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Source estimating of heavy metals in shallow groundwater based on UNMIX model: A case study

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ABSTRACT

Heavy metals in the groundwater can threaten the health and life of animals and human beings through food chains. In this study, the concentrations of eight kinds of heavy metals (Fe, Mn, Zn, Cr, Cd, Cu, Pb and Ni) of sixty-two shallow groundwater samples from the urban area of Suzhou, northern Anhui Province, China have been measured, and the data have been analyzed by UNMIX model for quantifying their sources. The results indicate that the concentrations of all of the heavy metals except for Mn and Pb can meet the guidelines for drinking water quality of World Health Organization. Four sources, including both anthropogenic sources (related to transportation/centralization and car industry) and geological sources (related to Fe and Mn hydroxides), have been identified by UMIX model, and their contributions for the total heavy metals are 29.3% and 70.7%, respectively. The study demonstrated that the UNMIX model can be applied for estimating the source of heavy metals in groundwater. Moreover, the study showed that more attention should be paid to the heavy metals (especially Zn and Cr) in the shallow groundwater in the study area because they have been affected by human activities.

KEYWORDS

Heavy metals; Shallow groundwater; Source approximation; UNMIX model.

INTRODUCTION

Heavy metals, the group of metals and metalloids with atomic density greater than 5 time of water, have long been concerned by environmentalists because of their special characteristics, e.g. wide range of sources, serious toxicities and difficulties of remediation. They did not only affect the production and quality of crops, but also influence the quality of the atmosphere and water bodies, and then threaten the health and life of animals and human beings by way of the food chains[1]. And therefore, a large number of studies have been processed in the natural environments, including evaluation of pollution degree, identification of sources and methods for remediation, etc.[2-4].

How to clean the environment in order to avoid their entrance into the food chain is an important work, because it is essential for protecting the health of animals and human beings. However, it is more realistic to understand the pollution status first, and then the sources of heavy metals, because not all of the heavy metals are released by anthropogenic activities, but they can also be produced by natural weathering processes of crust materials[5].

Groundwater has become an important strategic resource as most of the regions in the world use groundwater for drinking and irrigation, especially under the condition that the serious pollution of surface water. And therefore, heavy metal pollutions (including degree evaluation and source identification) in groundwater have been concerned by a large number of studies[6-8].

Groundwater is important for the development of Suzhou, a city located in northern Anhui Province, China, because most of the water resources used for domestic purpose, agriculture and industry in the city are supplied by groundwater. Understanding the pollution status and identifying the sources of them are therefore, important for the area. In this study, a total of sixty-two groundwater samples from the shallow wells in the urban area have been collected, and the concentrations of eight kinds of heavy metals (Fe, Mn, Zn, Cr, Cd, Cu, Pb and Ni) have been measured, and then the data were analyzed by UNMIX model for identifying and quantifying their sources.

EXPERIMENTAL

Sampling and analysis

A total of sixty-two samples were collected from wells in the urban area of Suzhou between September and October, 2013 (Figure 1). They were filtered through 0.45 μm pore-size membranes and collected into 2.0 L polyethylene bottles that had been cleaned in the laboratory. On collection, they were immediately acidified to pH<2 with HNO_3 to prevent element precipitation and/or adsorption by the bottle. The samples were sent to the laboratory for analysis within 24 hours of collection. Analysis was carried out at the Engineering and Technology Research Center of Coal Exploration in Anhui Province, China. Atomic absorption spectrometer (model: TAS-990, China) was used for analysis of Fe, Mn, Zn, Cr, Cd, Cu, Pb and Ni. Calibration curves were obtained using a series of different concentrations of metal standards and all eight calibration curves were linear, with a correlation coefficient higher than 0.99.

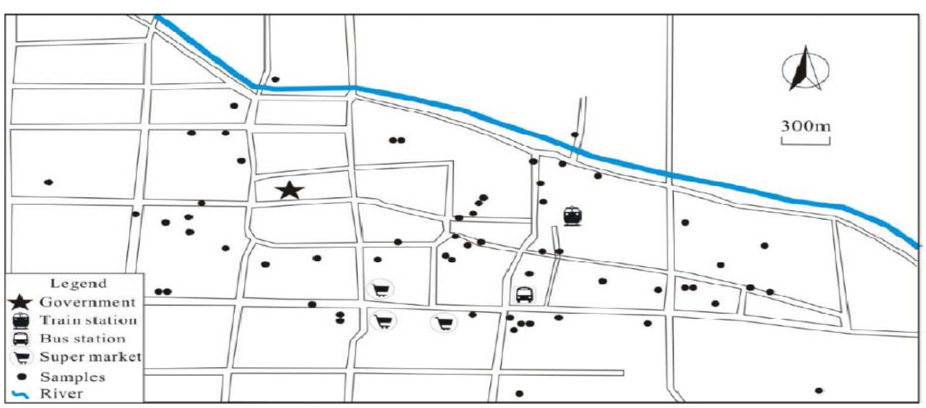

Figure 1: The distribution of sample locations

Data treatment

Identification of the source of anthropogenic and natural heavy metals in the environments is important for both environmental protection and remediation. Therefore, some methods for source identification and quantification have been proposed since the 60's of last century, including both qualitative analysis and quantitative calculation, and two kinds of models (the diffusion model and receptor model) have been widely applied[9,10]. And because of the easy application, the latter one (receptor model) is taken over gradually, such as CMB (chemical mass balance)[11], EF (Enriched factor)[12], PMF (positive matrix factorization)[13] and FA (factor analysis)[14] etc. These methods have been widely used in the environmental studies: including PM10 and 2.5 in the atmosphere and PAHs in coastal sediments and soils.

