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Source identification of heavy metals in peri-urban agricultural soils of southeast China: An integrated approach

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ABSTRACT

Intensive human activities, in particular agricultural and industrial production have led to heavy metal accumulation in the peri-urban agricultural soils of China threatening soil environmental quality and agricultural product security. A combination of spatial analysis (SA), Pb isotope ratio analysis (IRA), input fluxes analysis (IFA), and positive matrix factorization (PMF) model was successfully used to assess the status and sources of heavy metals in typical peri-urban agricultural soils from a rapidly developing region of China. Mean concentrations of Cd, As, Hg, Pb, Cu, Zn and Cr in surface soils (0–20 cm) were 0.31, 11.2, 0.08, 35.6, 44.8, 119.0 and 97.0 mg kg^{-1}, respectively, exceeding the local background levels except for Hg. Spatial distribution of heavy metals revealed that agricultural activities have significant influence on heavy metal accumulation in the surface soils. Isotope ratio analysis suggested that fertilization along with atmospheric deposition were the major sources of heavy metal accumulation in the soils. Based on the PMF model, the relative contribution rates of the heavy metals due to fertilizer application, atmospheric deposition, industrial emission, and soil parent materials were 30.8%, 33.0%, 25.4% and 10.8%, respectively, demonstrating that anthropogenic activities had significantly higher contribution than natural sources. This study provides a reliable and robust approach for heavy metals source apportionment in this particular peri-urban area with a clear potential for future application in other regions.

1. Introduction

There is an increasing public concern about the accumulation of heavy metals in agricultural soils which, in turn, has the potential to restrict the soil's function, cause toxicity to crops and ground water, and hence to threaten human health (Hou et al., 2014; Lu et al., 2015; Qu et al., 2016; Toth et al., 2016). Intensive human activities have led to heavy metal accumulation in peri-urban agricultural soils of China threatening soil environmental quality and food safety (Huang et al., 2006; Luo et al., 2009; Hu et al., 2013; Hu et al., 2017). Heavy metals can enter agro-ecosystems through geogenic sources and anthropogenic activities (Cloquet et al., 2006; Yang et al., 2016). Geogenic sources of heavy metals mainly come from weathering of the parent materials. Anthropogenic activities include inputs of heavy metals through application of fertilizers and organic manures, irrigation, atmospheric deposition, waste disposal, sewage application, and other human activities (Sharma et al., 2008; Hu et al., 2013; Hou et al., 2014; Pan and Wang, 2015). Inputs of heavy metals to soils through agricultural activities have increased within the past decades due to increasing food demands from a rapidly expanding population (Huang et al., 2015; Hu et al., 2017).

Heavy metal source apportionment is a crucial step towards

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prevention or reduction of heavy metal pollution (Huang et al., 2015). Identification of heavy metal sources in agricultural soils is a basis for undertaking appropriate actions to protect soil quality and to develop sustainable management strategies (Lu et al., 2012). In this context, peri-urban agricultural soils are priority areas for research of source apportionment as they are generally located close to multiple pollutant sources such as construction/excavation works, industry, traffic and urban waste disposal (Huang et al., 2015). Despite public concerns, quantitative knowledge of heavy metals in agricultural soils from different sources especially from different anthropogenic sources remains scarce. Discriminating the natural and different anthropogenic sources and their rates of contribution to heavy metal accumulation in soils are crucial for soil environmental protection and food safety (Pan and Wang, 2015).

The spatial distribution of heavy metals based on Geographical Information System (GIS) can be used as an aid to identify their possible sources and pollution hot spots (Chai et al., 2015). Identification of soil heavy metal sources and spatial delineation of areas with heavy metal pollution is important for decision makers to develop effective management strategies to improve environmental quality (Zhao et al., 2010; Pan and Wang, 2015). So far, studies on regional input and output fluxes of heavy metals are mostly based on model calculations, statistical yearbooks, and literature data (Luo et al., 2009; Belon et al., 2012; Lofts et al., 2013; Hou et al., 2014). This classical approach to source apportionment can be substantially improved by use of receptor models that are based on application of multivariate statistical methods to identify and quantify apportionment of pollutants to their sources (Wang et al., 2009). Although the positive matrix factorization (PMF) model has been successfully applied for pollutant source identification for atmospheric (Song et al., 2006; Alleman et al., 2010; Gupta et al., 2012; Jang et al., 2013) and sedimentary sources (Chen et al., 2013; Pekey and Dogan, 2013; Gonzalez-Macias et al., 2014), few studies have employed this approach to identify heavy metal sources in soils (Xue et al., 2014; Dong et al., 2015). Furthermore, stable Pb isotope ratio analysis is commonly used to trace the sources of Pb pollution in different environmental compartments at local to global scales (Wong et al., 2003; Cloquet et al., 2006; Komarek et al., 2008; Reimann et al., 2012; Yu et al., 2016). Although previous studies have been conducted to identify the sources of heavy metals in soils using the different individual method, integration of the different methods in the same area to accurately evaluate and validate the source identification results by the different approaches is lacking.

