Nature Environment and Pollution Technology
An International Quarterly Scientific Journal | ISSN: 0972-6268 | Vol. 12 | No. 3 | pp. 533-536 | 2013

Original Research Paper

Heavy Metals in Deep Seated Groundwater in Northern Anhui Province, China: Quality and Background

Linhua Sun, Herong Gui, Weihua Peng and Manli Lin
School of Earth Science and Engineering, Suzhou University, Suzhou 234000, China

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 10-4-2013
Accepted: 2-5-2013

Key Words:
Anhui Province
Heavy metal
Groundwater quality
Environmental background

ABSTRACT

Forty-five deep seated groundwater samples from three aquifers in two coal mines (Wolonghu and Baishan), northern Anhui Province, China have been measured for four kinds of heavy metal (Pb, Zn, Cr and Ni) concentrations for evaluation of quality and, establishment of environmental background values by using model based objective methods. The results suggest that these groundwater samples are of excellent quality relative to the quality standard of groundwater established by Chinese government, and most of them can be used for drinking directly according to their low concentrations of heavy metals. Moreover, they are considered to be representative of "pristine" state because they are far away from anthropogenic contribution and therefore, they can be used for environmental background estimation. The thresholds of Pb, Zn, Cr and Ni between natural and abnormal or anthropogenic are calculated to be 17.4, 64.9, 3.9 and 71.1µg/L by using model based objective methods, respectively.

INTRODUCTION

Water is the most important foundation of life, and groundwater is one of the main constituent of water resources on earth. Nowadays, more than 1.5 billion persons in the world take groundwater for drinking purpose. However, about 80% of the diseases and deaths in the developing countries are related to water contamination (UNESCO 2007); take an instance, low pH groundwater can cause gastrointestinal disorder (Laluraj & Gopinath 2006), whereas groundwater with high total dissolved solids (TDS) can brought to people calculus and other diseases (Fetters 1990). Therefore, a large number of studies have been focused on groundwater quality monitoring and evaluation for domestic and agricultural activities (Al-Bassam & Al-Rumikhani 2003, Jeevanandam et al. 2006, Pritchard et al. 2008, Ma et al. 2009, Choi & Lee 2011).

China's per capita water resources is only 1/4 of the world average, and 400 in 600 cities across the country are facing serious water shortage, especially in north and northwest of China. Groundwater accounts for 50% of the total water supply in most of the cities and, more than 80% for some of the cities. However, because of the discharging and usage of large amounts of untreated wastewater (about 48 million tons per year) (GSSSG 2009), shallow groundwater systems in some areas have been polluted and then exacerbated the shortage of groundwater resources. Under this situation, deep seated groundwaters in some of the areas in China were considered to be reliable water sources, take an instance, deep karst water has long been used for water supply in Xuzhou City, northern Jiangsu Province (Hu 1998).

As one of the most important coal producing area in China, Northern Anhui Province is also facing the problem of surface water shortage, and the government in Suzhou City, northern Anhui Province, tends to exploit the groundwater from Ordovician limestone aquifer with up to 900m depth. However, the environmental studies related to these groundwaters are limited, and the published papers are focused only on major ions (Sun & Gui 2013, Sun et al. 2013).

In this study, four kinds of heavy metals (Pb, Zn, Cr, Ni) have been analysed for 45 groundwater samples from four deep seated aquifers, and the goals of the study include: (1) identifying the heavy metal concentrations of groundwater and evaluating its suitability for drinking and irrigation and industrial usage, and (2) establishing the environmental background of heavy metals in deep seated groundwater.

MATERIALS AND METHODS

Hydrological background: Our study area is located in Suixiao coalfield in northern Anhui Province. The coalfield is located northwest to Suzhou with 45 km and near the boundary between Anhui and Henan Province, China with a total area of 4200 km^2. The area is bounded by Longhai railway in north, Subei fault in south, the boundary between Anhui and Henan province in west and Jinghu railway in east. The length from east to west is about 40-80 km, and the width from north to south is about 70 km. The climate of the area is warm and belongs to semi-humid climate with an annual average temperature of 14.3°C. The average annual rainfall is 820 mm and most of it is concentrated between June and August.

