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Original Research Paper

Health Risk Assessment of Heavy Metals in the Groundwater of a Coal Mining area in Northern Anhui Province, China

Lin Man-li*(**), **Gui He-rong***(**) **and Peng Wei-hua*****†
*School of Resources & Civil Engineering, Suzhou University, Suzhou 234000, Anhui, China
**National Engineering Research Center for the Control and Prevention of Coal Mine Water Hazards, Suzhou University, Suzhou 234000, Anhui, China
***School of Chemistry and Environment, Beihang University, No. 37 Xueyuan Road, Haidian District, Beijing 100191, P.R. China
†Corresponding author: Peng Wei-hua

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ABSTRACT

To investigate the health risk posed by heavy metals in the groundwater of a coal mining area in northern Anhui Province, China, six types of heavy metals (Cr, Cd, Cu, Pb, Zn, Ni) were identified and analysed by obtaining 59 water samples from four aquifers (UF, CA, TA, OA) through the use of an atomic absorption spectrophotometer. The values of these heavy metals were then compared with the permissible limits set by the Chinese Environmental Protection Agency (EPA) and World Health Organization (WHO) (2008). The health risk posed to adults and children was assessed based on the American Environmental Protection Agency's health risk assessment model. The concentrations of Cd, Cr, Cu, Zn, and Pb are within the permissible limits set by the Chinese EPA, but the concentration of Ni is higher than the permissible limits. The concentrations of Cr, Cu, Zn, and Ni are within the permissible limits set by the WHO (2008), whereas Cd and Pb concentrations are higher than the permissible limits. The health risk assessment performed shows that the HRI values of the selected heavy metals are in the order of Cd>Ni>Pb>Cu>Zn>Cr. Although most of the heavy metals pose no health risk (HRI<1), several HRI values of Cd in the selected water samples exceed 1, indicating a small health risk imposed on local people. This health risk assessment of heavy metals in a deep groundwater mining area can serve as a reference for groundwater resource exploitation and protection.

INTRODUCTION

As an important part of the Earth's water, groundwater is an indispensable resource for the development of the global social economy and people's lives. In China, the amount of exploited groundwater increased at a rate of 2.5 billion m^3 per year in the past three decades. A total of 40% of some (or even all) arable land relies on groundwater for irrigation, and water supply accounts for 20% of the total water supply in the country. Groundwater problems mainly include two aspects: excessive groundwater exploitation and groundwater pollution. It was reported that fully 90% of China's shallow groundwater is polluted, according to the Ministry of Land and Resources, and an alarming 37% is so foul that it cannot be treated for use as drinking water (Qui 2011). Moreover, excessive groundwater exploitation causes a decline in water levels and a change in groundwater movement patterns; thus, it eventually results in surface collapse. The pollution caused by human activities through various underground channels has caused serious groundwater pollution, particularly heavy metal pollution of groundwater. Groundwater contamination with heavy metals, such as Cd, Cr, Cu, Mn, Ni, Pb, and Zn, is a worldwide environmental problem (Muhammad et al. 2011a). Ingestion of water containing a certain amount of heavy metals may cause health problems in humans, including headaches, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, sideroblastic anaemia, intellectual disabilities, fatal cardiac arrest, and carcinogenesis (Kavcar et al. 2009, Jarup 2003, Muhammad et al. 2011a,b, Pekey et al. 2004). The processes of coal mining, coal washing, and coal cinder stacking easily cause the presence of heavy metal pollutants through runoff and infiltration as well as other forces in groundwater, which cause the pollution. Therefore, the physico-chemical parameters of heavy metals in drinking water are important, and their high or low concentration directly or indirectly affects humans (Muhammad et al. 2010).

As part of health risk assessment, groundwater environmental health risk assessment is based on the considerations of protecting human health and involves the correlation between pollutants in groundwater and human health to comprehensively consider the effect of pollutants on the health degree and its size estimates, which can provide necessary technical support and advice for the management and governance of contaminated areas. In our previous studies, although trace metals had been determined in order to understand their hydrogeochemical characteristics (Gui 2005), hydrological implications (Sun et al. 2013), quality and background (Sun et al. 2014, Lin et al. 2014a) in coal mining area in northern Anhui Province, China, together with preliminary health risk assessment of heavy metals (Lin et al. 2014b). However, no previous research on risk assessment of heavy metals in deep groundwater in the study area has been conducted to date, making a difference between children and adults. In addition, the evaluation results of health risk assessment for children and adults differ because of differences in water quantity required by children and adults. Only a few health risks for children have been analysed; thus, a more comprehensive reference for the utilization and protection of groundwater has not been provided. The present study investigates the concentrations of Cr, Cd, Cu, Pb, Zn, and Ni in four different aquifers in the groundwater environment of a coal mining area in northern Anhui Province. The health risk assessment model recommended the American Environmental Protection Agency (US EPA) for adults and children is utilized.