Therefore, a combination of spatial analysis (SA), isotope ratio analysis (IRA), input flux analysis (IFA), and positive matrix factorization (PMF) model has been used in this study to identify the status and sources of selected heavy metals (Cd, As, Hg, Pb, Cu, Zn and Cr) in typical peri-urban agricultural soils. The tested soils were from a rapidly developing region in southeast China, where a large number of samples of soils, crops, fertilizers and atmospheric depositions were collected and analysed. This work provides baseline information to develop effective policies and standards to control and reduce heavy metal inputs and long-term accumulation in agricultural soils as well as to provide the theoretical basis and technical support for sustainable agricultural production and management.

2. Materials and methods

2.1. Description of the study area

The selected study area is located on an alluvial island of the Yangtze River, a peri-urban area of Nanjing City (32°8′24″-32°13′37″ N, 118°46′24″-118°49′47″ E), Jiangsu Province, southeast China, with a total land area of 55.6 km^2 (Fig. 1). The area is within a subtropical monsoon climate zone with a mean annual temperature, precipitation, and potential evaporation of about 15–16 °C, 1100 mm and 1200 mm, respectively. The prevailing wind directions are northwest in winter and southeast in summer. The main soil type in this area is Cambosols (Fluvo-aquic soils) (CRGCST, 2001). The agricultural production is very intensive due to the increasing food demands from urban areas (Hu et al., 2014). Wheat, rice, maize and several types of vegetables are the main crops. The rotation patterns of the agricultural production include vegetable-vegetable rotation, crop-vegetable rotation and crop-crop rotation. According to our interviews with farmers and the available information at agricultural centers in the area, these intensive agricultural production practices are characterized by extensive fertilization which may result in heavy metal accumulation in the soils. Intensive industrial activity including iron and steel, chemical, thermo-electric, and medical industries, as well as sewage treatment plants built after 1990s are mainly located on the opposite side of the Yangtze River relative to the study area (Fig. 1).

2.2. Sampling, processing and analysis

Eighty-eight surface soil samples were collected in summer 2012 throughout the island based on land use and spatial homogeneity. The sampling sites covered nearly all land uses, including several uncultivated soils along the Yangtze River. All sampling sites were geo-located using a global positioning system receiver (Fig. 1). Each sample consisted of a mixture of five subsamples collected from five spots of an area of about 5 m^2. An amount of 1 kg fresh soil samples were collected to provide a representative sample of each soil. All soil subsamples were collected at a depth of 0–20 cm using a stainless steel shovel. Furthermore, three representative soil profile samples were taken at depths of 0–20, 20–40, 40–60, 60–80, and 80–100 cm. A total of nine typical crop samples (3 rice, 3 wheat and 3 leafy vegetable samples) were collected during soil sampling. Twenty eight chemical fertilizers and five commercial organic fertilizers were collected from adjacent agricultural stores or local farmers. For livestock manure, thirteen fresh samples were taken at 1 m depth from five points inside the manure pile using a soil sampler, and were mixed and transferred to the laboratory for analysis.

Seven atmospheric wet and dry deposition collection sites were established in the different direction of the study area (Fig. 1), and samples were collected monthly for one year from December 2011 to November 2012 using a conventional wet–dry automatic sampler. The wet–dry sampler was equipped with a 707 cm^2 aperture and a 177 cm^2 PUF-based glass bucket in separate containers to sample daily rainfall and monthly particulate dry deposition, respectively (Pan and Wang, 2015). All equipment in contact with the samples were carefully cleaned with 10% HCl solution, and kept in plastic bags until they were used for sample collection (Cui et al., 2014). All solid samples, including soils and potential source samples were ground in a mortar to pass through a 0.149 mm (100-mesh) polyethylene sieve and stored at room temperature until analysis. Soil samples were also crushed and passed through a 2-mm mesh sieve for soil pH and SOM determination.

Soil pH was measured by potentiometry on 1:2.5 (soil: water) paste using a glass electrode pH meter (PHS-3C, Shanghai, China). Soil organic matter (SOM, g kg^{-1}) was determined using the Walkley–Black method (Nelson and Sommers, 1996). To measure the contents of Cd, Pb, Cr, Cu and Zn in the soils, fertilizers and atmospheric wet and dry deposition, the 100-mesh sieved samples were digested by a mixture of HNO_3 (5 mL)-$HClO_4$ (1 mL)-HF (1 mL) in a poly-tetrafluoroethylene container. The mixture was heated to