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Research Article

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Heavy metals in groundwater from the coal bearing aquifer in northern Anhui Province, China: Concentrations and usability

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ABSTRACT

Water shortage is serious in the coal mining area of China, and the utilization of waste water during coal mining is considered to be a right choice for solving this issue. For tracing the hydro-chemical conditions of the groundwater from the coal bearing aquifer, thirty-five groundwater samples have been analyzed for heavy metal concentrations. The results suggest that either the concentrations or spatial distributions of the eight kinds of heavy metals (Pb, Cd, Cu, Ni, Cr, Zn, Fe and Mn) vary significantly. Fe, Ni and Mn are the dominant ones among these metals. Statistical analyses indicate that weathering of metal minerals, adsorption by iron hydroxides and dissolution of carbonate are responsible for these variations. Moreover, in comparison with the Chinese groundwater quality standards, the groundwater can be used for drinking if their Cd and Fe can be treated before application, whereas all of heavy metals except for Cu and Zn should be noticed in comparison with the standards of World Health Organization.

Key words: Groundwater, Heavy metals, Quality, Coal mine, Waste water.

INTRODUCTION

China is a coal consumption-based country. However, the water shortage in the coal mining area is a problem we have to face to, especially in the north China [1]. Previous studies revealed that more than 70% of the coal mining areas are facing the problem of water shortage and 40% of them are serious [2-4]. Therefore, increasing the utilization rate of the waste water during coal mining is considered to be a right choice for solving the problem of water shortage in the coal mining area [1], and a large number of studies have been paid towards the recycling technologies [5-7]. However, the study related to the natural condition (e.g. chemical and physical) of the waste water in the coal mining area is limited.

Five kinds of water are considered to be sources of the waste water in the coal mining area: atmospheric precipitation, surface water, groundwater from the deep aquifer, water related to fault and water from mined out area [1]. Among these water sources, the groundwater from the deep aquifers, especially the coal bearing aquifer, is considered to be the main source of the waste water, because the water from it is the first threaten people need to face during coal mining.

Because of their importance (either safety and environmental related), the groundwater from the deep aquifers have long been concerned by hydrologists and a large number of studies have been processed, especially the hydro-chemical studies, and most of them are concentrated in major ion concentrations and stable isotopes [8-10]. However, another important aspect, the heavy metals in the groundwater, which is considered to be important in environmental studies, has not been well determined.

In this study, thirty-five groundwater samples from the coal bearing aquifer in four different coal mines in northern Anhui Province, China have been collected and measured for their heavy metal concentrations (including Pb, Cd, Cu, Ni, Cr, Zn, Fe and Mn), and the usability of these groundwater has been discussed based on the comparison with

Chinese and WHO standards, which will be useful for the utilization and management of the groundwater resources in the area.

EXPERIMENTAL SECTION

Site Description

The study area is located in the northern Anhui Province, China (Fig.1). The area is one of the most important coal producing bases in China with its rich coal resources. The total mining area is 30000 km^2 and there are two large coal mining enterprises in the area: the Wanbei Coal-Electricity Group Co., Ltd and the Huaibei Mining Group, and the coal production in the area are more than 20 million tons per year.