In this study, the eight kinds of heavy metal concentrations were firstly analyzed by Mystat software (version 12), and the descriptive statistics were obtained, including minimum, maximum, median, mean, coefficient of variation and p-value of normality test. And then, all of the data were analyzed by UNMIX model (version 6.0) for calculating the source compositions and contributions in each sampling site. Moreover, the contributions of each site have been plotted as contour map along with their locations by Surfer software (version 11) for understanding their spatial variations.

RESULTS AND DISCUSSIONS

Descriptive statistics

The descriptive statistics of the heavy metal concentrations in this study are synthesized in TABLE 1. As can be seen from the table, the concentrations of Fe, Mn, Zn, Cr, Cd, Cu, Pb and Zn are 1.64-273, 19.0-728, 2.54-225, 0.56-11.1, 0.21-2.42, 3.15-37.1, 3.92-11.5 and 1.17-48.2 μg/l, respectively, and their mean concentrations are Mn > Fe > Zn > Ni > Cu > Pb > Cr > Cd. Moreover, as suggested by previous studies, a low coefficient of variation (< 10%) indicates the low degree of anthropogenic contribution, whereas a high coefficient of variation (> 90%) indicates high degrees of anthropogenic contribution[15]. In this study, the coefficients of variations (CVs) of Fe, Mn, Zn, Cr, Cd, Cu, Pb and Zn are 0.83, 0.52, 0.94, 1.04, 0.59, 0.71, 0.26 and 0.84, respectively, which indicate that most of the heavy metals have been affected by human activities with moderate degrees, and Zn and Cr have high degrees of anthropogenic contributions. More information can also be obtained from their p-values of Anderson-Darling test, all of the heavy metals have p-values lower than 0.05, implying that all of them cannot pass the normality test, and therefore, they might have been affected by anthropogenic contributions.

TABLE 1: Descriptive statistics (μg/l)

Species	Min	Max	Median	Mean	CV	p-value
Fe	1.64	273	46.0	57.0	0.83	<0.01
Mn	19.0	728	242	262	0.52	<0.01
Zn	2.54	225	34.5	40.2	0.94	<0.01
Cr	0.56	11.1	1.02	1.35	1.04	<0.01
Cd	0.21	2.42	0.51	0.65	0.59	<0.01
Cu	3.15	37.1	7.14	8.55	0.71	<0.01
Pb	3.92	11.5	6.30	6.53	0.26	<0.01
Ni	1.17	48.2	8.75	11.1	0.84	<0.01
Mass	89.2	810	361	387	0.38	0.03

Quality of groundwater

In comparison with the guidelines for drinking water quality[16], the results suggest that all of the samples can meet the requirement of Fe (300 μg/l), Zn (3000 μg/l), Cr (50 μg/l), Cd (3 μg/l), Cu (2000 μg/l) and Ni (70 μg/l), respectively, and only six and three samples cannot meet the requirements of Mn

(400 μg/l) and Pb (10 μg/l), respectively, which suggest that the concentrations of Mn and Pb should be treated before the application of drinking.

Source approximation by UNMIX model

Based on the calculation of UNMIX model, four sources have been identified and the results are listed in Table 2. These four sources have Min Rsq = 0.83, representing that more than 83% of the variance information can be explained by the modeling and it is higher than the minimum requirement of the model (Min Rsq > 0.8). Moreover, the Min Sig/Noise is 2.07, also higher than the minimum requirement (Min Sig/Noise > 2). It can also be obtained from Figure 2 that the relationship between predicted and observed concentrations of total heavy metals is significant (r^2 = 0.47, higher than the critical value r^2 = 0.06, α=0.05, n =62), suggesting that the efficiency of modeling is good. Therefore, the results of source approximation based on UNMIX model is considered to be reliable[17].

