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Research Article

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Groundwater in rural area of Suzhou, northern Anhui Province, China: Heavy metal concentrations and statistical analysis

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ABSTRACT

The issue of water contamination is becoming more serious in nowadays, especially the heavy metal pollution. For revealing the groundwater quality in rural area of Suzhou, northern Anhui Province, China, a total of seventy samples have been collected and analyzed for six kinds of heavy metal concentrations. The results indicate that all of the heavy metals have low concentrations with significant spatial variations. In comparison with the quality standards of World Health Organization and Chinese government, they are classified as excellent. Statistical analyses, including correlation, cluster and factor analysis, suggest that two factors are responsible for the heavy metals in the groundwater. One is responsible for Fe and Mn, and another is responsible for Cr, Cd, Pb and Ni, and both of them are related to geological conditions, rather than anthropogenic activities.

Key words: Statistical analysis, Heavy metals, Groundwater, Quality, Source

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INTRODUCTION

Water is essential for living beings. However, previous studies revealed that more than one billion people in the world do not have suitable drinking water, and about three to five millions die annually from water related diseases [1, 2]. Two kinds of water resources, including surface water and groundwater are considered to be dominant in the world. However, the issue of water contamination is becoming more serious in nowadays, and human activities (e.g. agricultural, industrial and domestic) have long been identified to be the contributors of pollutants. Take an instance, nitrate pollution, heavy metal pollution and organic pollution [3-5].

Among these pollutions, heavy metals are considered to be the major pollutants of water sources, especially due to the industrial activities [6, 7]. Some of these metals are essential for living organisms, whereas others are non-essential as they are indestructible and most of them are categorized as toxic species on organisms. For instance, zinc and iron are essential elements and are generally considered to be non-toxic below certain levels, whereas cadmium, copper and lead are classified to be toxic elements because of their adverse health effects [8-10].

Just because of the importance of groundwater for human beings, as well as the effects of heavy metals for human health, a large number of studies related to heavy metals in groundwater have been processed, including quality assessment, source identification and remediation etc. [11-13], which have brought to us useful information for the management of groundwater resources.

In this study, a total of seventy groundwater samples from the wells in the rural area of Suzhou, northern Anhui Province, China have been collected, and the concentrations of six kinds of heavy metals (including Fe, Mn, Cr, Cd, Pb and Ni) have been measured. The results were compared with the maximum contaminant levels specified by World Health Organization (WHO) and quality standards of groundwater in China. Moreover, the multivariate statistical analysis was conducted to identify the source of the heavy metals.

EXPERIMENTAL SECTION

SITE DESCRIPTION:
Suzhou is a city located in northern Anhui Province, China (Fig. 1). The length from east to west is 195 km and the width from south to north is 151 km, and the total area of the city is 9787 km^2. The city's land area is 7.8 million acres and the plant area is 15.6 million acres with 200% multiple cropping index. The main crops in the area include wheat, corn, soybean, cotton, potato, rapeseed, peanuts and fruit etc. Moreover, the industry is mostly coal related because the coal production in the area is up to one hundred million tons per year. The city is located in the transition zone of warm and subtropical climate, and belongs to warm temperature monsoon climate. The annual rainfall is 774 - 895 mm, and the average temperature is 14 – 14.5 centigrade.

Almost all of water resources used for agriculture, industry and domestic purpose in the city was supplied by groundwater, and previous investigations revealed that there are three types of groundwater in the area, including shallow groundwater in the loose layer aquifer, deep groundwater in the limestone aquifer and bedrock fissure water. The average storage is 1.86 billion m^3 per year.

Fig. 1: Location of the Suzhou city

SAMPLING AND ANALYSIS:
A total of seventy shallow groundwater samples from the wells located in the rural area east to the Suzhou city, northern Anhui Province, China have been collected between September and October, 2013. 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, China. Atomic absorption spectrometer (AAS) has been applied for analysis of six kinds of heavy metals (Fe, Mn, Cr, Cd, Pb and Ni). 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.

DATA PROCESSING:
SPSS statistical package (Window version 11.5) was used for data analysis. The analysis of the experimental data was carried out by using descriptive statistics, Pearson correlation matrix and cluster analysis, as well as factor analysis.

The descriptive statistics was used for obtaining the min, max, mean, median, standard deviation, coefficient of variation and normality test. Pearson correlation analysis was used for determining the strength and direction of the association between two variables. Cluster analysis was applied for grouping the metals, and factor analysis was used for identifying the source of metals.