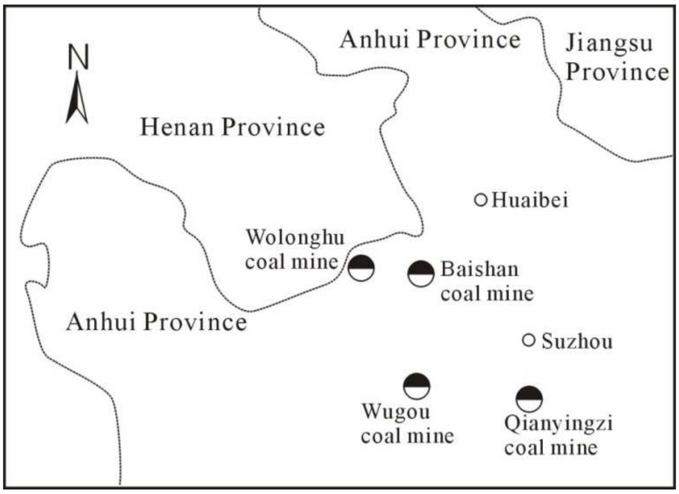

Fig.1: Location of the study area

Previous investigation revealed that there are three main aquifer systems related to coal mining in the area: the loose layer aquifer system, the coal bearing sandstone aquifer system, the limestone aquifer. The groundwater from the coal bearing sandstone aquifer system is the main contribution for the waste water during coal mining because they are included in the same strata with coal. Before coal mining, they should be firstly discharged. In most cases, the water storage in the aquifer system is limited. As to their wall rock compositions, sandstone, siltstone and mudstone are the main rock types, to a lesser extent, limestone.

Sampling and Analysis

A total of thirty-five groundwater samples from the coal bearing aquifer system in four different coal mines (7- Wugou coal mine; 8- Qianyingzi coal mine; 12- Wolonghu coal mine; 8- Baishan coal mine) in northern Anhui Province, China have been collected between June and August, 2012. Water samples were filtered through 0.45 μm pore-size membrane and collected into a 2.0L polyethylene bottles that had been cleaned in the laboratory, and immediately acidified to pH < 2 by HNO_3 for prevention of element precipitation and/or adsorption by the bottle. Then the samples were sent to the laboratory for analysis in 24 hours.

Analytical processes were taken place in the Engineering and Technology Research Center of Coal Exploration in Anhui Province. Atomic absorption spectrometer (AAS) has been applied for analysis of eight kinds of heavy metals (Pb, Cd, Cu, Ni, Cr, Zn, Fe and Mn). Calibration curves were obtained using a series of varying concentrations of the standards for the metals, all of the eight calibration curves were linear with a correlation coefficient higher than 0.99.

RESULTS AND DISCUSSION

Metal Concentrations

The analytical results are listed in Table-1. As can be seen from the table, the concentrations of Pb, Cd, Cu, Ni, Cr and Zn are 6.21-49.0, 1.26-9.07, 2.75-68.3, 19.0-393, 0.068-47.4 and 30.3-92.7 ug/l, respectively. Their mean concentrations are 15.7, 4.68, 13.7, 92.7, 5.41 and 52.3 ug/l, respectively. And following the order of Ni>Zn>Pb>Cu>Cr>Cd. However, the groundwater samples show much higher Fe concentrations than other seven kinds of heavy metals, their Fe concentrations are 535-1158 ug/l (mean= 579 ug/l). Moreover, the groundwater samples have variable Mn concentrations (1-882 ug/l, mean= 68 ug/l).

It is also noticed that the groundwater samples from different coal mine have variable concentrations of heavy metals (Fig.2). The highest mean concentrations of Pb, Cd, Cu, Ni, Cr, Zn and Fe are observed in the Qianyingzi coal mine, whereas the highest mean Mn concentration is observed in the Wolonghu coal mine. Comparatively, the lowest mean concentrations of Pb, Cd, Ni and Zn are identified in the Baishan coal mine, and the lowest Cu and Cr concentrations are observed in the Wolonghu coal mine, the lowest Fe and Mn concentrations are identified in the Wugou coal mine. Because most of these heavy metals are considered to be originated from the water rock interactions, most of the heavy metals show highest concentrations in the Qianyingzi coal mine are most probably related to its condition that it is the newest coal mine among the four ones, and the groundwater in the aquifer is relatively "closed" with no significant recharge from other aquifers (e.g. limestone aquifer that can increase the concentration of Mn). The highest Mn concentration of groundwater in the Wolonghu coal mine is consistent with its mining status that the coal bearing aquifer in the coal mine has been affected by other aquifers. Moreover, the lowest heavy metal concentrations in the Baishan coal mine is also an indication of "open" condition that the coal bearing aquifer has been affected by other aquifers.

