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Heavy Metals Characteristics in Deep Groundwater of Coal Mining Area, Northern Anhui Province

Manli Lin[1,2], Herong Gui[1,2,3], Weihua Peng[1,2], Song Chen[1,2]
1 School of earth science and engineering, Suzhou University, Suzhou 234000;
2 Suzhou University, Anhui Province Coal Mine Exploration Engineering Technology Research Center, Suzhou 234000;
3 Institute of earth and environment, Anhui University of Science and Technology, Huainan 232001

Abstract The concentrations of heavy metals (HMs) such as Cd, Cr, Cu, Zn, Pb and Ni were investigated in deep groundwater of different aquifers (unconsolidated formation, coal measure aquifer, Taiyuan limestone aquifer and Ordovician limestone aquifer), which collected from four typical coal mines, northern Anhui province, China. The characterization (rangeability, distribution) and source apportionment of HMs were also studied. HMs concentrations were analysed using atomic absorption spectrometer and compared with permissible limits set by China State Bureau of Technology Supervision. The concentration orders of HMs were different from each other in the four aquifers, and for the entire study area, the concentrations of HMs were found in the order of Ni＞Zn＞Pb＞Cu＞Cd＞Cr, the same as Taiyuan limestone aquifer. Cu had the minimum variable coefficient value, and Ni has the maximal rangeability. Cr and Ni got the maximal value in coal measure aquifer mainly due to etching effects of parent rock and bed rock. The concentrations of Cr, Cu and Zn were observed within their respective limits, while Cd, Pb and Ni concentrations were higher than their respective permissible limits, which should be considered as the monitoring and control targets. Cr should as be pay much attention, because it had almost approach the permissible limit in coal measure aquifer in the study area.
Keywords northern Anhui mining areas, groundwater, heavy metals, concentration characteristics

Introduction

“Heavy metal” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4000 kg/m^3, or 5 times more than water (Garbarino et al. 1995), and they are natural components of the earth’s crust (Hashim et al. 2011). Although some HMs are essential micro nutrients for living beings at specific concentrations, at higher concentrations they can lead to severe poisoning (Lenntech 2004), which are considered as severe pollutants owing to their toxicity, persistence and bioaccumulative nature in 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). Investigation of water contamination with HMs has become the prime focus of environmental scientists in recent years (Muhammad et al. 2011). In China, quality-induced water shortage has become an important problem of the water resources, under the effect of various pollution sources, the shallow groundwater pollution become more and more serious, and its pollution speed is very quickly. For the mining area, water resources problem is becoming more and more serious, on the one hand, it is quantity shortage of water resources, and the statistics show that there are 70% mining areas facing water shortages, in which 40% mining areas need water badly (Yuan 2000), on the other hand, the water quality of mining areas is deteriorating, taking excavation works for instance, it has become a key effect factor for groundwater pollution (Ma 2011), thus the water resource is restricting the sustainable development of coal mine areas (Gui et al. 2011).

Concerning the study of HMs in water systems, much attention has been paid to the characteristics and source apportionment of HMs in surface water and shallow groundwater (Muhammad et al. 2011; Leung and Jiao 2006; Wang et al. 2008; Liu 2010), but a relative small number of studies focus on the study of HMs in deep groundwater from different aquifers. In the area focused in this study, some trace metals and rare earth elements in deep groundwater from different aquifers has been measured in order to discuss geochemical and hydrogeochemical characteristics (Gui, 2005; Yan et al., 2012), however, in our knowledge, so far this is the first comprehensive study of HMs for their characteristics and source apportionment in deep groundwater from different aquifers of coal mining area，northern Anhui Province. The present study is designed to investigate the concentrations of heavy metals in deep groundwater from four aquifers, which were sampled from four typical coal mines located at northern Anhui mining area, and the characteristics of HMs and their source apportionment were also analyzed, in order to provide reference for the utilization and protection of groundwater resources in coal mining area.