Previous investigations revealed that the groundwater system in the area is mainly divided into three aquifers from up to down: loose layer aquifer, coal bearing sandstone aquifer and the underlying limestone aquifer. The loose layer aquifer (LA) is subdivided into two aquifers, the Tertiary and Quaternary aquifers with a depth up to 234 m and the wall rocks are mainly composed of clay, sandstone and conglomerate, and the water storage is limited. The coal bearing aquifer (CA) is subdivided into four aquifers and its wall rocks are composed of grey-white sandstones with a large number of cracks, the total thickness of the coal bearing aquifer is near 240 m and the water is enriched in the fifth and seventh aquifers. The limestone aquifer (TA) is mainly composed of limestone and can be subdivided into Taiyuan Formation and Ordovician limestone aquifers. Among all of these aquifers, TA is the major threat for the safety of coal mining.

Sampling and analysis: Forty-five groundwater samples from LA, CA and TA have been collected from the alley in Wolonghu and Baishan coal mine, and Suixiao coalfield 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 have 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 used for analysis of four kinds of heavy metals (Pb, Zn, Cr, Ni), and the standard solutions after dilution have been applied for calibration, and the relative standard deviation is limited to less than 3%.

Data treatment: The analytical results were firstly examined by SPSS (version 16) for data description, including min, max, mean, median, standard deviation, coefficient of variation, skewness and examination of normal distribution. Then the data were processed by model based objective methods (iterative 2σ technique and the calculated distribution function) for background estimation, the software (Excel macro) was provided by Nakic et al. (2007). In comparison with other environmental background estimation methods (Singh et al. 2001, Gemitzi 2012, Molinari et al. 2012), model based objective methods do not requiring normal or log-normal distribution and can be applied to small datasets (n > 30), they can be applied to scattered distributions if the Lilliefors test statistic T is lower than the critical value of T with 95% confidence (Lepeltier 1969).

RESULTS AND DISCUSSION

Heavy metal concentrations: The analytical results are presented in Table 1. As can be seen from the table, lead, zinc, chromium and nickel concentrations are 2.87-31.8, 30.3-109, 0.07-7.28 and 14.1-187 μg/L, and their mean concentrations are 12.8, 52.7, 2.24 and 51.5μg/L, respectively. The decreasing order of metal concentrations is Zn > Ni > Pb > Cr. As to their coefficients of variation, except for Zn which possesses a low CV value (0.23), other three metals have very high CV values higher than 0.50, indicating that Pb, Cr and Ni have obvious spatial variation relative to Zn. Moreover, all of the concentrations show positive bias as they all have skewness values higher than zero. It is also noticed that they do not have normal distribution because their Kolmogorov-Smirnov values are all lower than 0.05.

Chinese government has 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 is the worse which cannot be used for drinking, either irrigation or industrial use and must be carefully selected. Based on this standard, all the samples can be subdivided to class III or better according to the concentrations of Pb, Zn and Cr. However, there are only 28 samples which can pass the class III criterion and they are concentrated in LA and CA. Moreover, only four samples have higher Ni concentrations higher than the criterion of class IV and are all CA samples. Because the water supplies in the coal mining area are extracted from LA and CA, these results suggest that the groundwater quality in these two coal mines can be considered to be excellent according to their heavy metal concentrations.

Environmental background estimation: Determination of environmental background is a concern of scientists and government, because it is the basis for either pollution degree evaluation or future environmental protection. Therefore, a large number of studies focused on this issue have been published and cited (Singh et al. 2001, Gemitzi 2012, Molinari et al. 2012). Among these methods, they have a common objective: how to identify the threshold between anthropogenic and natural background? And the best answer is defined to be "finding out the pristine samples" (Urresti-Estala et al. 2013).