MATERIALS AND METHODS

Study area: The study area, Wanbei coal mining area, is located in north of Anhui Province, China. The area stretches from 114°55' to 118°10' E longitude and from 32°25' to 34°35' N latitude (Fig. 1a). It is bordered by Jiangsu Province in the east, Huaihe River in the south, Henan Province in the west, and Shangdong Province in the north and includes Fuyang, Bengbu, Xuzhou, Suzhou and Huaibei (Gui 2005). The study area has a monsoon climate, which is warm in summer and very cold in winter. The annual average temperature is 14°C to 14.5°C. The average rainfall in the study area varies from 774 mm to 895 mm per year, and Huaihe River is the main river. The coal mining area, which is one of the important coal bases in China, has abundant coal resources and two big mining groups (Wanbei Coal-Electricity Group Co., Ltd., and Huaibei Mining Group Co., Ltd.), with a total area of 30000 km^2. According to the Huaibei coalfield integrated hydrogeological histogram, the Cenozoic group in the study area contains four aquifers, as shown in Fig. 1b. The first aquifer has a thickness of 3.73 m to 63.42 m (mean of 27.92 m), the second aquifer has a thickness of 0 m to 52 m (mean of 19.45 m), the third aquifer has a thickness of 5.2 m to 71.6 m (mean of 33.84 m), and the fourth aquifer has a thickness of 0 m to 51.97 m (mean of 17.5 m). The fifth aquifer (thickness of 0 m to 100 m; mean of 10.08 m) of the Mesozoic Jurassic group is found only in Zhu Xianzhuang coal mining area in Suzhou City. Dyas, an upper Palaeozoic coal measure aquifer, basically has three coal crannies between sandstone aquifers (thickness of 1.29 m to 157 m, average of 34.67 m), 7-8 coal top and bottom aquifers (thickness of 0 m to 74.2 m, average of 19.2 m), and 10 coal and fractured sandstone aquifers (thickness of 0 m to 66.1 m, mean of 22.23 m). The thickness of carboniferous Taiyuan formation limestone aquifer ranges from 21.27 m

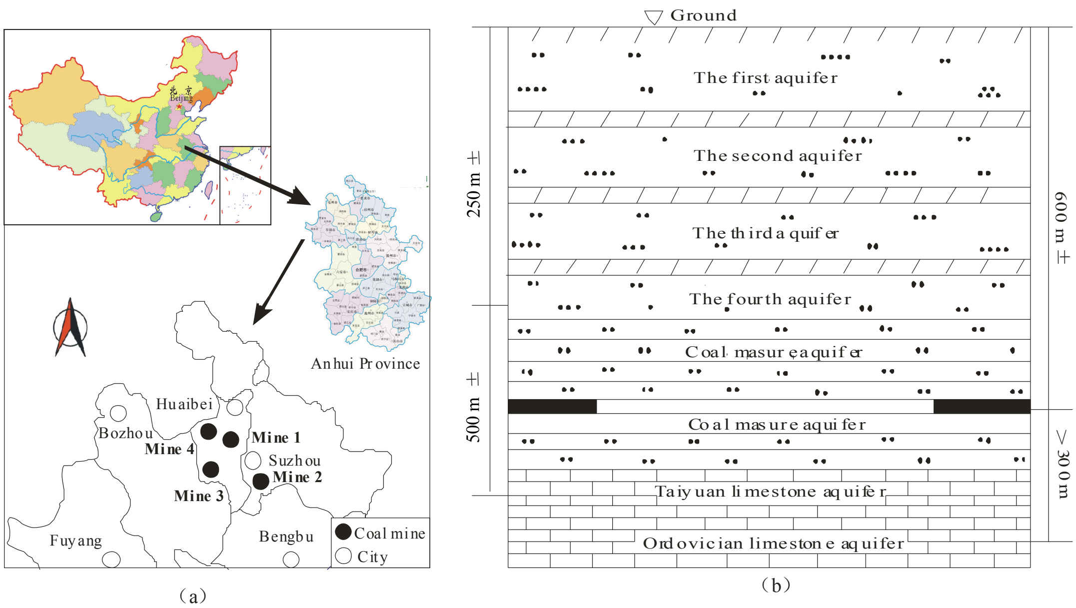

Fig. 1: Location of the study area and distribution of sampling points.

to 135 m, with an average of 54.9 m. The thickness of Ordovician limestone aquifer is unknown.