Materials and methods

Study area description

Northern Anhui mining area was located in the north in Anhui province (fig.1, a), longitude 114°55′~118°10′, latitude 32°25′~34°35′, borders Shandong province in the north, Jiangsu province to the east, and Henan province to the east, mainly including Fuyang, Bozhou, Suzhou and Huaibei city (Gui 2005). As an important coal base in China, the mine area has rich coal resources, and there are two big mining groups namely Wanbei coall-electicity group co., LTD and Huaibei mining (group) co., LTD, with 30000 km^2 and more than 30 coal mines. The area stratum is part of Xu Huai stratigraphic division in stratigraphic regions of north China, excepting northeast part with a small amount of bedrock exposed, the others are all covered by the quaternary strata, and its geological tectonic unit is in the south of Sino Korean paraplatform, which is fault basin formed since Cenozoic Era, with the structural system mainly including east-west fault zone, north-north-east new huaxia structure and Xusu arc structure. According to the Huaibei coalfield integrated hydrogeological histogram (ACGET 3 2012), there were four water aquifer in cainozoic group (fig.1, b), the first aquifer, the second aquifer, the third aquifer and the four aquifer in top-down order, and its average thickness were 27.92 m, 19.45 m, 33.84 m and 17.5 m, respectively.

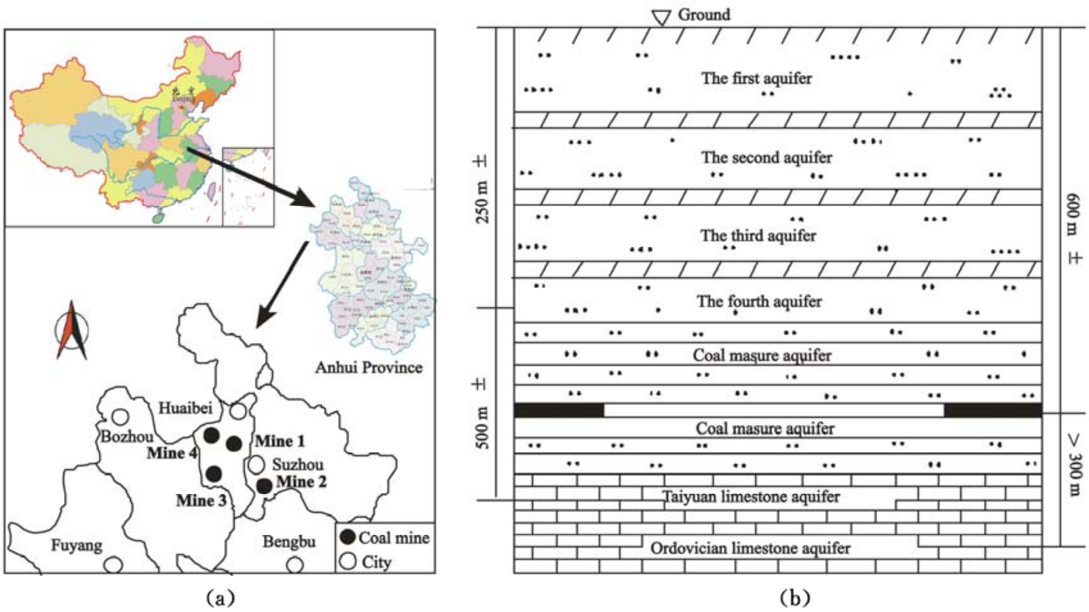

Fig. 1 *Location of study area and the distribution of sampling points*

Sampling and monitoring

The representative groundwater samples were selected from four locations (Mine 1, Mine 2, Mine 3 and Mine 4) of the study area shown in fig. 1 (a). A total of 59 groundwater samples were collected from four aquifers in the study area in October 2012, with single sampling quantity over 2.5 L. The four aquifers were unconsolidated formation (16 samples, primarily sampled from the third aquifer and the fourth aquifer), coal measure aquifer (26 samples), Taiyuan limestone aquifer (12 samples) and Ordovician limestone aquifer (5 samples), and their sampling depth were 223.8~349.95 m, 250~649.5 m, 430~538.49 m and 200~440 m, respectively. Each water sample was filtered through 0.45 μm filter paper and acidified with ultrapure HNO_3 (2 ml/L) to keep pH＜2. All the samples were transported to laboratory within 24 h and stored in a refrigerator at 4℃ for further analyses. The main physicochemical parameters (T, pH and TDS) were measured on the spot. The six selected HMs (Cd, Cr, Cu, Zn, Pb and Ni) in acidified water samples were analysed using atomic absorption spectrometer (Pgeneral, TAS-990) under standard operating conditions having r >0.999, and Cd, Cr, Cu, Pb and Ni were detected by graphite furnace-AAS, while Zn were detected by flame method. External standard method was used for quantitative analysis, and the test recovery of Cd, Cr, Cu, Pb, Ni and Zn were 93.64%, 105.84%, 101.83%, 111.92%, 95.50% and 96.96%, respectively.