The deep seated groundwater system can meet this requirement because it is buried deeper than hundreds of meters and far away from anthropogenic activities. As in the study area, the only approach might be coal mining activities. However, as can be seen from their low concentrations of metals, especially the comparison with the groundwater

Table 1: Analytical results of heavy metals concentrations (µg/L).

	Min	Max	Mean	Median	SD	SK	CV	KS
Pb	2.87	31.8	12.8	10.3	7.84	1.32	0.61	0.000
Zn	30.3	109	52.7	50.4	12.0	2.27	0.23	0.008
Cr	0.07	7.28	2.24	1.70	1.97	1.04	0.88	0.004
Ni	14.1	187	51.5	38.1	40.2	1.95	0.78	0.001

Note: SD- Standard deviation, SK- Skewness, CV- coefficient of variation (SD/Mean), KS- Kolmogorov-Smirnov (95% confidence).

Table 2: Quality standards for groundwater in China (µg/L, GB/T 14848-9).

	Class I	Class II	Class III	Class IV	Class V
Pb	≤ 5	≤ 10	≤ 50	≤ 100	< 100
Zn	≤ 50	≤ 500	≤ 1000	≤ 5000	< 5000
Cr	≤ 5	≤ 10	≤ 50	≤ 100	< 100
Ni	≤ 5	≤ 10	≤ 50	≤ 100	< 100

Table 3: Environmental background values (µg/L) calculated by iterative 2σ technique (F1) and the calculated distribution function (F2).

	F1	T	$T_{Critical}$	F2	T	$T_{Critical}$
Pb	2.7-16.1	0.072	0.148	3.2-17.4	0.070	0.134
Zn	38.5-64.0	0.080	0.142	35.8-64.9	0.099	0.137
Cr	0-3.0	0.088	0.152	0-3.9	0.065	0.131
Ni	3.3-71.1	0.127	0.144	8.7-67.5	0.066	0.131

quality standard (Table 1 and 2), they have not, or only slightly affected by coal mining. Therefore, these samples are considered to be good choice for environmental background estimation.

The calculated environmental background values of Pb, Zn, Cr and Ni are given in Table 3. Because natural conditions are non-homogeneous, therefore, the environmental background values are sets of range rather than fixed values (Nakic et al. 2007), concentrations higher than the upper limit are considered to be abnormal (e.g. natural or anthropogenic). Goodness of fit of background data to a normal distribution is tested by using Lilliefors test for the level of significance a = 0.05, the bin width is calculated to be $2*IQR/n^{1/3}$, where IQR is the difference between values of 75 and 25 percentiles. The environmental background values of Pb, Zn, Cr and Ni, calculated by iterative 2σ technique, are 2.7-16.1, 38.5-64.0, 0-3.0 and 3.3-71.1 µg/L, respectively, whereas environmental background values of Pb, Zn, Cr and Ni calculated by calculated distribution function are 3.2-17.4, 35.8-64.9, 0-3.9 and 8.7-67.5 µg/L, respectively. They all can pass the Lilliefors test because their T values are lower than $T_{Critical}$. In comparison with this result, nine, four, nine and seven samples are considered to have abnormal Pb, Zn, Cr and Ni concentrations, respectively.

CONCLUSION

1. Most of the deep seated groundwater samples from three aquifers in two coal mines, northern Anhui Province, China can be classified as class III or better according to their Pb, Zn and Cr concentrations relative to quality standards for groundwater in China, and only four samples have higher Ni concentrations higher than the criterion of class IV.
2. The deep buried aquifers are far away from anthropogenic activities, they are considered to be representative of "pristine" state free of anthropogenic contribution, and therefore, they can be used for environmental background estimation.
3. The environmental background ranges of Pb, Zn, Cr and Ni between natural and abnormal or anthropogenic have been established, the thresholds for them are 17.4, 64.9, 3.9 and 71.1µg/L, respectively, and higher values can be considered to be abnormal or anthropogenic.

