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Statistical and Spatial Analyses of Zinc Concentrations in the Shallow Groundwater of Urban Area and Their Implications on Environmental Background Establishment

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ABSTRACT

Based on the systematic collection of the shallow groundwater samples in the urban area of Suzhou, Anhui province, China, the concentrations of zinc have been analysed by statistical and spatial methods. The results show that the zinc concentrations in the groundwater samples are low, and all the samples can meet the national groundwater quality standard of China with Class I and II, which means that the groundwater can be used for drinking purpose. However, the zinc concentration has high coefficient of variation and low p-values of normal distribution, implying that it has been affected by anthropogenic activities, which was also demonstrated by the consistency of the distribution of the samples with high zinc concentrations and the areas with high density of human and transportation, as well as the high-high cluster of the spatial autocorrelation analysis of zinc. Based on the statistical analysis, the environmental background has been calculated to be 0-62.6 μg/L, whereas the environmental background has been calculated to be 0-69.8 μg/L with spatial analysis. They are different because of the different basis of the two methods, the former based on the hypothesis of normal distribution of the background values, whereas the latter do not need such a hypothesis.

INTRODUCTION

Groundwater is the main water supply for the industrial, agriculture and domestic use in most cities in north China. However, because of the irrational exploitation and anthropogenic pollution, the quality of the groundwater in the areas with a high density of people has been dramatically affected (Liu et al. 2005). Therefore, the scientific issues related to the groundwater have attracted a great deal of attention, and a series of scientific or engineering discoveries have been reported, such as regional hydro-geology, hydrochemistry, groundwater pollution, modelling and management (Zhang et al. 1996, Zhang et al. 2003, Kemper 2004, Zhang et al. 2012, Rodríguez-Lado et al. 2013).

The environmental background is the concentration (mostly, the range of concentrations) of the chemical elements in a relatively clean area (with low contribution of anthropogenic activities), and is the basis to determine the pollution degree of a regional environment (Reimann et al. 2005, Reimann & Garrett 2005). For the management of groundwater, environmental background is important, because it is needed for identifying the pollution of the groundwater and, it is also the destination of the environmental protection (Liu et al. 2014).

Suzhou is an important city with coal production in northern Anhui Province, China, and it is also a city with a long period of groundwater utilization. The water for industrial and domestic purposes is mainly obtained from the underground, especially from the shallow and deep pore water. In recent years, with the continuous development of the urban economy and the scale of the city, the demand for industrial and domestic water is increasing, and the problems related to the development and utilization of groundwater resources are exposed more and more, which restricts the sustainable development of the city and the health of the people in the area (Li et al. 2004, Liu & Liang 2014, Lin & Peng 2016).

Because of the importance of groundwater for the development of the Suzhou city, the shallow groundwater in the urban area has been taken as the research object. Based on systematic sampling and the measurement of the zinc concentrations, statistical and spatial autocorrelation analyses have been applied to the data, for getting the statistical information about the zinc concentration and their spatial distribution, as well as the environment background of zinc in the groundwater, which can provide scientific information for the protection and utilization of the shallow groundwater in the area. For the shallow groundwater in the urban area, the transportation has long been identified to be one of the main sources of pollution because of the penetration of the recharge water from the surface to the underground, and zinc has long been identified to be the typomorphic element related to the wearing of tire (Sarkar et al. 2011), that is why we chose zinc as the study element therein.

MATERIALS AND METHODS

Study Area

Suzhou is the north gate of the Anhui province, China. It is located at the south of the Huang-Huai plain, adjacent to Xuzhou of Jiangsu and Heze of Shandong in the north, Yongcheng of Henan in the west, and Suqian of Jiangsu in the east. There are many rivers in the area, including the Kui, Sui, Tuo and Hui rivers, all of them flow from northwest to southeast, and ended in the Huai River or the Hongze lake. The annual precipitation is 857 mm, with an average temperature of 14.4 degrees (centigrade).

There are three aquifer systems in the study area, including the loose layer, the coal bearing sandstone and the limestone aquifer systems from shallow to deep. However, most of the water supply in the city is taken from the first one (loose layer aquifer system), which can also be subdivided into four aquifers (1^{st}- 4^{th}) from shallow to deep. All the groundwaters in the loose layer aquifer system of the urban area are recharged by the water from two ways: (1) the horizontal runoff from the mountain area located in the north of the city, and (2) the penetration from the vertical direction in the urban area, that is why the anthropogenic activities in the surface can affect the groundwater environment.

