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Source identification and spatial distribution of arsenic and heavy metals in agricultural soil around Hunan industrial estate by positive matrix factorization model, principle components analysis and geo statistical analysis

Xiaowen Zhang[1], Shuai Wei[1], Qianqian Sun, Syed Abdul Wadood, Boli Guo*

Institute of Food Science and Technology, Chinese Academy of Agriculture Sciences/ Key Laboratory of Agro-products Quality and Safety Control in Storage and Transport Process, Ministry of Agriculture, Beijing 100193, PR China

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ABSTRACT

Characterizing the distribution and defining potential sources of arsenic and heavy metals are the basic preconditions for reducing the contamination of heavy metals and metalloids. 71 topsoil samples and 61 subsoil samples were collected by grid method to measure the concentration of cadmium (Cd), arsenic (As), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr). Principle components analysis (PCA), GIS-based geostatistical methods and Positive Matrix Factorization (PMF) were applied. The results showed that the mean concentrations were 9.59 mg kg^{-1}, 51.28 mg kg^{-1}, 202.07 mg kg^{-1}, 81.32 mg kg^{-1} and 771.22 mg kg^{-1} for Cd, As, Pb, Cu and Zn, respectively, higher than the guideline values of Chinese Environmental Quality Standard for Soils; while the concentrations of Ni and Cr were very close to recommended value (50 mg kg^{-1}, 200 mg kg^{-1}), and some site were higher than guideline values. The soil was polluted by As and heavy metals in different degree, which had harmful impact on human health. The results from principle components analysis methods extracted three components, namely industrial sources (Cd, Zn and Pb), agricultural sources (As and Cu) and nature sources (Cr and Ni). GIS-based geo-statistical combined with local conditions further apportioned the sources of these trace elements. To better identify pollution sources of As and heavy metals in soil, the PMF was applied. The results of PMF demonstrated that the enrichment of Zn, Cd and Pb were attributed to industrial activities and their contribution was 24.9%; As was closely related to agricultural activities and its contribution was 19.1%; Cr, a part of Cu and Ni were related to subsoil and their contribution was 30.1%; Cu and Pb came from industry and traffic emission and their contribution was 25.9%.

1. Introduction

Heavy metals contamination and accumulation in agricultural soil have evoked a worldwide attention for their non-biodegradability, toxicity, and persistence. Heavy metals pollution cannot be ignored as it poses a significant threat to humans, animal life, soil ecosystem and water reservoirs (Bastami et al., 2014; Ke et al., 2017; Wang et al., 2016). The accumulation of heavy metals in soils not only leads to a decline in production and quality of cereal but also pose a serious threats to human health through the food chain as their detrimental impact appears after several years of exposure (Guan et al., 2018). The arable land contaminated by heavy metals in China is up to 100 thousand km^2. Whereas; grain contaminated by heavy metals surpasses 10 million tons, causing considerable economic loss of over 3 billion dollars (Cai et al., 2012, 2014). In order to effectively reduce heavy metal pollution of soil, it is necessary to demonstrate the source of trace metals and spatial pattern of soil.

The concentration of heavy metals in soil largely depends on the parent material and variety of anthropogenic activities (Facchinelli et al., 2001; Lu et al., 2012). In China, many factors such as rapid industrialization, urbanization, heavy traffic, non-judicial use of agrochemicals and untreated waste water for irrigation put an immense stress on local environment. These factors have led to decline the quality of local environment and ultimately increase heavy metals pollution over the last few decades (Cai et al., 2012; Chen et al., 2008; Lu et al., 2012; Ning et al., 2017; Xiao et al., 2015). These

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* Corresponding author.
E-mail address: guoboli2007@126.com (B. Guo).
[1] Xw.Z. and S.W. contributed equally.

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anthropogenic activities coupled with natural input and additionally heterogeneity of the soil itself make difficult to identify the source of heavy metals. Previous studies were focused on heavy metal toxicity and associated risk assessment (Chen et al., 2016a, 2016b; Niu et al., 2013). Relatively little information is available about source, spatial variability and spatial relationship of soil heavy metals at regional scale. Current research have gradually drawn attention to quantify levels of contamination in different situations and apportion the source of soil contaminants by multivariate statistical methods (Cai et al., 2015, 2014; Chen et al., 2008; Guan et al., 2018; Lv et al., 2015). Positive matrix factorization model along with the combination of multivariate statistics, and geo-statistics is very effective and widely used to apportion the source of heavy metals (Guan et al., 2018). In this study, three apportionment methods were used. Principle components analysis (PCA) was applied to approximately determine the source of harmful elements. Geographical statistical analysis intuitively reflects the local situation and verifies whether the results of PCA are reasonable. Positive matrix factorization model was used to further analyze the type of pollution source and contribution rate based on the former results. Ultimately, these three methods combined each other were very good for analyzing pollution sources.

In Hunan province, it has been estimated that smelting, mining and other industrial discharge contributed approximately 610, 136 and 31 t per year of Pb, Cr and Cd, respectively, into the Yangtze River (Liu et al., 2010). Zhuzhou is the largest transportation hub in the south of the Yangtze River. After 50 years of development, Zhuzhou has become an industrial hub having metallurgical, mechanical, chemical, building materials, raw materials manufacturing industries, high-tech and state owned large and medium sized enterprises (Xi et al., 2008). Arsenic (As) and heavy metals concentration in this locality had been found exceeding the permissible limits. Crops grown in this region is vulnerable to heavy metals accumulation which can pass toxic residues to human body through ingestion so it is necessary to investigate and apportion the source of heavy metals and metalloids in soil of Zhuzhou. The main objectives of this research were to (1) investigate the concentration of As and heavy metals; (2) characterize the distribution and apportion the potential source of As and heavy metals; (3) accurately define the sources of As and heavy metals and quantify their contributions.