Results and discussion

HMs concentration

In the 59 groundwater samples, the detection rate of Cd, Cr, Cu, Pb, Ni and Zn were all 100%, its concentrations characteristics, were listed in table 1, including range, mean, standard deviation (SD) and variable coefficient (CV) of six HMs from different aquifers and the total groundwater (Total).

Table 1 shows that, the mean concentrations of six HMs vary with the different aquifers, its concentrations order in SS, MX, TH and AH were Zn＞Ni＞Pb＞Cu＞Cd＞Cr, Ni＞Zn＞Pb＞Cu＞Cr＞Cd, Ni＞Zn＞Pb＞Cu＞Cd＞Cr, Zn＞Ni＞Pb＞Cu＞Cr＞Cd, in this six HMs, the concentrations of Pb and Cu changed stable, in other words Pb＞Cu in all aquifers, and that their concentrations are always in the middle place, less than Zn or Ni, while greater than Cd or Cr. The concentrations of the six HMs in the total groundwater were the same order as the Taiyuan limestone aquifer. Liu (Liu 2010) collected and detected 151 shallow groundwater samples, with the sampled depth among 8-60 m, from Huaibei plain during 2008-2009, and the results showed that Zn＞Cu＞Pb＞Ni＞Cd. It shows that, the concentrations of HMs were different between shallow and deep groundwater, farther more, it is still different in deep groundwater with aquifers change. Taking the Cr for example, its concentrations were in the order of MX＞SS＞TH＞AH. Predecessors' research results have shown that, aquifers and crustal rock had the same curve shape in microelement abundance (Gui 2005; Shen 1993), and the crustal rock was the final source for microelement in groundwater (Gui 2005). However, the HM in water could be derived from both natural (i.e., weathering, erosion of bed rocks, ore deposits and volcanic activities) and anthropogenic (i.e., mining, smelting, industrial influx, wastewater irrigation and agriculture activities) sources (Demirak et al. 2006; Chanpiwat et al. 2010; Muhammad et al. 2010; Khan et al. 2013), of which, mines is an important source for trace metals (Cantor 1997). HMs concentrations change with the different aquifers in this study, besides natural factors (i.e., hydrogeological condition, lithology of aquifer and water-resisting layer), that can also be ascribed to human factors, maybe the concentration and geochemical behavior of HMs had been disturbed by coal mining activities.