Sampling and Analysis

A total of 62 shallow groundwater samples were collected from the shallow wells of the local residents (<30m), that is why the locations of the samples look random. The sample locations are shown in Fig. 1. Before sampling, a 2.0 L polyethylene bottle that has been cleaned in the laboratory has been rinsed three times with the well water similar to the samples. The samples were acidified to be pH<2 by HNO_3 to prevent the adsorption of the elements by the bottle, and finally labelled and sent to the laboratory for processing. The GPS location and site conditions (including the flow of people, life, industry, and traffic related information) have been recorded.

In the laboratory, all the samples were filtered through 0.22 μm film before analysis, for removing debris. The concentration of zinc was analyzed by atomic absorption spectrometer, and the quality control was carried out by standard sample (the correlation coefficient between actual and measured concentrations was higher than 0.99). All the analysis was conducted in the Engineering Research Center of Coal Mine Exploration, Anhui province, China.

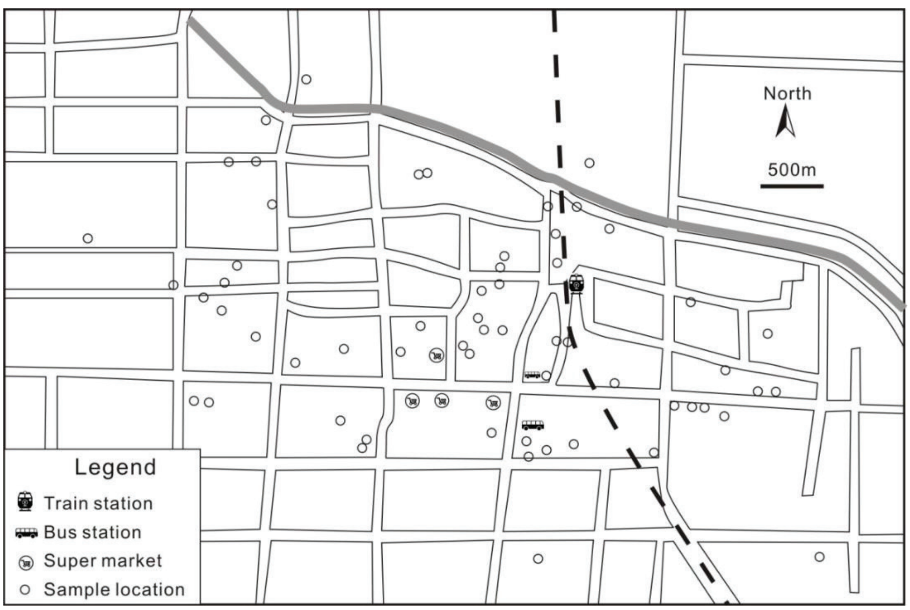

Fig. 1: Locations of the groundwater samples.

Data Treatment

Firstly, all the data were processed for statistical analysis by the Mystat 12 software, for calculating the maximum, minimum and mean values, standard deviation, coefficient of variation and the p-value of the normal distribution test, and then the contour map of the zinc concentrations was constructed by the Surfer 11 software (with natural neighbour grid method), and finally the spatial autocorrelation analysis by the Geoda 1.8.3 software. For avoiding the influence of the non normal distribution data for the spatial cluttering, all the zinc concentrations were firstly transformed by Box-cox with the Minitab 14 software. Finally, the local spatial autocorrelation (LISA) is processed to obtain the significant map and the spatial clustering map.

At present, there are two kinds of methods for determining environmental background values, including the geochemical method and statistical method. Among these two, the statistical method is the most commonly used one, because it is hard to find a place without anthropogenic influence, which was needed for the geochemical method. There are some kinds of methods related to the statistical method, e.g. the relative cumulative frequency, the normal distribution, the regression analysis, the outlier test, the iterative standard deviation and so on (Reimann et al. 2005, Reimann & Garrett 2005), and all of these methods have a same basis that the background values of the sample obey the normal distribution (or lognormal distribution).

In this study, two kinds of methods have been applied for the establishment of the environment background value:

(1) The box plot by the Mystat 12, which based on the assumption that the environmental background value in line with the normal distribution. After processing, the samples outside the lower and upper hinge of the box plot were removed (repeated until no abnormal samples), and then the mean and standard deviation of the rest of the samples were calculated. The environmental background value was then calculated to be mean ± 2*standard deviation.

(2) Based on the spatial autocorrelation analysis, the basis is that there is no significant change of the concentrations in the sample relative to its adjacent samples. Therefore, the samples for calculating the environmental background values only consider the non significant samples (without high-high, low-low, high-low and low-high clusters) after spatial autocorrelation analysis, then the environmental background values were calculated by the mean ± 2*standard deviation.

