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Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China☆

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A B S T R A C T

In this study, we investigated the pollution degree and spatial distribution of heavy metals and determined their sources in topsoil in a typical coal mine city, Lianyuan, Hunan Province, China. We collected 6078 soil surface samples in different land use types. And the concentrations of Zn, Cd, Cu, Hg, Pb, Sb, As, Mo, V, Mn, Fe and Cr were measured. The average contents of all heavy metals were lower than their corresponding Grade II values of Chinese Soil Quality Standard with the exception of Hg. However, average contents of twelve heavy metals, except for Mn, exceeded their background level in soils in Hunan Province. Based on one-way analysis of variance (ANOVA), the contents of Cu, Zn, Cd, Pb, Hg, Mo and V were related to the anthropogenic source and there were statistically significant differences in their concentrations among different land use patterns. The spatial variation of heavy metal was visualized by GIS. The PMF model was used to ascertain contamination sources of twelve heavy metals and apportion their source contributions in Lianyuan soils. The results showed that the source contributions of the natural source, atmospheric deposition, industrial activities and agricultural activities accounted for 33.6%, 26.05%, 23.44% and 16.91%, respectively.

1. Introduction

Soil heavy metal contamination attracts great attention around the world due to rapid urbanization and industrialization (Chen et al., 2009). In a large number of soil pollutants, heavy metals already turn into an important contaminant because of their toxicity and difficult degradation (Zhong et al., 2014). Heavy metals accumulate in soils as time goes on, which can lead to the loss of soil nutrient component and the degeneration of soil biology and function (Zhang et al., 2016; Zhao et al., 2013). For instance, if the Fe concentration in soils is too high, it will affect the growth of rice. Additionally, high contents of soil heavy metal cause a serious threat to human and animals health, because heavy metal ions can be easily enter human and animals bodies by inhalation, dermal absorption or ingestion (Sun et al., 2010). For example, Cu in soils can be absorbed by the roots of crops, when Cu accumulates to a certain extent in the human body, it will be harmful to human health (the normal Cu content in soils is 2–200 mg kg^{-1}).

It is generally considered that natural and human activities are the two major origins of heavy metals. Natural sources of soil heavy metals are mainly controlled by the geological parent material (Liu et al., 2015). In addition, anthropogenic inputs of soil heavy metals are attributed to metalliferous industries, mining, vehicle exhaust, agricultural practices, coal combustion and atmospheric deposition (Alloway, 2013; Zhang, 2006). Therefore, it is very necessary to identify metal inputs before taking effective measures to protect soil quality. The spatial distribution of heavy metals in topsoil is largely influenced by natural inputs and human activities (Lu et al., 2012). Multivariate statistics combined with geostatistical methods are used to identify sources and the spatial variation of heavy metals in soils (Liang et al., 2016b; Maas et al., 2010). Positive matrix factorization (PMF) was applied to source apportionment of atmospheric particles in the early 1990s (Paatero and Tapper, 1994). And it is also effectively employed to apportion source contribution in sediments, soils and aquatic systems in recent years (Chen et al., 2016; Hua et al., 2015). Thus, this research applied the PMF model to identify twelve heavy metal's sources in soils in the Lianyuan

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city.

Lianyuan, a famous old industrial base in Hunan Province (China), possesses rich mineral resources and is known as “the sea of coal, the township of building materials, the hometown of metals and nonmetals”. Coal combustion is regarded as the most vital input of heavy metal pollution (Liaghati et al., 2004). In the Lianyuan city, many heavy industries (for instance, chemical manufacturing, metallurgical industries, iron and steel plants and so on) are related to coal combustion. What is more, there are a number of small-scale coal mines in the Lianyuan city. Coal mining can cause heavy metal pollution in different land use patterns directly or through atmospheric sedimentation. Previous studies have paid close attention to soil contamination in a single land use pattern (e.g. agricultural soil, industrial district soil, etc.), but have focused less on heavy metal pollution in soils in the coal mine city (Li et al., 2013). Consequently, it is the necessary to investigate heavy metal pollution in the surface soils from different land use patterns in a typical coal mine city, Lianyuan. This study area includes three land use patterns, which are woodland, farmland and land for construction. Our specific objectives are as follows: (1) to estimate the contamination extent of heavy metals in soils, (2) to ascertain the spatial variation characteristics of soil heavy metal concentration using geostatistics, and (3) to quantitatively identify various sources of soil heavy metals based on positive matrix factorization (PMF). This work will provide effective information to prevent further heavy metal pollution in soils in some coal mine cities.