Table 1 *Summary of heavy metals in aquifers and the total groundwater*

Aquifers		Cd	Cr	Cu	Zn	Pb	Ni
SS	Range	0.0020-0.0057	0.0001-0.0051	0.0033-0.0145	0.0449-0.0689	0.0033-0.0297	0.0141-0.0578
	Mean	0.0035	0.0012	0.0068	0.0543	0.0093	0.0308
	SD	0.0008	0.0013	0.0031	0.0078	0.0058	0.0132
	CV（%）	22.86	108.33	45.59	14.36	62.37	42.86
MX	Range	0.0013-0.0091	0.0001-0.0474	0.0028-0.0683	0.0303-0.0927	0.0062-0.0490	0.0190-0.3932
	Mean	0.0048	0.0061	0.0139	0.0522	0.0164	0.1019
	SD	0.002	0.0106	0.0143	0.0132	0.0096	0.0838
	CV（%）	41.67	173.77	102.88	25.29	58.54	82.24
TH	Range	0.0015-0.0190	0.0004-0.0064	0.0040-0.0280	0.0479-0.0665	0.0029-0.0757	0.0147-0.1927
	Mean	0.0074	0.0034	0.0163	0.0590	0.0276	0.0622
	SD	0.0046	0.0019	0.0086	0.0063	0.0197	0.0462
	CV（%）	62.16	55.88	52.76	10.68	71.38	74.28
AH	Range	0.0026-0.0040	0.0019-0.0059	0.0078-0.0096	0.0443-0.1089	0.0093-0.0153	0.0244-0.0286
	Mean	0.0035	0.0036	0.0088	0.0606	0.0129	0.0269
	SD	0.0006	0.0019	0.0008	0.0273	0.0025	0.0016
	CV（%）	17.14	52.78	9.09	45.05	19.38	5.95
Total	Range	0.0013-0.0190	0.0001-0.0474	0.0028-0.0683	0.0303-0.1089	0.0029-0.0757	0.0141-0.3932
	Mean	0.0049	0.0040	0.0120	0.0549	0.0164	0.0682
	SD	0.0028	0.0074	0.0109	0.0126	0.0128	0.0673
	CV（%）	57.14	184.25	90.88	22.99	77.96	98.64

Note: *SS, MX, TH and AH respectively represented the water samples collected from unconsolidated formation, coal measure aquifer, Taiyuan limestone aquifer and Ordovician limestone aquifer*

HMs rangeability and distribution

The range change condition of Cd, Cr, Cu, Pb, Ni and Zn and their distribution in different aquifers were showed in fig. 2. Combining fig. 2 (a) and table 1, it is not difficult to conclude that, Cd and Cr have the smaller rangeability, Cu, Zn and Pb have the medium rangeability, while Ni has the maximal rangeability, its range is 0.0028-0.0683 mg/L, and its mean value is 0.0132 mg/L. The distribution of six HMs in different aquifers were showed in fig. 2 (b), Cr and Ni get the maximal value in coal measure aquifer, Cd, Cu and Pb get the maximal value in Taiyuan limestone aquifer, while Zn get the maximal value in Ordovician limestone aquifer. Researches show that, The enhanced Cr and Ni concentrations in water samples can be attributed to the occurrence of ultramafic rocks (Ashraf 1982; Miller 1991), and according to the Huaibei coalfield integrated hydrogeological histogram (ACGET 3 2012), the bottom of Plx (including 4, 5, 6, 7, 8 coal bed) is aluminum mudstone in study area. It can thus be seen, Cr and Ni get the maximal value in coal measure aquifer mainly due to etching effects of parent rock and bed rock. In the total groundwater samples, Cu has the minimum variable coefficient value (table 1, CV=22.95%), He (He et al. 2011) took the shallow groundwater as the study object, and proceeded HMs characteristic study in Huainan city in 2009, and also gave the same conclusion that Cu has the minimum variable coefficient value (CV=2.7%), so, we can draw a conclusion that Cu concentration in ground water was relatively stable, and its change gently in different aquifers.