TABLE-1 Heavy metal concentrations

ID	Pb (ug/l)	Cd (ug/l)	Cu (ug/l)	Ni (ug/l)	Cr (ug/l)	Zn (ug/l)	Fe (mg/l)	Mn (mg/l)
WG-1	13.292	4.172	13.841	72.698	6.085	57.734	0.545	0.005
WG-2	15.968	5.004	16.105	71.731	4.183	62.824	0.553	0.004
WG-3	19.102	5.317	11.625	70.437	3.674	53.044	0.555	0.001
WG-4	17.465	5.158	13.683	71.081	3.920	57.727	0.554	0.002
WG-5	15.509	5.523	22.850	72.058	2.790	77.695	0.558	0.006
WG-6	15.236	4.639	13.762	71.885	4.884	57.731	0.549	0.003
WG-7	17.511	5.160	13.804	71.083	3.926	57.865	0.554	0.002
QYZ-1	11.510	3.884	15.719	95.585	7.585	46.762	0.546	0.003
QYZ-2	16.850	4.532	3.415	34.612	0.731	60.427	0.562	0.005
QYZ-3	30.818	8.056	44.798	259.006	29.755	57.280	0.562	0.005
QYZ-4	49.035	9.068	68.252	393.188	47.350	60.767	0.592	0.006
QYZ-5	12.104	3.786	8.615	59.224	1.385	92.669	1.158	0.015
QYZ-6	7.739	3.026	3.212	32.380	0.068	43.968	0.540	0.005
QYZ-7	29.444	8.874	4.582	100.845	1.441	48.707	0.535	0.005
QYZ-8	26.074	7.075	25.530	197.062	19.231	60.395	0.591	0.050
WLH-1	11.723	4.338	3.738	99.917	1.072	50.473	0.554	0.005
WLH-2	11.794	4.087	2.753	109.023	3.331	46.549	0.575	0.002
WLH-3	17.460	4.911	6.593	61.298	1.560	56.665	0.565	0.066
WLH-4	21.277	6.570	11.834	38.087	2.444	61.561	0.582	0.860
WLH-5	26.004	5.559	11.628	37.606	2.269	63.617	0.577	0.882
WLH-6	11.366	4.238	3.668	187.241	1.158	42.878	0.546	0.014
WLH-7	15.551	5.277	6.588	84.448	1.682	51.377	0.564	0.110
WLH-8	6.319	2.879	5.456	19.030	0.475	57.792	0.574	0.013
WLH-9	18.008	5.642	8.693	163.877	0.697	32.383	0.560	0.024
WLH-10	17.837	5.773	9.391	166.294	0.162	30.305	0.557	0.027
WLH-11	14.831	5.226	5.746	92.028	2.741	41.957	0.604	0.029
WLH-12	14.885	5.415	5.302	87.146	0.294	42.765	0.575	0.028
BSH-1	9.007	2.747	16.536	53.889	4.064	43.742	0.558	0.025
BSH-2	7.546	1.260	10.266	49.175	7.281	47.377	0.557	0.023
BSH-3	6.213	3.135	9.844	51.966	5.279	45.716	0.548	0.025
BSH-4	7.445	2.839	13.161	53.953	3.650	43.996	0.553	0.025
BSH-5	8.600	2.509	17.083	54.921	2.538	44.069	0.565	0.025
BSH-6	9.094	2.934	15.540	51.844	6.545	45.189	0.557	0.026
BSH-7	8.921	2.571	17.595	56.015	2.524	42.341	0.559	0.025
BSH-8	8.291	2.448	16.586	53.849	2.553	45.867	0.572	0.025

Quality and Usability

The Chinese government have subdivided groundwater into five classes based on the concentrations of pollutants (Table-2): Class I, II and III can be used for drinking, irrigation and industry, and class IV can be used for irrigation and industry directly, but must be treated before drinking, whereas class V and the worse cannot be used for drinking, and either irrigation or industrial use must be carefully selected.

According to these standards, all of samples show better quality than class III according to their Pb, Cd, Cu, Cr and Zn concentrations, and six and thirty-three samples can pass the class III criterion according to their Cd and Mn concentrations, respectively. Moreover, all of the samples have Fe concentrations higher than the class III criterion but they can meet the requirement of class IV. Therefore, if the groundwater from the coal bearing aquifer is considered to be used for drinking, Cd and Fe should be firstly treated.