Sampling: A total of 59 groundwater samples were collected from four coal mining sampling points in the coal mining area in northern Anhui Province in October 2012. Hydrogeological types of the four mines were all of medium-complexity level, so they had relatively well represented the mines in the study areas. The area includes four aquifers, namely, unconsolidated formation (UF) (16 samples, primarily sampled from the third and fourth aquifers), coal measure aquifer (CA) (26 samples), Taiyuan limestone aquifer (TA) (12 samples), and Ordovician limestone aquifer (OA) (5 samples); their sampling depths were 223.8 m to 349.95 m, 250 m to 649.5 m, 430 m to 538.49 m, and 200 m to 440 m, respectively (Fig. 1b). Clean and unmixed water samples were required in this study. The samples were selected preferentially under the coal mine, for example, the water samples from Taiyuan limestone aquifer and Ordovician limestone aquifer were sampled through drain holes. When the sampling under coal mine was not convenient, a tailor-made sampler was used to collect groundwater samples from observation wells above the ground, which were constructed for pumping test and groundwater regime observation of different aquifers. Of course, the obviously mixed or contaminated water samples were all abandoned. In general, majority of water samples were collected under coal mine in our study while only small number were pulled out directly from observation well by hand pump on the ground. Before sampling, the bottles were washed with double deionized water containing 20% HNO_3 (Khan et al. 2013). Each water sample was collected in a clean polyethylene plastic bottle (2.5 L), to which a few drops of 5% HNO_3 was added. Each water sample was filtered through 0.45 μm filter paper and acidified with ultrapure HNO_3 (2 mL/L) to maintain pH<2. All the water samples were transported to the Research Center of Coal Mine Exploration Engineering and Technology in Anhui Province and stored at 4°C for further analyses.

Chemical analysis: The concentrations of Cd, Cr, Cu, Pb, and Ni in the water samples were analysed with a graphite furnace atomic absorption spectrophotometer (Pgeneral, TAS-990) under standard operating conditions. The concentration of Zn in the water samples was analysed with a flame atomic absorption spectrophotometer. Quantitative methods that adopt the external standard methods were employed with test recovery of 93.64%, 105.84%, 101.83%, 111.92%, 95.50%, and 96.96%. To reduce the error of the test results, each water sample was analysed thrice to calculate the average concentration of heavy metals.

Health Risk Assessment: ***Chronic daily intakes of metals***: Heavy metals enter the human body through several pathways, including food chain, dermal contact, and inhalation; in comparison with oral intake, all other means are considered negligible. The chronic daily intake (CDI) through water intake was calculated according to eq. (1) (Shah et al. 2012, Muhammad et al. 2011a,b).

$$CDI = \frac{C_m \times I_w}{W_b}, \qquad ...(1)$$

Where, C_m (μg/L) represents the heavy metal concentration in water, I_w (L/day) denotes the average daily intake of water (assumed to be 2 L/day for adults and 1 L/day for children) (US EPA 2011), and W_b (kg) is the average body weight (assumed to be 70 kg for adults and 10 kg for children) (US EPA 2011).

Health risk indexes of metals: To estimate the chronic health risks, HRIs were calculated according to eq. (2) (Shah et al. 2012, Muhammad et al. 2010).

$$HRI = \frac{CDI}{RfD}, \qquad ...(2)$$

Where, the oral toxicity reference dose [RfD, μg/(kg·day)] values for Cd, Cr, Cu, Zn, Pb, and Ni, are 5.0E-01, 1.5E+03, 3.7E+01, 3.0E+02, 3.6E+01, and 2.0E+01, respectively (Shah et al. 2012, Muhammad et al. 2010, US EPA 2005). An HRI value less than 1 is considered safe for consumers (Khan et al. 2008).