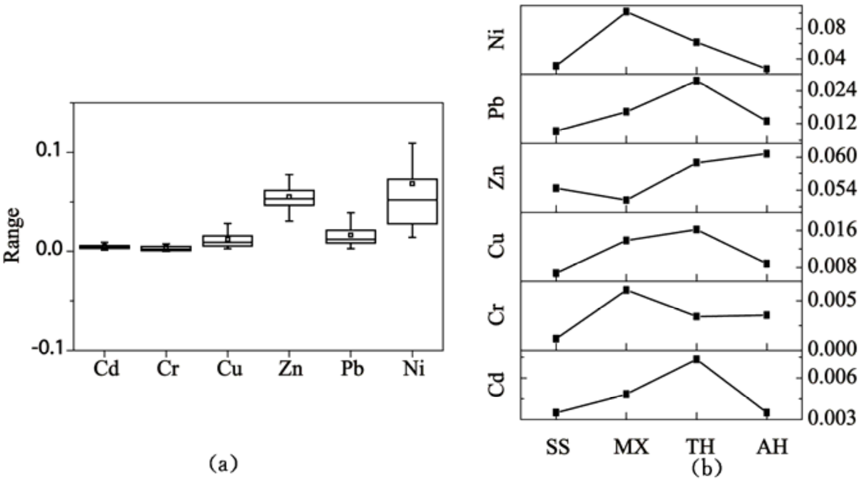

Fig. 2 *Range of heavy metal and its distribution in aquifers*

Water quality

China domestic quality standard for ground water (GB/T 14848－93(Ⅲ)) was used to investigate the quality of groundwater, since its water function area is applicable primarily for centralized drinking water supplies, industrial and agricultural sectors. Compared with GB/T 14848－93(Ⅲ), there is only one water sample in Taiyuan limestone aquifer, in which the concentrations of Cd and Pb beyond the standard limit (fig.3, a, e), furthermore that is the same water sample, and the over standard rate of Cd is 1.70%. The concentrations of Cr, Cu and Zn are all below standard line in four aquifers, however, Cr in coal measure aquifer is much higher (fig.3, b), while Cu and Zn are change relatively stable and far below the standard value (fig.3, c, d). Except Ordovician limestone aquifer, Ni is beyond the standard limit in some water samples in the other aquifers (fig.3, f), and the over standard rates of Ni are 6.25%, 76.92% and 66.67% in unconsolidated formation, coal measure aquifer and Taiyuan limestone aquifer, respectively.

Gui (Gui et al. 2002) had researched the shallow groundwater quality condition of Huainan city in 2002, the results proved that in the six HMs (Cu, Zn, Pb, Hg, Cr and Cd), only Pb exceeded the standard limit. The study of He (He et al. 2011) gave the results that Cu and Zn were all below standard line, and the over standard rate of Cd and Ni were 5.98% and 9.16%. Liu (Liu 2010) also drawed a conclusion that Cu was below standard line in the shallow groundwater of Huibei Plain. Combining previous research results and it is not hard to find that, Cu, Zn and Cr generally do not exceed the standard limit, while Cd, Pb and Ni exceeded the standard limit frequently, so, the latter three HMs should be pay much attention seriously, especially when groundwater was considered as the water source for domestic water in drinking way. To this study area, Cr should as be pay much attention, because it has approach the permissible limit in coal measure aquifer.

Conclusions

Concentrations of Cd, Cr, Cu, Pb, Ni and Zn vary in the different aquifers, and the concentrations orders were Zn＞Ni＞Pb＞Cu＞Cd＞Cr, Ni＞Zn＞Pb＞Cu＞Cr＞Cd, Ni＞Zn＞Pb＞Cu＞Cd＞Cr, and Zn＞Ni＞Pb＞Cu＞Cr＞Cd, respectively. The concentrations of the six HMs in the total groundwater were the same order as the Taiyuan limestone aquifer.