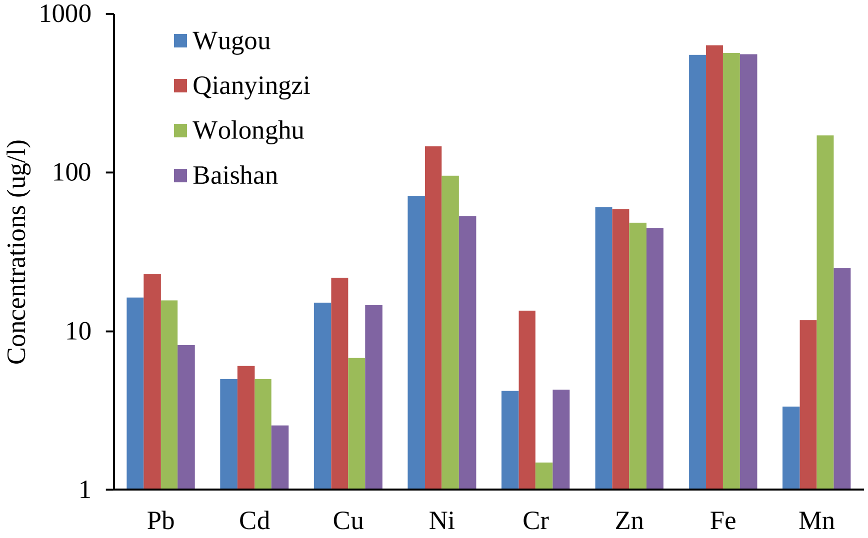

Fig.2: Concentration variations of heavy metals in groundwater from different coal mines

Moreover, comparisons of heavy metal concentrations in the groundwater with the World Health Organization guidelines for drinking water quality [11] suggest that no sample can meet the requirement of Fe (300 ug/l), and only ten and eight samples can meet the requirements of Pb (10 ug/l) and Cd (3 ug/l), respectively. However, only fifteen and seven samples can meet the requirements of Ni (70 ug/l) and Mn (400 ug/l). Therefore, different with those of the Chinese standards, all of the heavy metals except for Cu and Zn should be noticed before the application of drinking.

TABLE-2 Quality standards for groundwater in China (GB/T 14848-9)

	Class I	Class II	Class III	Class IV	Class V
Pb(μg/l)	≤5	≤10	≤50	≤100	>100
Cd(μg/l)	≤0.1	≤1	≤10	≤10	>10
Cu(μg/l)	≤10	≤50	≤1000	≤1500	>1500
Ni(μg/l)	≤5	≤10	≤50	≤100	>100
Cr(μg/l)	≤5	≤10	≤50	≤100	>100
Zn(μg/l)	≤50	≤500	≤1000	≤5000	>5000
Fe(mg/l)	≤0.1	≤0.2	≤0.3	≤1.5	>1.5
Mn(mg/l)	≤0.05	≤0.05	≤0.1	≤1.0	>1.0

Statistical Analysis

Statistical analyses (e.g. factor, cluster and correlation analysis) have long been used for hydro-chemical and environmental studies [9, 12]. In this study, correlation analysis has been firstly processed by using the heavy metal concentrations, and the result is listed in Table-3. As can be seen from the table, Pb, Cd, Cu and Cr are significantly correlated with each other, suggesting that they have a similar source and/or, similar forms. Moreover, Fe and Zn are significantly correlated, indicating that Zn is probably adsorbed by iron hydroxides.

Three factors with eigen values higher than one after varimax rotation have been obtained (Table-4), the total variance explanation is 85.1%. The first factor (FA1), which accounts for 48.6% of total information, has high positive loadings of Pb, Cd, Cu, Ni and Cr, the second factor (FA2) accounts for 20.3% of the total information, and is dominated by Zn and Fe, whereas Mn is participated mainly in the third factor (FA3) with 16.2% information.

