coal mining activity. Free ions were the dominant species of the selected HMs in a 'closed' system (TA and OA) due to common reduction property of groundwater, while soluble metallic hydroxides were the main species of HMs in a relatively 'open' system (QA), where high pH existed and the aquifer was easily influenced by complex human activities. In CA, the main species of Ni and Zn were $CuCO_3(aq)$ and $PbCO_3(aq)$, respectively, indicating more CO_2 had been flooded and dissolved in groundwater from

the ground atmospheric environment, moreover, the hydraulic connection between CA and QA might have been enhanced. In general, from the perspectives of concentration, temporal variation and speciation, the 'closed' characteristics of CA in the Renlou coal mine might have been broken due to coal mining activity, where oxidation and deoxidization status had been changed. Moreover, the analysis of concentration and speciation of HMs in groundwater of different aquifers might provide a possible method for water source discrimination in future studies, which is extremely important for coal mine production and safety.

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