RESULTS AND DISCUSSION

METAL CONCENTRATIONS:

The descriptive statistics of analytical results are listed in Table-1. As can be seen from the table, the decreasing order of the concentrations of heavy metals is Mn > Fe >Pb > Ni > Cr > Cd, their median concentrations are 63.0, 14.7, 3.92, 3.88, 0.468 and 0.274 ug/l, respectively. However, it is also noticed from Table-1 that all of the heavy metals except for Fe have mean concentrations higher than median concentrations. Moreover, Fe, Mn and Pb have relative lower coefficients of variations (CVs). Their CVs are 0.65, 0.64 and 0.40, respectively, indicating that the spatial distributions of them are relatively homogeneous. Comparatively, Cr, Cd and Ni show high CVs (0.93, 1.00 and 1.29, respectively), suggesting that their spatial distribution are inhomogeneous, which might be an indication of anthropogenic effect.

Either skewness or kurtosis values are good indicators of concentration distributions. As can be seen from Table-1, Fe has the lowest skewness value (near to zero), whereas others have skewness values higher than one, implying that the distribution of Fe is near normal, whereas other have right bias relative to normal distribution. However, it can be obtained from the p-value of Anderson-Darling test that all of the heavy metal concentrations cannot pass the normality test, which might be related to their variable Kurtosis values.

TABLE-1 Descriptive statistics of heavy metal concentrations

	N	Min	Max	Mean	SD	Median	CV	Skewness	Kurtosis	p-value
Fe	70	0.47	33.0	14.3	9.31	14.7	0.65	0.08	-1.32	<0.01
Mn	70	39.0	297	93.2	59.9	63.0	0.64	1.71	2.68	<0.01
Cr	70	0.022	3.52	0.623	0.582	0.468	0.93	2.95	10.8	<0.01
Cd	70	0.009	2.35	0.390	0.391	0.274	1.00	2.65	9.30	<0.01
Pb	70	2.02	10.3	4.37	1.75	3.92	0.40	1.63	2.45	<0.01
Ni	70	0.034	45.5	7.19	9.31	3.88	1.29	2.77	8.30	<0.01

Note: Unit – ug/l. SD – standard deviation; CV – coefficient of variation; p-value is obtained by Anderson-Darling test (a normal distribution should be higher than 0.05).

EXTENT OF CONTAMINATION:

In comparison with the World Health Organization guidelines for drinking water quality [14], the results suggest that all of the sample can meet the requirement of Fe (300 ug/l), Mn (400 ug/l), Cd (3 ug/l) and Ni (70 ug/l), and only one sample has Pb concentration higher than the guideline of Pb (10 ug/l), indicating that the quality of the shallow groundwater in the area are excellent.

According to the groundwater quality standards of Chinese government (Table-2), only the Class I, II and III groundwater 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 Fe, Cr, Cd, Pb and Ni concentrations, whereas twenty samples cannot pass the Class III criterion of Mn concentrations.

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

	Class I	Class II	Class III	Class IV	Class V	N
Fe(ug/l)	≤100	≤200	≤300	≤1500	>1500	70
Mn(ug/l)	≤50	≤50	≤100	≤1000	>1000	50
Cr(μg/l)	≤5	≤10	≤50	≤100	>100	70
Cd(μg/l)	≤0.1	≤1	≤10	≤10	>10	70
Pb(μg/l)	≤5	≤10	≤50	≤100	>100	70
Ni(μg/l)	≤5	≤10	≤50	≤100	>100	70

Note: N means samples can pass the Class III criterion.

CORRELATIONS BETWEEN HEAVY METALS:

To deduce the probable common source of metals in water samples, the bivariate correlation procedure was used (Table-3). This procedure computes the pair wise associations for a set of metals and displays the results as a matrix. It is useful for determining the value of association of the investigated metals. Because, obtained data was not normally distributed, Spearman method was applied. As can be seen from Table-3, the close relationships between the Cr, Cd, Pb and Ni have been identified, which indicate that they have probable common source. However, there is no significant correlation between Fe, Mn and others, implying that Fe and Mn have different origin with other heavy metals.

TABLE-3 Results of correlation analysis

	Fe	Mn	Cr	Cd	Pb
Mn	0.18				
Cr	-0.18	0.02			
Cd	-0.09	-0.02	0.48*		
Pb	0.08	-0.02	0.51*	0.69*	
Ni	0.12	0.09	0.43*	0.85*	0.65*

*Note: * means correlation significant at the 0.01 level.*

CLUSTER ANALYSIS:
Cluster analysis grouped the studied heavy metals into clusters on the basis of similarities within a group and dissimilarities between different groups. In this study, Ward's method and Pearson distance have been applied during calculation, and the result is shown in Fig. 2. As can be seen from the figure, six studied heavy metals were classified into two groups based on spatial similarities and dissimilarities. The first one is Fe and Mn, whereas the second one includes Cd, Ni, Pb and Cr, which suggests that Fe and Mn have a common origin, probably related to the rocks in the aquifer, whereas other four kinds of heavy metals have another origin.