RESULTS AND DISCUSSION

Physico-chemical characteristics: The physico-chemical characteristics of groundwater in the study area are summarized in Table 1. The concentration of Cd in the four aquifers in a decreasing order was as follows: TA>CA>UF=OA. Cd concentration in groundwater samples from UF, CA, TA, and OA ranged from 2.0-5.7, 1.3-9.1, 1.5-19.0 and 2.6-4.0 μg/L, with mean concentrations of 3.5, 4.8, 7.3 and 3.5 μg/L, respectively. The highest Cd concentration (19.0 μg/L) was found in TA, and the lowest (1.3 μg/L) in CA. The concentration of Cr in the four aquifers in a decreasing order was as follows: CA>OA>TA>UF. Cr concentration in groundwater samples from UF, CA, TA, and OA ranged from 0.07-5.1, 0.1-47.4, 0.4-6.4 and 1.9-5.9 μg/L, with mean concentrations of 1.2, 6.1, 3.4 and 3.6 μg/L, respectively. The highest Cr concentration (47.4 μg/L) was found in CA, and the lowest (0.07 μg/L) in UF. The concentration of Cu in the four aquifers in a decreasing order was as follows: TA>CA>OA>UF. Cu concentration in the groundwater samples from UF, CA, TA and OA ranged from 3.2-14.5, 2.8-68.3, 4.0-28.0 and 7.8-9.6 μg/L, with mean concentrations of 6.8, 13.9, 16.3 and 8.8 μg/L, respectively. The highest Cu concentration (68.3 μg/L) and the lowest one (2.8 μg/L) was found in CA. The concentration of Zn in the four aquifers in a decreasing order was as follows: OA>TA>UF>CA. Zn concentration in groundwater samples from UF, CA, TA, and OA ranged from 44.9-68.9, 30.3-92.7, 47.9-66.5 and 44.3-108.9 μg/L, with mean concentrations of 54.4, 52.2, 59.0 and 60.6 μg/L, respectively. The highest Zn concentration (108.9 μg/L) was found in OA, and the lowest (30.3 μg/L) in CA. The concentration of Pb in the four aquifers in a decreasing order was as follows: TA>CA>OA>UF. Pb concentration in ground water samples from UF, CA, TA and OA ranged from 3.3-29.7, 6.2-49.0, 2.9-75.7 and 9.3-15.3 μg/L, with mean concentrations of 9.3, 16.4, 27.6 and 12.9 μg/L, respectively. The highest Pb concentration (75.7 μg/L) was found in TA, and the lowest (3.3 μg/L) in UF. The concentration of Ni in the four aquifers in a decreasing order was as follows: CA>UF>TA>OA. Ni concentration in groundwater samples from UF, CA, TA and OA ranged from 14.1-57.8, 19.0-393.7, 14.7-192.7 and 24.4-28.6 μg/L, with mean concentrations of 30.8, 101.9, 62.2 and 26.9 μg/L, respectively. The highest Ni concentration (393.3 μg/L) was found in CA, and the lowest (14.1 μg/L) in UF.

The mean concentrations of Cd, Cr, Cu, Zn and Pb were found to be within the permissible limits set by Chinese EPA, but the concentration of Ni was higher than the permissible limits (Fig. 2). The mean concentration of Cd, Cr Cu, Pb, Ni and Zn in study area was 4.9, 4.0, 12.0, 54.9, 16.4 and 68.2 μg/L, respectively. The concentrations of Cd, Pb and Ni in all the water samples exceeded the permissible limit set by the Chinese EPA by 1.69%, 1.69% and 47.46%, respectively. Ni exhibited the maximum exceed rate and should thus be regarded as the priority pollutant in this coal mining area (northern Anhui Province). Relevant departments should therefore implement active measures to prevent and control pollution and reduce or avoid the occurrence of nickel poisoning among local residents. The concentrations of Cr, Cu, Zn and Ni were all within the permissible limits set by the WHO (2008), whereas the concentrations of Cd and Pb were higher than the permissible limits (Fig. 2).

Health risk assessment: Coal cinder in Wanbei mining area has piled up for a long period of time. Under the action of rainfall and gravity, coal cinder and heavy metal pollutants in wastewater have formed a new pollution source in the groundwater environment. The pollution range increases with time and would eventually result in a wide range of elevated heavy metal content in groundwater. Groundwater is the main source of drinking water in the study area, so heavy metal pollutants in the groundwater cause serious health hazards to local residents. This study is based on groundwater monitoring data for heavy metals in combination with the health risk assessment model recommended by the US EPA. The chronic daily intakes (CDIs) and health risk indexes (HRIs) of heavy metals were calculated for adults and children.

Chronic daily intake of selected heavy metals: The CDI values of selected heavy metals in the study area calculated for adults and children are summarized in Table 2. The CDI values of selected heavy metals were in a decreasing order: Ni>Zn>Pb>Cu>Cd>Cr. Several CDIs of Cd in TA samples for children exceeded the RfD value limit set by the US EPA (2005), and several CDIs of Ni in CA samples for children exceeded the RfD value limit. However, the CDIs of Cr, Cu, Pb and Zn were within their respective RfD limit.