TABLE 2: Source compositions (μg/l)

Species	Source 1	Source 2	Source 3	Source 4
Fe	6.920	1.150	58.900	-9.880
Mn	48.700	11.200	12.300	177.000
Zn	39.000	0.241	-6.090	7.920
Cr	0.179	0.740	0.117	0.329
Cd	0.150	0.006	-0.041	0.536
Cu	0.148	-0.041	6.960	1.610
Pb	1.130	0.337	0.940	3.770
Ni	0.425	-0.246	0.613	11.100
Mass	96.6	13.4	73.7	192

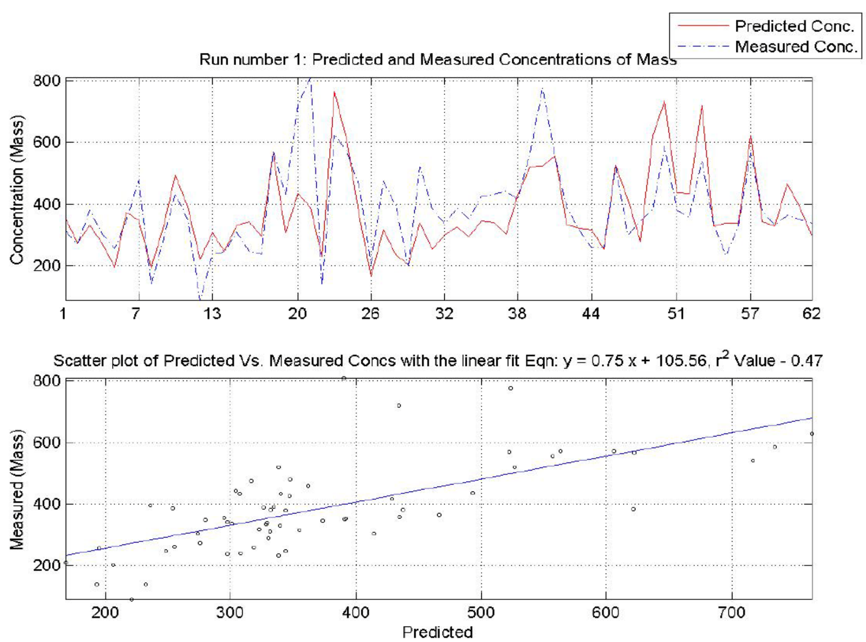

Figure 2: Predicted versus observed concentrations of total heavy metals (Mass)

The detailed explanations about the four sources are as follows:

Source 1 has the highest loading of Zn and moderate loadings of Fe, Mn, Cd and Pb among the four sources. This source has 25.7% contribution for the total heavy metals, and the spatial distribution of contribution of this source is inhomogeneous as suggested by its CV (0.99). Moreover, according to the spatial distribution of contributions of this source (Figure 3), the areas with high contributions of this source is located in the area with high densities of populations, including train station, bus station and super market. Therefore, this source can be explained to be an anthropogenic source related to transportation/centralization, because: (1) zinc is an essential component of tire manufacturing, and the wearing of tire is a main contribution for releasing the zinc into the environment[18] and (2) most of the lead in the current world is released by combustion of gasoline and diesel.

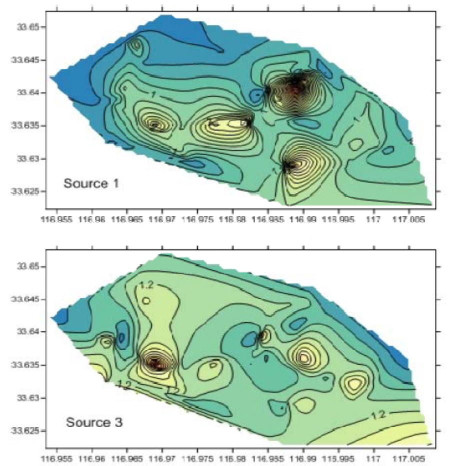

Figure 3: Spatial distributions of source contributions (method: natural neighbour)

Source 2 has the highest loading of Cr among the four sources, and other heavy metals possess the lowest loadings. This source has only 3.57% contribution for the total heavy metals. However, this source has the highest CV (1.97), which means that the spatial distribution of contribution of this source is inhomogeneous, and it has been dramatically affected by human activities. This consideration can also be demonstrated by the spatial distribution of contributions of this source (Figure 3) that the area with high contribution of this source is located in the south-west part of the study area, where the repair depots and trading markets of cars are concentrated. Therefore, this source can be explained to be another anthropogenic source related to car industry.

Source 3 and 4 has the highest loadings of most kinds of the heavy metals, including Fe, Mn, Cd, Cu, Pb and Ni among the four sources. These two sources have 70.7% contribution for the total heavy metals and, although their CVs (0.68 and 0.66, respectively) indicate that the distributions of these two sources are also inhomogeneous, their CVs are the lowest ones among the four sources. Therefore, these two sources can be explained to be geological sources related to Fe and Mn hydroxides. Such a consideration can also be achieved by Figure 3 that there is no significant centralized area with high contribution of source 3. Moreover, the distribution of contributions of source 4 is similar to the distribution of total dissolved solids in the groundwater from the study area[19], which was explained to be the result of geological heterogeneity.

Further discussions

In all, the results suggest that the heavy metal concentrations in the shallow groundwater from the urban area of Suzhou, northern Anhui Province, China are contributed by multi-sources, including both geological and anthropogenic. Although geology is the main source for some of the heavy metals (70.7% contribution), the contributions from human activities (e.g. transportation, centralization and industry) have high contribution for all of the heavy metals (29.3%), especially for Zn and Cr, which suggest that human activities have had a significant impact on the ecological environment of the shallow groundwater system in the area. And therefore, more attention should be paid to for protection.

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