RESULTS AND DISCUSSION

Concentrations

According to the groundwater quality status, health of people and the goal of environmental protection, the quality of the groundwater has been classified into five degrees according to the National Standard of China (GB/T 14848-93): Class I and II (≤0.5 mg/L), natural background; Class III (≤1.0 mg/L), suitable for drinking, industrial and agricultural use; Class IV (≤5.0 mg/L), suitable for industrial and agricultural use (can also be used for domestic purpose after treatment); Classes V (>5.0 mg/L), not suitable for any purpose. In this study, the zinc concentrations of the groundwater are 2.54-225 μg/L (mean = 40.4 μg/L) (Table 1). In comparison with the National Standard of China, all the samples can be classified to be Class I and II. However, does it mean that the zinc in the groundwater has not been affected by human activities?

In environmental studies, coefficient of variation (CV) is always used for analyzing the degree of anthropogenic contribution of pollutants: when CV < 0.10, it means low anthropogenic contribution, whereas CV > 0.90 means high anthropogenic contribution (Peters et al. 1997, Xie et al. 2011). In this study, the groundwater samples have a relatively high CV (0.937), which probably means that the zinc in the groundwater has been influenced by anthropogenic activities. Moreover, the p-value of normal distribution test is <0.01, which means that the zinc concentrations in this study cannot pass the normal distribution test (p> 0.05), which also indicates the anthropogenic contribution (Reimann et al. 2005, Reimann & Garrett 2005). Even after log transformation, the CV is also > 0.10 and the p-value < 0.05, which also means anthropogenic influence.

Spatial Distribution of Zinc

The contour map of the zinc concentrations in this study is shown in Fig. 2. As can be seen from the figure, three areas with high zinc concentrations can be found in the central and central-east of the study area. In comparison with the sample locations in the Fig. 1, it can be found that the groundwater samples with high zinc concentrations are located near the train station, bus station and the business area. During the period of sampling, we found that the three areas are characterized by high density of people and transportation. Because, except for the geogenic origin (weathering of rocks), another important source of zinc in the environment is the transportation related tire erosion, which can release Zn, Pb and Cu simultaneously (Sarkar et al. 2011).

Table 1: Statistical description of zinc in this study (μg/L).

N	Min	Max	Mean	SD	CV	p-value
62	2.54	225	40.4	37.8	0.937	<0.01

Spatial Autocorrelation Analysis

According to the classification of Moran'I index (Anselin 1995), all the samples can be subdivided into two

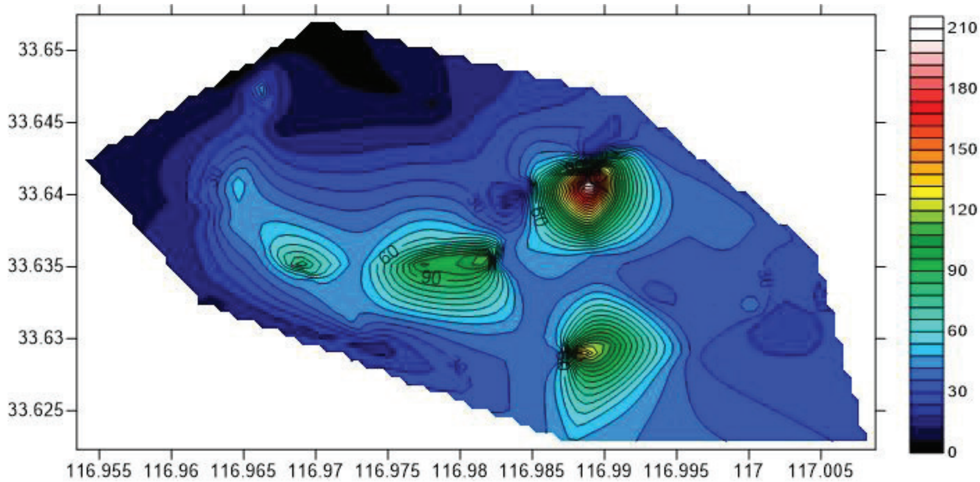

Fig. 2: Contour map of zinc concentrations (μg/L).

major categories: one is "not significant", and another is "significant". Samples classified into the former are considered as the environmental background samples in this study, and the samples classified into the latter can be divided into four sub categories: high-high, low-low, low-high and high-low, which represent the relationship between the concentration of a sample and its surrounding ones. The hot spot includes the high-high samples, and the freezing spot includes the low-low samples, whereas the low-high and high-low samples are abnormal ones, which may be related to the influence of other factors (Moran 1948, Ord & Getis 1995, Diniz-Filho et al. 2003, Zhao et al. 2009). The result of spatial autocorrelation analysis is shown in Fig. 3.