In the four aquifers, the range of the CDIs of Cd for adults

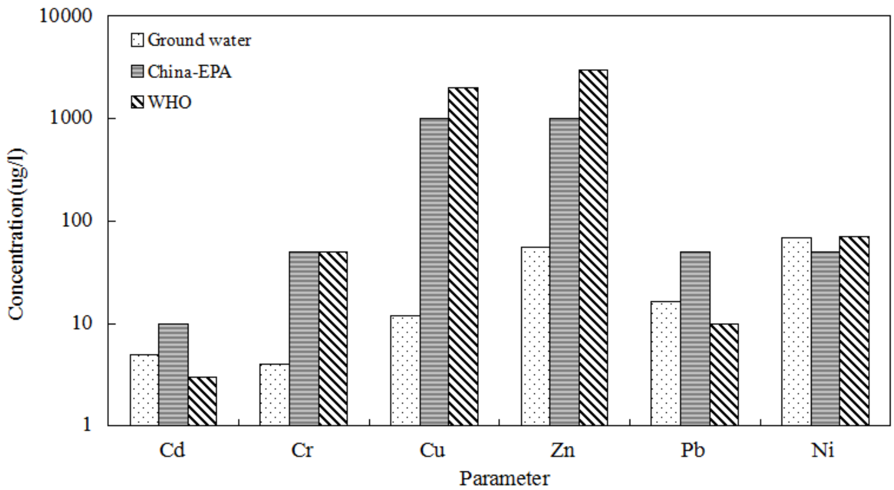

Fig. 2: Comparison of selected heavy metals in groundwater together with their permissible limits.

Table 1: Concentrations (μg/L) of selected heavy metals in groundwater (n=59).

Parameter	Statistics	UF (n[a]=16)	CA (n=26)	TA (n=12)	OA (n=5)	Chinese EPA[b]	WHO[c]
Cd	Range	2.0-5.7	1.3-9.1	1.5-19.0	2.6-4.0	10.0	3.0
	Mean	3.5	4.8	7.3	3.5		
Cr	Range	0.07-5.1	0.1-47.4	0.4-6.4	1.9-5.9	50.0	50.0
	Mean	1.2	6.1	3.4	3.6		
Cu	Range	3.3-14.5	2.8-68.3	4.0-28.0	7.8-9.6	1000.0	2000.0
	Mean	6.8	13.9	16.3	8.8		
Zn	Range	44.9-68.9	30.3-92.7	47.9-66.5	44.3-108.9	1000.0	3000.0
	Mean	54.4	52.2	59.0	60.6		
Pb	Range	3.3-29.7	6.2-49.0	2.9-75.7	9.3-15.3	50.0	10.0
	Mean	9.3	16.4	27.6	12.9		
Ni	Range	14.1-57.8	19.0-393.2	14.7-192.7	24.4-28.6	50.0	70.0
	Mean	30.8	101.9	62.2	26.9		

[a] Number of water samples; [b] source: Quality standard for groundwater (III) from National Standard of the People's Republic of China (China State Bureau of Technology Supervision 1993); [c] source: World Health Organization (WHO 2008)

Table 2: Chronic daily intakes [CDIs, μg/(kg·day)] of selected heavy metals.

Parameters	Individuals	Statistics	UF (n[a]=16)	CA (n=26)	TA (n=12)	OA (n=5)
Cd	Adults	Range	0.057-0.163	0.037-0.26	0.043-0.543	0.074-0.114
		Mean	0.1	0.137	0.209	0.1
	Children	Range	0.2-0.57	0.13-0.91	0.15-1.9	0.26-0.4
		Mean	0.35	0.48	0.73	0.35
Cr	Adults	Range	0.002-0.163	0.003-1.354	0.011-0.183	0.054-0.169
		Mean	0.034	0.174	0.097	0.103
	Children	Range	0.007-0.51	0.01-4.74	0.04-0.64	0.19-0.59
		Mean	0.12	0.61	0.34	0.36
Cu	Adults	Range	0.094-0.414	0.08-1.951	0.114-0.8	0.223-0.274
		Mean	0.194	0.397	0.466	0.251
	Children	Range	0.33-1.45	0.28-6.83	0.4-2.8	0.78-0.96
		Mean	0.68	1.39	1.63	0.88
Zn	Adults	Range	1.283-1.968	0.866-2.649	1.369-1.9	1.266-3.111
		Mean	1.554	1.491	1.686	1.731
	Children	Range	4.49-6.89	3.03-9.27	4.79-6.65	4.43-10.89
		Mean	5.44	5.22	5.9	6.06
Pb	Adults	Range	0.094-0.849	0.177-1.4	0.083-2.163	0.266-0.437
		Mean	0.266	0.469	0.788	0.769
	Children	Range	0.33-2.97	0.62-4.9	0.29-7.57	0.93-1.53
		Mean	0.93	1.64	2.76	1.29
Ni	Adults	Range	0.403-1.651	0.543-11.23	0.42-5.506	0.697-0.817
		Mean	0.88	2.911	1.777	0.769
	Children	Range	1.41-5.78	1.9-39.32	1.47-19.27	2.44-2.86
		Mean	3.08	10.19	6.22	2.69