Clastic rocks (including sandstones, siltstone and mudstone) in the coal bearing aquifer are enriched in metal minerals, and therefore, the first factor can be explained to be a weathering factor, which indicates the contribution from weathering of the metal minerals in the clastic rocks. Moreover, previous studies revealed that clay minerals and/or iron hydroxides are good carrier for heavy metals [20]. Therefore, the close correlation between Zn and Fe suggests that zinc is adsorbed by iron hydroxides. As to the third factor, it should be assigned as a carbonate factor because Mn is more enriched in limestone aquifer than in the other aquifers.

TABLE-3 Results of correlation analysis

	Pb	Cd	Cu	Ni	Cr	Zn	Fe
Cd	0.911**						
Cu	0.683**	0.459**					
Ni	0.749**	0.662**	0.737**				
Cr	0.732**	0.518**	0.936**	0.823**			
Zn	0.265	0.223	0.227	-0.056	0.178		
Fe	-0.020	-0.047	-0.025	-0.036	-0.024	0.602**	
Mn	0.222	0.186	-0.053	-0.190	-0.094	0.198	0.003

*Note: ** & * mean correlation significant at the 0.01 and 0.05 levels, respectively.*

TABLE-4 Results of factor analysis

	FA1	FA2	FA3
Pb	0.93	0.09	0.27
Cd	0.80	0.08	0.35
Cu	0.87	-0.06	-0.21
Ni	0.88	-0.26	-0.16
Cr	0.91	-0.11	-0.22
Zn	0.25	0.87	-0.13
Fe	0.01	0.80	-0.43
Mn	0.04	0.41	0.82
Eigen value	3.9	1.6	1.3
Variance explained	48.6%	20.3%	16.2%

CONCLUSION

Based on the heavy metal concentrations in groundwater from the coal bearing aquifer in four different coal mines, northern Anhui Province, China, the following conclusions have been made:

(1) The concentrations of the eight kinds of heavy metals vary significantly and following the decreasing order of Fe>Ni>Mn>Zn>Pb>Cu>Cr>Cd;

(2) In comparison with the Chinese groundwater quality standards, most of the heavy metal concentrations can meet the requirement of class III criterion, and only Cd and Fe should be firstly treated before the application for drinking. However, all of heavy metals except for Cu and Zn should be noticed in comparison with the standards of WHO;

(3) Correlation and factor analyses revealed that the weathering of metal minerals, adsorption by iron hydroxides and dissolution of carbonate are responsible for the heavy metal concentrations in the groundwater.

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REFERENCES

[1] HR Gui, EQ Yao, XM Song, ZH Yuan, G Zhang. Research on recycling technology of coalmine water, 1st Edition, China University of Mining and Technology Press, Xuzhou, **2011**, 3-6.
[2] LH Shi; LQ Wang, *Mining Technolgy*, **2008**, 8(1), 86-88.
[3] JW Xu; DY Yu; L Sun; *Jiangxi Coal Science & Technology*, **2010**, 3(3), 92-94.
[4] XW He; J Yang; LN Shao; FQ Li; X Wang; *Journal of China Coal Society*, **2008**, 33(1), 63-66.
[5] P Qi; Q Wu; XX Li; XL Wu, *Technology of Water Treatment*, **2010**, 36(4), 125-126.
[6] HR Gui; WH Peng; WL He, *Journal of Ecology and Rural Environment*, **2012**, 28(5), 605-608.
[7] XW He; FQ Li, *Coal Science and Technology*, **2010**, 38(11), 17-22.
[8] HR Gui; L H Sun, *Asian Journal of Chemistry*, **2013**, 25(11), 5941-5944.
[9] LH Sun; HR Gui; ML Lin, *Fresenius Environmental Bulletin*, **2013**, 22(2a), 537-543.
[10] LW Chen; HR Gui; XX Yin, *Journal of China Coal Society*, **2008**, 33(5), 537-542.
[11] World Health Organization (WHO). Guidelines for drinking water quality, 3rd Edition, Available at: http://www.who.int/water_sanitation_health/dwq/fulltext.pdf. **2008**.
[12] AK Krishna, M Satyanarayanan; PK Govil, *Journal of Hazardous Materials*, **2009**, 167(1), 366-373.