As can be seen from the figure the 31 samples are classified to be "non significant" samples, whereas the sample numbers classified to be high-high, low-low, low-high and high-low clusters are 20, 4, 3 and 4, respectively. It can also be noticed from the figure that the samples divided into the high-high cluster are mainly concentrated in the area between the train station (north), bus station (south)

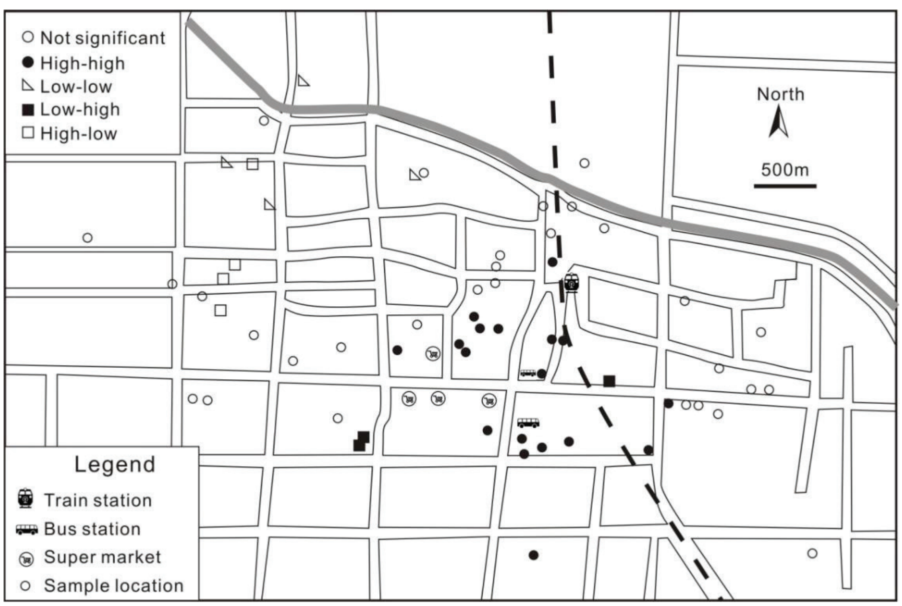

Fig. 3: Results of spatial autocorrelation analysis.

and the commercial district (west). Therefore, this area can be called as "hot spot". This area is consistent with the distribution of the samples with high zinc concentrations in Fig. 2, which implies that the high density of human and transportation is the main influencing factor. In contrast, the low-low cluster samples are located in the north of the study area, where there is the newly constructed urban area with low density of humans. Further, for the low-high and high-low abnormal samples, they reflect that the concentrations of zinc in these samples are "mutation" relative to the surrounding ones, and may be a reflection of natural or anthropogenic disturbance (Moran 1948, Ord & Getis 1995, Diniz-Filho et al. 2003, Zhao et al. 2009).

Establishment of the Environmental Background

Fig. 4 is the density plot of zinc concentrations. It can be seen from the figure that the concentrations of the zinc have three peaks, which probably indicates that the zinc in the groundwater without anthropogenic influence might follow the normal distribution (the first peak in the Fig. 4). Based on the box plot of the zinc concentrations, there are 6 samples with zinc concentrations higher than 100 μg/L can be considered as outliers (Fig. 5). After removing them, the remaining 56 samples were calculated and the average value was 30.0 μg/L with standard deviation of 16.3 μg/L (Table 2). Therefore, the background value calculated by the statistics method is 0-62.6 μg/L (less than 0 and replaced by 0).

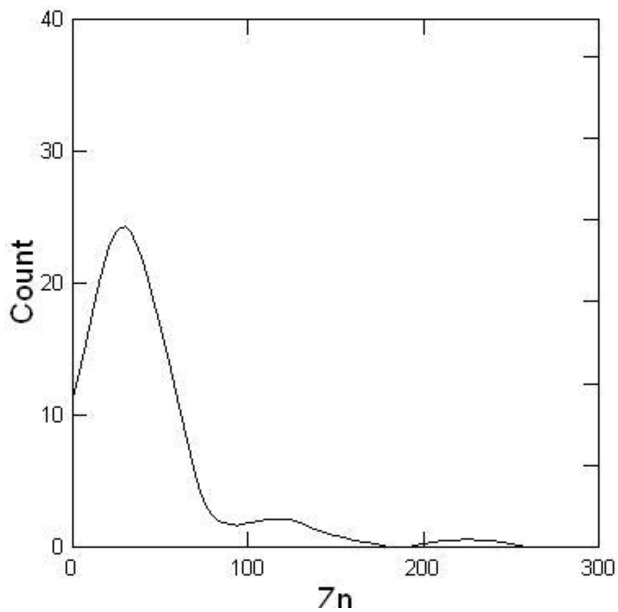

Fig. 4: Density plot of the zinc concentrations.