[a]Number of water samples

was 0.0057-0.163, 0.037-0.26, 0.043-0.543 and 0.074-0.114 μg/(kg·day), with mean CDIs of 0.1, 0.137, 0.209 and 0.1 μg/(kg·day), respectively. For children, the range of the CDIs of Cd were 0.2-0.57, 0.13-0.91, 0.15-1.9 and 0.26-0.4 μg/(kg·day), with mean CDIs of 0.35, 0.48, 0.73 and 0.35 μg/(kg·day), respectively. The range of the CDIs of Cr for adults were 0.002-0.163, 0.003-1.354, 0.011-0.183 and 0.054-0.169 μg/(kg·day), with mean CDIs of 0.034, 0.174, 0.097 and 0.103 μg/(kg·day), respectively. For children, the range of the CDIs of Cr were 0.007-0.51, 0.01-4.74, 0.04-0.64 and 0.19-0.59 μg/(kg·day), with mean CDIs of 0.12, 0.61, 0.34, and 0.36 μg/(kg·day), respectively. The range of the CDIs of Cu for adults were 0.094-0.414, 0.08-1.951, 0.114-0.8 and 0.223-0.274 μg/(kg·day), with mean CDIs of 0.194, 0.397, 0.466 and 0.251 μg/(kg·day), respectively. For children, the range of the CDIs of Cu were 0.33-1.45, 0.28-6.83, 0.4-2.8 and 0.78-0.96 μg/(kg·day), with mean CDIs of 0.68, 1.39, 1.63 and 0.88 μg/(kg·day), respectively. The range of the CDIs of Zn for adults were 1.283-1.968, 0.866-2.649, 1.369-1.9 and 1.266-3.111 μg/(kg·day), with mean CDIs of 1.554,

Table 3: Health risk indexes (HRIs) of selected heavy metals.

Parameter	Individuals	Statistics	UF (n[a]=16)	CA (n=26)	TA (n=12)	OA (n=5)
Cd	Adults	Range	1.1E-01-3.3E-01	7.4E-02-5.2E-01	8.6E-02-1.09	1.5E-01-2.3E-01
		Mean	2.0E-01	2.7E-01	2.1E-01	2.0E-01
	Children	Range	4.0E-01-1.14	2.6E-01-1.82	3.0E-01-3.8	5.2E-01-8.0E-01
		Mean	7.0E-01	9.6E-01	1.5	7.0E-01
Cr	Adults	Range	1.3E-06-1.1E-04	2.0E-06-9.0E-04	7.3E-05-1.2E-04	3.6E-05-1.1E-04
		Mean	2.3E-05	1.2E-04	6.4E-05	6.9E-05
	Children	Range	4.67E-06-3.4E-04	6.67E-06-3.16E-03	2.67E-05-4.27E-04	1.27E-04-3.93E-04
		Mean	8.0E-05	4.1E-04	2.3E-04	2.4E-04
Cu	Adults	Range	2.54E-03-1.12E-02	2.16E-03-5.27E-02	3.08E-03-2.2E-02	6.03E-03-7.41E-03
		Mean	5.2E-03	1.1E-02	1.3E-02	6.8E-03
	Children	Range	8.92E-03-3.92E-2	7.57E-03-1.84E-01	1.08E-02-7.57E-02	2.11E-02-2.59E-02
		Mean	1.8E-02	3.8E-02	4.4E-02	2.4E-02
Zn	Adults	Range	4.28E-03-6.56E-03	2.89E-03-8.8E-03	4.56E-03-6.33E-03	4.22E-03-1.04E-02
		Mean	5.2E-03	5.0E-03	5.6E-03	5.8E-03
	Children	Range	1.5E-02-2.3E-02	1.01E-02-3.09E-02	1.59E-02-2.22E-02	1.48E-02-3.63E-02
		Mean	1.8E-02	1.7E-02	2.0E-02	2.0E-02
Pb	Adults	Range	2.67E-03-2.41E-02	4.92E-03-3.89E-02	2.3E-03-6.01E-02	7.39E-03-1.21E-02
		Mean	7.4E-03	1.3E-02	2.2E-02	2.1E-02
	Children	Range	9.17E-03-8.25E-02	1.72E-02-1.36E-01	8.6E-03-2.1E-01	2.58E-02-4.25E-02
		Mean	2.6E-02	4.6E-02	7.7E-02	3.6E-02
Ni	Adults	Range	2.02E-02-8.26E-02	2.72E-02-5.6E-01	2.1E-02-2.75E-01	3.48E-02-4.09E-02
		Mean	4.4E-02	1.5E-01	8.9E-02	3.9E-02
	Children	Range	7.05E-02-2.89E-01	9.5E-02-1.97	7.35E-02-9.4E-01	1.2E-01-1.4E-01
		Mean	1.5E-01	5.1E-01	3.1E-01	1.3E-01