ACKNOWLEDGMENT

This work was financially supported by National Natural Science Foundation of China (No. 41173016) and Natural Science Foundation of Anhui Province (No. 1308085QE77), and the Key Project of Natural Science of the Department of Education, Anhui Province, China (No. KJ2013A246).

REFERENCES

Al-Bassam, A. M. and Al-Rumikhani, Y. A. 2003. Integrated hydrochemical method of water quality assessment for irrigation in arid areas:

Application to the Jilh aquifer, Saudi Arabia. Journal of African Earth Sciences, 36: 345-356.

Choi, H. M. and Lee, J. Y. 2011. Groundwater contamination and natural attenuation capacity at a petroleum spilled facility in Korea. Journal of Environmental Sciences, 23(10): 1650-1659.

Fetters, C. W. (ed.) 1990. Applied Hydrogeology. CBS, New Delhi.

Gemitzi, A. 2012. Evaluating the anthropogenic impacts on groundwater, a methodology based on the determination of natural background levels and threshold values. Environmental Earth Science, 67(8): 2223-2237.

Groundwater Science Strategy Study Group (GSSSG) (ed.) 2009. Opportunities and Challenges of Chinese Groundwater Science. Scientific Press, Beijing.

Hu, C.L. 1998. Environmental geological problems in the karstic water exploitation process in Xuzhou city. Hydrogeology and Engineering Geology, 25(5): 36-38.

Jeevanandam, M., Kannan, R., Srinivasalu, S. and Rammohan, V. 2006. Hydrogeochemistry and groundwater quality assessment of lower part of the Ponnaiyar River basin, Cuddalore district, south Inida. Environmental Monitoring and Assessment, 132(1-3): 263-274.

Laluraj, C. M. and Gopinath, G. 2006. Assessment on seasonal variation of groundwater quality of phreatic aquifer - A river basin system. Environmental Monitering and Assessment, 117: 45-47.

Lepeltier, C. A. 1969. Simplified treatment of geochemcial data by graphical representation. Economic Geology, 64: 538-550.

Ma, J., Ding, Z., Wei, G., Zhao, H. and Huang, T. 2009. Sources of water pollution and evolution of water quality in the Wuwei basin of Shiyang River, Northwest China. Journal of Environmental Management, 90: 1168-1177.

Molinari, A., Guadagnini, L., Marcaccio, M., Guadagnini, A. 2012. Natural background levels and threshold values of chemical species in three large-scale groundwater bodies in Northern Italy. The Science of the Total Environment, 425: 9-19.

Nakic, Z., Posavec, K. and Bacani, A. 2007. A visual basic spreadsheet macro for geochemical background analysis. Ground Water, 45(5): 642-647.

Pritchard, M., Mkandawire, T. and O'Neill, J.G. 2008. Assessment of groundwater quality in shallow wells within the southern district of Malawi. Physics and Chemistry of the Earth, 33: 812-823.

Singh, K., Bartolucci, A. and Bae, S. 2001. Mathematical modeling of environmental data. Mathematical and Computer Modelling, 33: 793-800.

Sun, L.H., Gui, H.R. and Lin, M.L. 2013. Major ion chemistry of groundwater from limestone aquifer in Taoyuan coal mine, northern Anhui Province, China. Fresenius Environmental Bulletin, 22(2): 537-543.

Sun, L.H. and Gui, H.R. 2013. Groundwater quality and evolution in a deep limestone aquifer, northern Anhui Province, China: Evidence from hydrochemistry. Fresenius Environmental Bulletin, 22(4): 1126-1131.

UNESCO 2007. UNESCO water portable no. 161: Water related disease. http://www. Unesco.org/water/news/newsletter/161.shtml.

Urresti-Estala, B., Carrasco-Cantos, F., Vadillo-Pérez, I. and Jiménez-Gavilán. 2013. Determination of background levels on water quality of groundwater bodies: A methodological proposal applied to a Mediterranean River basin (Guadalhorce River, Malaga, southern Spain). Journal of Environmental Management, 117: 121-130.