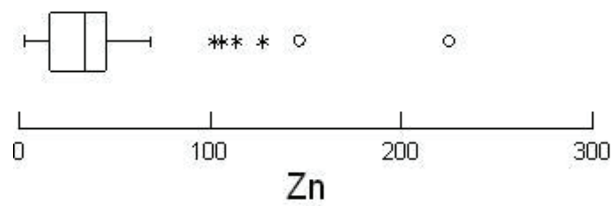

Fig. 5: Box plot of the zinc concentrations.

As to the spatial autocorrelation analysis, the above mentioned 31 samples belonging to the "non significant" category were calculated, the mean value was 29.1 μg/L with the standard deviation of 20.3 μg/L (Table 2). Therefore, the background value calculated by the spatial autocorrelation analysis method is 0-69.8 μg/L (less than 0 and replaced by 0).

Table 2: Statistical descriptive of zinc samples after outlier remover(μg/L).

	N	Min	Max	Mean	SD	CV	p-value
Zn^1	56	2.54	69.1	30.0	16.3	0.544	>0.15
Zn^2	31	2.54	102	29.1	20.3	0.699	<0.01

Note: 1 and 2 are the samples after outlier remover based on the box plot and spatial autocorrelation analysis, respectively.

COMPARISON AND DISCUSSION

For comparison, the iterative standard deviation, distribution function method (Nakić et al. 2007) and QQ plot (Panno et al. 2006) have also been applied for calculation. The results show that the environmental background values of zinc in the groundwater are 0-58.9 μg/L (iterative standard deviation) and 0-72.9 μg/L (distribution function). As can be seen from the QQ diagram (Fig. 6), there was an inflection point at the 69.1 μg/L, and therefore, it can be determined that the environmental background value was 2.54 to 69.1 μg/L.

According to the results obtained by the above methods, it can be synthesized that the calculated environmental background values are different with each other, and the main reason for this difference is their different basis: for the statistical methods (including box plot, QQ plot and iterative standard deviation, distribution function), the basis is that the background samples follow the normal distribution, whereas the spatial analysis focused on the "non mutation" feature (no significant spatial autocorrelation).

During the application, if the distribution of the element/pollutant can be determined or demonstrated, the statistics method (or the method with same principle, such as the iterative standard deviation and the probability distribution plot (Panno et al. 2006, Nakić et al. 2007) can be considered. However, if the distribution of data is uncertain, the method of spatial analysis should be chosen.

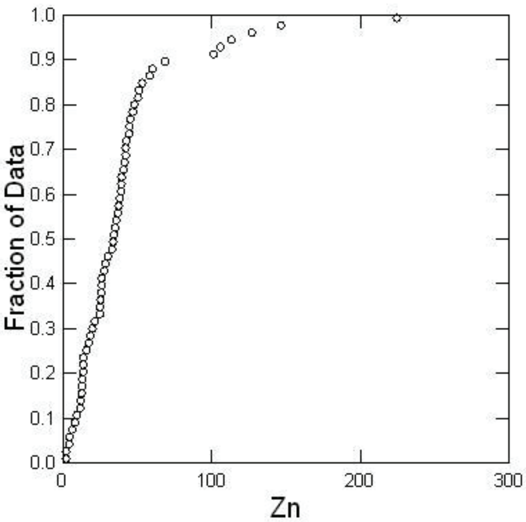

Fig. 6: QQ plot of the zinc concentrations.

CONCLUSIONS

Based on the systematic sampling and the measurement of the zinc concentrations of the shallow groundwater in Suzhou, Anhui province, China, the statistical and spatial autocorrelation analyses have been processed for the zinc concentrations, and the following conclusions have been obtained:

1. All the groundwater samples can meet the requirement of zinc concentrations of the Class I and II of the national groundwater quality standard of China, which means that they can be used for drinking purpose, however, they have medium CV and low p-value of normal distribution test, implying that the groundwater have been influenced by human activities;
2. The spatial distribution of the zinc concentration suggests that the samples with high concentrations of zinc are located near the train station, bus station and the business area, consistent with the hot spot identified by spatial autocorrelation analysis, and indicating that high density of human and transportation are the main factors influencing the zinc in groundwater;
3. The environmental background calculated by statistical and spatial analyses is 0-62.6 and 0-69.8 μg/L, respectively. They are different because of the different basis of the two methods. And during the application, they can be used with different conditions.

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