[a] Number of water samples

1.491, 1.686 and 1.731 μg/(kg·day), respectively. For children, the range of the CDIs of Zn were 4.49-6.89, 3.03-9.27, 4.79-6.65 and 4.43-10.89 μg/(kg·day), with mean CDIs of 5.44, 5.22, 5.9 and 6.06 μg/(kg·day), respectively. The range of the CDIs of Pb for adults were 0.094-0.849, 0.177-1.4, 0.083-2.163 and 0.266-0.437 μg/(kg·day), with mean CDIs of 0.266, 0.469, 0.788 and 0.769 μg/(kg·day), respectively. For children, the range of the CDIs of Pb were 0.33-2.97, 0.62-4.9, 0.29-7.57 and 0.93-1.53 μg/(kg·day), with mean CDIs of 0.93, 1.64, 2.76 and 1.29 μg/(kg·day), respectively. The range of the CDIs of Ni for adults were 0.403-1.651, 0.543-11.23, 0.42-5.506 and 0.697-0.817 μg/(kg·day), with mean CDIs of 0.88, 2.911, 1.777 and 0.769 μg/(kg·day), respectively. For children, the range of the CDIs of Ni were 1.41-5.78, 1.9-39.32, 1.47-19.27 and 2.44-2.86 μg/(kg·day), with mean CDIs of 3.08, 10.19, 6.22 and 2.69 μg/(kg·day), respectively.

Health risk indexes of selected heavy metals: The HRI values of selected heavy metals for adults and children are summarized in Table 3. The HRI values of selected heavy metals were in a decreasing order: Cd>Ni>Pb>Cu>Zn>Cr. Several HRI values of Cd in the TA samples for adults and in the three aquifer water samples (UF, CA, and TA) for children exceeded 1. Several HRI values of Ni in the TA samples for children exceeded 1, and the HRI values of Cr, Cu, Pb and Zn were less than 1, indicating less health risk to local people who drink the water.

The mean HRI values of Cd were 2.0E-01, 2.7E-01, 2.1E-01 and 2.0E-01 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Cd were 7.0E-01, 9.6E-01, 1.5 and 7.0E-01 in the selected four aquifers, respectively. The high HRI value of Cd was 3.8 (which exceeds 1) in the TA for children. The low HRI value of Cd (7.4E-02, for adults) was recorded in CA. The mean HRI values of Cr were 2.3E-05, 1.2E-04, 6.4E-05 and 6.9E-05 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Cr were 8.0E-05, 4.1E-04, 2.3E-04 and 2.4E-04 in the selected four aquifers, respectively. The high HRI value of Cr was 3.16E-03 in the CA for children. The low HRI value of Cr (1.3E-06, for adults) was recorded in UF. The mean HRI values of Cu were 5.2E-03, 1.1E-02, 1.3E-02 and 6.8E-03 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Cu were 1.8E-02, 3.8E-02, 4.4E-02 and 2.4E-02 in the selected four aquifers, respectively. The high HRI values of Cu was 1.84E-01 (which is within 1) in CA for children. The low HRI value of Cu (7.41E-03, for adults) was recorded in OA. The mean HRI values of Zn were 5.2E-03, 5.0E-03, 5.6E-03 and 5.8E-03 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Zn were 1.8E-02, 1.7E-02, 2.0E-02 and 2.0E-02 in the selected four aquifers, respectively. The high HRI value of Zn was 3.63E-02 in OA for children. The low HRI value of Zn (2.89E-03, for adults) was recorded in CA. The mean HRI values of Pb were 7.4E-03, 1.3E-02, 2.2E-02 and 2.1E-02 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Pb were 2.6E-02, 4.6E-02, 7.7E-02 and 3.6E-02 in the selected four aquifers, respectively. The high HRI value of Pb was 2.1E-01 in TA for children. The low HRI value of Pb (2.3E-03, for adults) was recorded in TA. The mean HRI values of Ni were 4.4E-02, 1.5E-01, 8.9E-02 and 3.9E-02 for adults in the selected four aquifers (UF, CA, TA and OA), respectively; for children, the mean HRI values of Ni were 1.5E-01, 5.1E-01, 3.1E-01 and 1.3E-01 in the selected four aquifers, respectively. The high HRI value of Ni was 1.97 (which exceeds 1) in CA for children. The low HRI value of Ni (2.02E-02, for adults) was recorded in UF.

Uncertainty analysis: Uncertainty analysis has always been the main problem in health risk assessment. Hence, the health risk assessment results in this study also exhibit a certain degree of uncertainty mainly from three aspects. First, the weight and daily water consumption of children and adults were obtained from the US EPA standard, and the actual situation in the study area was not investigated. These conditions may have caused uncertainty in risk assessment. Second, health risk assessment was implemented only for children and adults, not for men and women. Hence, the results are not comprehensive. Lastly, the parameters in the risk assessment, such as RfD, were obtained from the US EPA database and may thus differ when applied to the study area; this condition may have also caused uncertainty. Investigation of local drinking habits would reduce uncertainty.