2. Materials and methods

2.1. Study area

Lianyuan (27°27′-28°2′N, 111°33′-112°2′E), including one residential district and nineteen towns, is located in the geometrical center of Hunan province, South Central China. The city's terrain is largely mountainous, and low-lying the west to the east. The city has a subtropical humid monsoon climate. Furthermore, the annual mean temperature and rainfall are 16–17.3 °C and 1406 mm, respectively. Major industries are mining, iron and steel manufacturing, coking, machine manufacturing, metal smelting, pharmaceuticals industry, chemical planting and so on. These industry activities are closely related to heavy metal pollution in soils in the Lianyuan city.

2.2. Sample collections and concentration determination

We collected 6078 surface soil samples in the whole city from May to October, 2015 (Fig. 1). Sampling points were selected with the density of about seven every 1 km^2. In order to improve the sampling efficiency and the quality of the investigation work, the GeoSurveyPad digital survey system was applied to record geographic coordinates of the sampling points. All samples were open-air dried at room temperature in a room and selected through a 2-mm sifter after removing root and plant materials. Finally, these samples were stored in plastic bottles for concentration determination.

The soil samples were digested using the method of HNO_3-$HClO_4$-HF (Chen et al., 2009). The concentration of Fe, Cu, Zn, Cr, Pb, Mn and V was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Oral et al., 2016). The inductively coupled plasma mass spectrometer (ICP-MS) was used to analyze the concentration of Cd and Mo (Huang et al., 2008; Ivanova et al., 2001). A portion of soil samples were digested with HNO_3: HCl = 1:3, after that Hg, As and Sb concentration was determined by atomic fluorescence spectrometry (AFS) (Lin et al., 2010). Soil standard reference materials, GSS-1 and GSS-4 purchased from the Center of National Reference Materials of China, were used for quality assurance and quality control (QA/QC). Recoveries ranged from 84% to 98%. Each set of 50 samples, including 1 duplicate sample, 2 standard samples and 2 external monitor samples, was used for evaluate the accuracy of analysis methods. Every soil sample was tested in triplicate ($n = 3$). The standard deviation was lower than 7% of all batch treatments. Detection limits were 2, 0.017, 0.0005, 3, 0.5, 0.05, 4, 0.3, 8, 0.03, 4 and 0.9 mg kg^{-1} for Pb, Cd, Hg, Zn, As, Fe, Cr, Mo, Mn, Sb, V and Cu, respectively.

2.3. Statistical and geostatistical analyses

The descriptive statistical analysis was conducted by applying SPSS 19.0 (IBM, USA), while the correlations between heavy metals were described by using Spearman correlation analysis. Prior to One-way analysis of variance (ANOVA) and geostatistical analyses, a normality test (Kolmogorov-Smirnov test) was accomplished in order to assess the normality of original concentration data. The original concentration data, which does not meet the normal distribution, was normalized by the Box-Cox transformation. The differences of heavy metal concentrations were compared from the different land use types using the ANOVA. The kriging interpolations of soil heavy metal contents were calculated using the ArcGIS 9.3 (ESRI, Redlands, California, USA).

2.4. PMF model

In our research, PMF 5.0 was adopted to source apportionment of heavy metals in soils. According to EPA PMF 5.0 user guide:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where x_{ij} is a measurement matrix of the j_{th} heavy metal element in i number of samples; g_{ik} is a contribution matrix of the k_{th} source factor for i number of samples; f_{kj} is a source profile of j_{th} heavy metal element for the k_{th} source factor; and e_{ij} refers to the residual value for the j_{th} metal element in i number of samples. The minimum value of the objective function Q can be computed by the following formula.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right)^2 \tag{2}$$

where u_{ij} refers to the uncertainty in the j_{th} heavy metal element for sample i.

The remarkable feature of PMF is using uncertainty to analyze the quality of every concentration data individually. If the concentration of heavy metal does not exceed the MDL value, the uncertainty is calculated using the following formula.

$$Unc = \frac{5}{6} \times MDL \tag{3}$$

If the concentration of heavy metal exceeds its corresponding MDL value, the calculation is

$$Unc = \sqrt{(Errorfraction \times concentration)^2 + (0.5 \times MDL)^2} \tag{4}$$