2. Materials and methods

2.1. Site description and sampling

This study was conducted in Shifeng District, Zhuzhou city, which is located in the north side of Yangtze River. The study site covers an area of 47.1 km^2 and experiences subtropical monsoon climate. The annual average temperature is 17.6 ℃ and annual rainfall is 1409 mm (Li et al., 2013). There are many local industrial enterprises mainly conducted smelting and chemical production. Rice and vegetables are dominant crops which are cultivated in this region.

A detailed investigation of soil was performed in April 2017. The samples were collected from agricultural and industrial fields of the study area (Fig. 1). Considering the geomorphological characteristics and soil types of Qingshuitang industrial zone, the soil samples were collected by grid method. Soil sampling was carried out with drilling of 5 cm diameter. At each sampling point, the topsoil was removed and then mixed to obtain a composite soil sample with a quartile. Soil samples consisted of topsoil (0–20 cm depth) and subsoil (40–60 cm depth) (Zhi et al., 2016). The samples were collected using GPS equipment and kept in sealed packages, and then transferred to the laboratory for subsequent analysis. A total of 133 soil samples (72 topsoil and 61 subsoil) were collected from 72 different sampling sites.

All soil samples were air-dried at room temperature (20–23 ℃) in the laboratory. Impurities like stones, plant roots and other contaminants were removed. The samples were crushed with a semi-circular planetary mill and passed through 0.074 mm mesh for the determination of As and heavy metals and organic matter (Zhang et al., 2017). Then the prepared soil samples were stored in polyethylene bottles for further analysis.

2.2. Chemical analysis

Samples were analyzed for organic matter (OM), pH, and As and heavy metals namely Cr, Ni, Cu, Zn, Cd and Pb. Soil pH was measured in a soil: water (1:2.5) suspension by pH meter (S220, Mettler Toledo, Switzerland) proposed by Micó (Micó et al., 2006). The organic matter concentration of the soil was determined by the low-temperature external heat potassium dichromate oxidation-colorimetric method, and the organic substance was measured by wet oxidation at 180 °C with a mixture of potassium dichromate and sulfuric acid (BV-III grade, Beijing Institute of Chemical Reagents, Beijing, China) as reported by Chen (Chen and Lu, 2012). Arsenic and heavy metals content in soil were analyzed after digestion by a mixture of concentrated HNO_3 and HF (8/2 v/v) (BV-III grade, Beijing Institute of Chemical Reagents, Beijing, China) and microwave digestion instrument (CEM MARS Xpress, CEM, USA). The digestion procedure follows three steps: the temperature was raised to 120 ℃ within 10 min and kept for 4 min; the temperature was heated to 160 ℃ within 8 min and maintained for 4 min; then the temperature was increased to 185 ℃ within 5 min and maintained for 25 min; and then samples were allowed to cool at room temperature. After cooling, the digested solution were diluted to 100 mL volume with ultrapure water (Mill-Q, Millipore, Bedford, MA, USA) and stored in a plastic bottle. All glassware and polyethylene containers were washed with 10% HNO_3 (v/v) to avoid cross-contamination.

Heavy metals were measured by Inductively Coupled Plasma Mass Spectrometry (Agilent 7700 ICP-MS, Agilent Technologies, Santa Clara, CA), following the procedure described by Zhang et al. (2017). The Environmental Calibration Standard (Part #5183-4688) provided by the Agilent Co. was used as the standard stock solution. The standard working solutions were diluted the stock solution with 5% HNO_3 (v/v). In order to compensate the possible changes in instrument performance and avoid matrix effects during analysis, the online internal standard solution ^{72}Ge, ^{115}In and ^{209}Bi (1 ng L^{-1}, part #5183-4680, Agilent) was used. Instrumental condition was as follows: RF power of 1280 W, atomization chamber temperature of 2 ℃, sampling depth of 8 mm, cooler flow rate of 1.47 L min^{-1}, carrier gas flow rate of 1 L min^{-1}, auxiliary the flow rate is 1 L min^{-1}. The standard soil (GBW 07446) was analyzed to confirm the accuracy during the entire procedure. The recovery rates of samples were more than 85%. Limits of detection and quantification were affirmed depend on the criteria of 3 σ and 10 σ and the standard deviation (σ) of 11 blank measurements. The accuracy of the method expressed by RSD is assessed in terms of repeatability. The RSDs of all elements obtained from four independent digestions ranged from 1% to 6%.

2.3. Statistical methods

2.3.1. Principal component analysis (PCA)

Principal component analysis is a dimension reduction technique which is widely applied in environmental science studies. It is very effective to demonstrate potential source and spatial distribution of heavy metals (Chen et al., 2003; Jianjun et al., 2006; Li et al., 2016; Lin et al., 2007; Xiaobo et al., 2009). Principal component analysis extracts effective information from multidimensional data. By orthogonal transformation, the original stochastic vector related to its components is transformed into a new random vector whose components are irrelevant (Gallego et al., 2002; Jing et al., 2012). In this study, the common components were extracted by principle components analysis to get the correlation matrix. To better interpret the results, a varimax rotation was applied to reduce the number of heavy metals that have