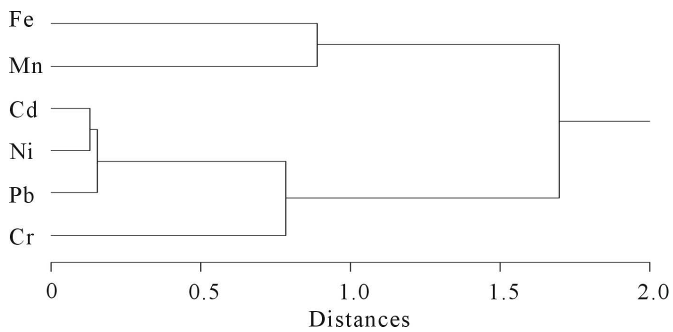

Fig. 2: Dendrogram of heavy metals (R-mode)

FACTOR ANALYSIS:
Factor analysis (coupled with principle component analysis) reduces the dimensionality of data by a linear combination of original data to generate new latent variables which are orthogonal and uncorrelated to each other [15]. Before the application of factor analysis, the raw data was normalized by using SPSS for avoiding misclassifications due to the different order of magnitude and range of variation of the analytical parameters. The rotation of the principal components was executed by the varimax method.

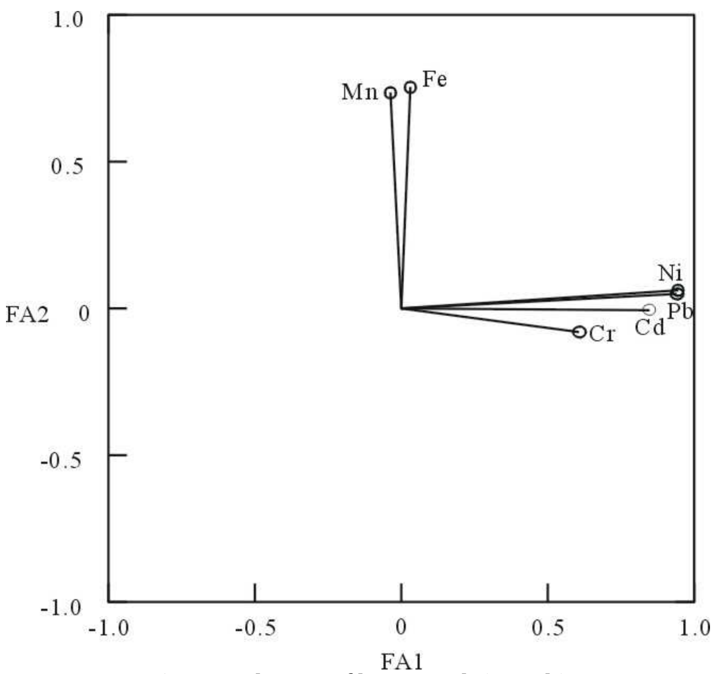

Fig. 2: Dendrogram of heavy metals (R-mode)

Two factors are obtained for heavy metals with eigenvalue higher than one (Table-4 and Fig. 3). This indicates that two main controlling factors influenced the quality of groundwater in the study area, which is similar to the results obtained by cluster analysis (Fig. 2). Factor analysis of the whole data set yielded two data sets explaining 68.5% of the total variance. The first factor explains 49.8% of the total variance and is correlated with Ni, Pb, Cd and Cr. The second factor is due to Fe and Mn with 18.7% of variance explained.

TABLE-4 Results of factor analysis

Factors	Ni	Pb	Cd	Cr	Fe	Mn	Eigenvalue	Variance explained
FA1	0.946	0.941	0.916	0.607	0.032	-0.036	2.990	49.8
FA2	0.061	0.050	-0.005	-0.081	0.753	0.735	1.119	18.7

The results obtained in this study are different with previous study [11], in which the groundwater samples were collected from the deep seated sandstone aquifer, where the sandstones are the main rocks in it. However, the groundwater samples in this study were collected from the loose layer aquifer, where the main rock types in it were mudstone and siltstone, and most of them are dominated by the mineral of quartz. Therefore, the groundwater samples in this study show relative lower heavy metal concentrations than the groundwater from the deep seated sandstone aquifer.

Moreover, Fe and Mn are always originated from geological sources, and Ni, Pb, Cd and Cr can be originated from either geological or anthropogenic sources. However, as can be seen from Table-4, these four metals have very high positive loadings on FA1 but very low or negative loadings on FA2. Therefore, they are also considered to be geological origin because: if they are only originated from anthropogenic origin, there loadings on FA2 should be identical because geological contribution is inevitable. Moreover, almost all of the groundwater samples in this study show excellent quality, which can also rule out the significant anthropogenic contribution.

CONCLUSION

Based on the statistical analysis of six kinds of heavy metals in shallow groundwater samples from the rural area of Suzhou, northern Anhui Province, China, the following conclusions have been made:

(1) The groundwater samples show low concentrations of heavy metals and therefore, they can be used for drinking according to either WHO or China’s quality standards;

(2) Correlation, cluster and factor analysis suggest that two factors are responsible for the heavy metals in the groundwater samples, Fe-Mn and Cr-Cd-Pb-Ni, both of them are related to geological conditions.

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