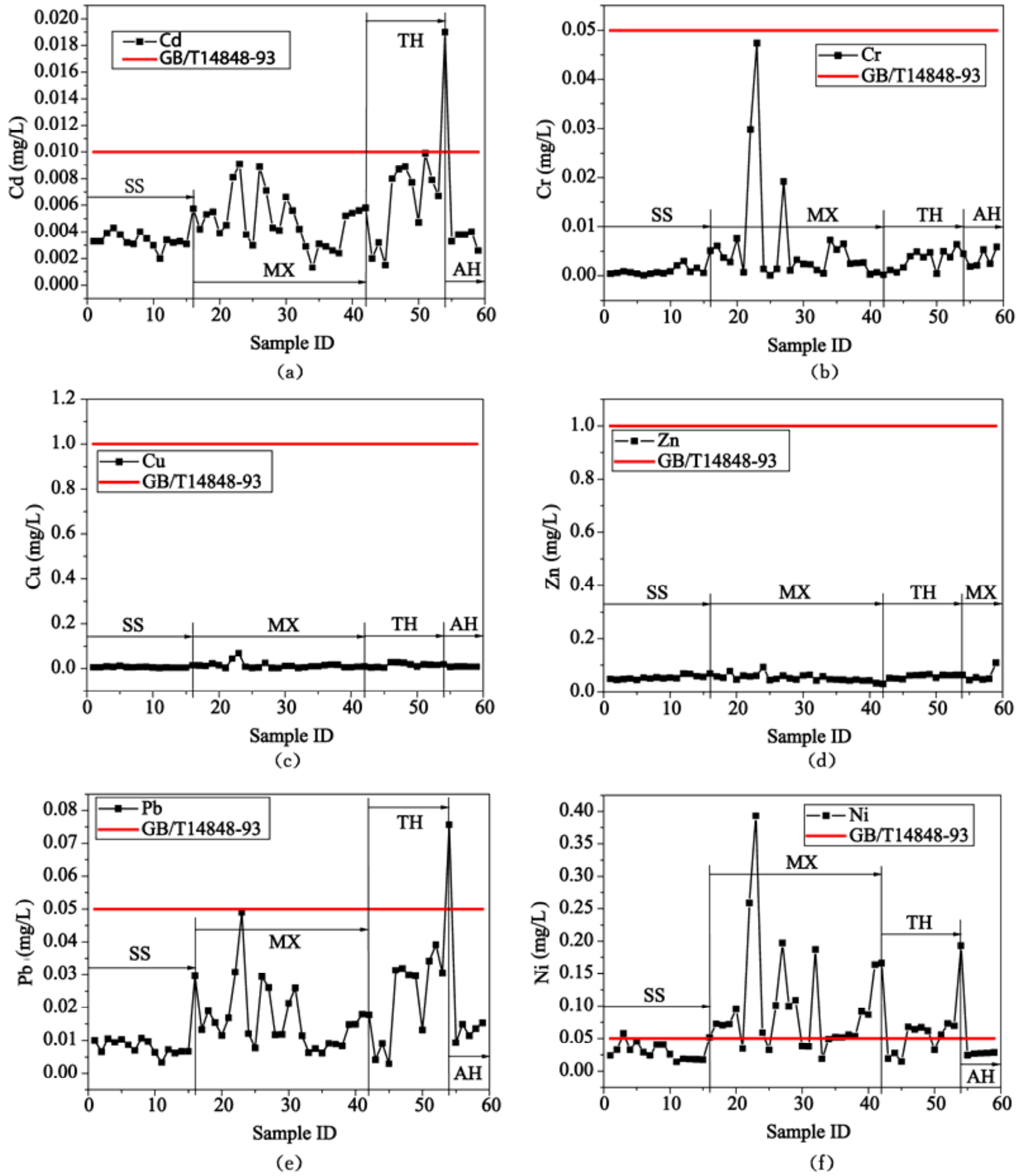

***Fig. 3** Distribution of heavy metals in the groundwater samples and pollution levels*

In the six HMs, Cu has the minimum variable coefficient value, and Ni has the maximal rangeability. Cr and Ni get the maximal value in coal measure aquifer mainly due to etching effects of parent rock and bed rock.

The concentrations of Cr, Cu and Zn are all within permissible limits (GB/T 14848－93(Ⅲ)) in four aquifers, while Cd, Pb and Ni are higher than the standard limit in some water samples, and Ni has the maximum standard over rates. The latter three HMs, together with Cr, should be taken as the priority monitoring and control targets in this study area, when the groundwater used as domestic water, especially in drinking way.

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