CONCLUSIONS

In the northern mining area of Anhui province, the mean concentrations of Cd, Cr, Cu, Zn and Pb were found to be within the permissible limits set by the Chinese EPA. However, the concentration of Ni was higher than the permissible limits; Ni is thus the priority pollutant in this coal mining area. Relevant departments should take active measures to prevent and control Ni pollution and reduce or avoid the occurrence of nickel poisoning among local residents. The concentrations of Cr, Cu, Zn and Ni were all within the permissible limits set by the WHO, whereas Cd and Pb concentrations were higher than the permissible limits. The health risk assessment conducted in this study revealed that the HRI values of the selected heavy metals are in a decreasing order, i.e., Cd>Ni>Pb>Cu>Zn>Cr. Although most of the heavy metals pose no health risk (HRI<1) according to the US EPA standards, several HRI values of Cd in the selected water samples exceed 1, indicating a small health risk to local people. Therefore, feasible measures should be adopted to prevent and control groundwater pollution. Such measures include dealing with coal cinder and wastewater produced by stacking and then discharged into the environment. The government should implement measures that combine mining technology improvement with the establishment of an environment management system to reduce or eliminate the hazards imposed by heavy metals to local residents.

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REFERENCES

China State Bureau of Technology Supervision 1993. GB/T 14848-93 National Standard of the People's Republic of China: Quality standard for ground water. Standards Press of China, Beijing.

Gui, H.R. 2005. Hydrogeochemical characteristics discrimination of groundwater in mining district of north Anhui province. University of Science and Technology of China, Hefei.

Jarup, L. 2003. Hazards of heavy metal contamination. British Medical Bulletin, 68(1): 167-182.

Kavcar, P., Sofuoglu, A. and Sofuoglu, S.C. 2009. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. International Journal of Hygiene and Environmental Health, 212(2): 216–227.

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z. and Zhu, Y.G. 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollution, 152(3): 686-692.

Khan, K., Lu, Y.L., Khan, H., Zakir, S., Ihsanullah., Khan, S., Khan, A.A. and Wang, T.Y. 2013. Health risks associated with heavy metals in the drinking water of Swat northern Pakistan. Journal of Environmental Science, 25(10): 2003-2013.

Lin, M.L., Gin, H.R. and Peng, W.H. 2014a. Study on content characteristics and water quality assessment of heavy metals in deep groundwater from northern Anhui mining areas. Journal of Safety and Environment, 14(6): 266-271.

Lin, M.L., Gin, H.R., Peng, W.H., Sun, L.H., Chen, S. and Li, Z.C. 2014b. Health risk assessment of heavy metals in deep groundwater from different aquifers of a typical coal mining area: A case study of a coal mining area in northern Anhui Province. Acta Geoscientica Sinica, 35(5): 589-598.

Muhammad, S., Shah, M.T. and Khan, S. 2010. Arsenic health risk assessment in drinking water and source apportionment using multivariate

statistical techniques in Kohistan region, northern Pakistan. Food and Chemical Toxicology, 48(10): 2855-2864.
Muhammad, S., Shah, M.T. and Khan, S. 2011a. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchemical Journal, 98(2): 334-343.
Muhammad, S., Shah, M.T. and Khan, S. 2011b. Heavy metal concentrations in soil and wild plants growing around Pb-Zn sulfide terrain in Kohistan region, northern Pakistan. Microchemical Journal, 99(1): 67-75.
Pekey, H., Karaka, D. and Bakoglu, M. 2004. Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analysis. Marine Pollution Bulletin, 49(9): 809-818.
Qui, J. 2011. China to spend billions cleaning up groundwater. Science, 334(6057): 745.
Shah, M.T., Ara, J., Muhammad, S., Khan, S. and Tariq, S. 2012. Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan. Journal of Geochemical Exploration, 118: 60-67.
Sun, L.H., Gui, H.R., Peng, W.H. and Lin, M.L. 2013. Heavy metals in deep seated groundwater in Northern Anhui Province, China: quality and background. Nature Environment and Pollution Technology, 12(3): 533-536.
Sun, L.H., Gui, H.R. and Peng, W.H. 2014. Heavy metals in groundwater from the Wolonghu coal mine, northern Anhui Province, China and their hydrological implications. Water Practice & Technology, 9(1): 80-87.
US EPA (US Environmental Protection Agency) 2005. Guidelines for Carcinogen Risk Assessment. Risk Assessment Forum, Washington, DC. EPA/630/P–03/001F.
US EPA (US Environmental Protection Agency) 2011. Exposure Factors Handbook. United States Environmental Protection Agency, Washington, DC. EPA/600/R–09/052F.
WHO (World Health Organization). 2008. Guidelines for Drinking Water Quality, 3rd ed. Recommendations, vol. 1. WHO Press, World Health Organization, 20 Avenue Appia, 1211 Geneva 27, Switzerland.