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Combining emission inventory and isotope ratio analyses for quantitative source apportionment of heavy metals in agricultural soil

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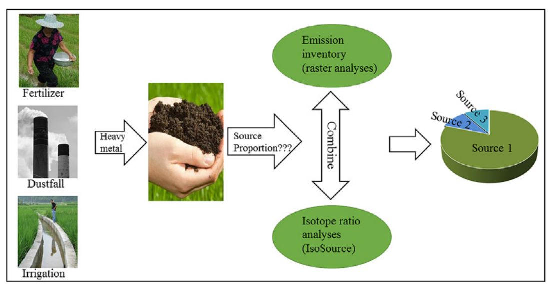
HIGHLIGHTS

- Emission inventory and IRA were combined for source apportionment of heavy metals.
- Raster analysis was used to calculate the input rate for each source type.
- IsoSource was used to quantify the source contributions in the IRA method.
- The results obtained using the two methods were similar.

GRAPHICAL ABSTRACT



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ABSTRACT

Two quantitative methods (emission inventory and isotope ratio analysis) were combined to apportion source contributions of heavy metals entering agricultural soils in the Lihe River watershed (Taihu region, east China). Source apportionment based on the emission inventory method indicated that for Cd, Cr, Cu, Pb, and Zn, the mean percentage input from atmospheric deposition was highest (62–85%), followed by irrigation (12–27%) and fertilization (1–14%). Thus, the heavy metals were derived mainly from industrial activities and traffic emissions. For Ni the combined percentage input from irrigation and fertilization was approximately 20% higher than that from atmospheric deposition, indicating that Ni was mainly derived from agricultural activities. Based on isotope ratio analysis, atmospheric deposition accounted for 57–93% of Pb entering soil, with the mean value of 69.3%, which indicates that this was the major source of Pb entering soil in the study area. The mean contributions of irrigation and fertilization to Pb pollution of soil ranged from 0% to 10%, indicating that they played only a marginally important role. Overall, the results obtained using the two methods were similar. This study provides a reliable approach for source apportionment of heavy metals entering agricultural soils in the study area, and clearly have potential application for future studies in other regions.

1. Introduction

Agricultural soil is a long-term sink for potentially toxic elements including cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) (Nicholson et al., 2003; Zhu et al., 2013; Hou et al., 2014; Chen et al., 2015, 2017a; Cao et al., 2016; Ding and Xu, 2016; Jeon et al., 2017; Nedelescu et al., 2017). Heavy metals

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including these enter the agro-ecosystem through both natural and anthropogenic processes (Hou et al., 2014; Yang et al., 2016; Jiang et al., 2017; Li et al., 2017; Lin et al., 2017; Xia et al., 2017). Natural sources include weathering, desertification, erosion, and other geological processes. Anthropogenic processes may include inputs of heavy metals through fertilization and irrigation, and atmospheric deposition (Dach and Starmans, 2005; Luo et al., 2009; Sheppard et al., 2009; Yang et al., 2009; Xia et al., 2014; Lin et al., 2017). Atmospheric deposition has been identified as a principal source of metals entering soil (Gray et al., 2003; Loyola et al., 2007; Rothwell et al., 2011; Xia et al., 2014); agricultural activities, including fertilization and irrigation using sewage wastewater are also very important pollution sources (Kachenko and Singh, 2006; Lu et al., 2012). Previous studies have indicated that inputs of heavy metals to soils through agricultural activities have increased in recent decades because of world population expansion (Li et al., 2008; Niu et al., 2013; Huang et al., 2015).

As a result of the diverse routes of entry of heavy metals into agricultural soils, there is a growing public concern about heavy metal accumulation in agricultural products, and the consequent human health effects through the agricultural food chain (Luo et al., 2011; Yu et al., 2017; Bi et al., 2018; Han et al., 2018). Action is required to control pollution by heavy metals to reduce the risks of their accumulation. Source apportionment is a crucial step in this process (Lu et al., 2012; Jiang et al., 2017). Methods commonly used for heavy metal source apportionment include multivariate statistical analysis and geographic information system (GIS) mapping (Qu et al., 2013; Huang et al., 2015; Zhou et al., 2016; Li et al., 2017; Lin et al., 2017). Multivariate statistics and GIS mapping are highly subjective and cannot be used for quantitative source apportionment (Chen et al., 2015; Huang et al., 2015; Wang et al., 2016; Hou et al., 2017; Bi et al., 2018; Han et al., 2018); however, emission inventory methods can be used for this purpose. The emission inventory approach involves initial source identification, quantitation of the input of heavy metals to agricultural soil from the sources (including atmospheric deposition, fertilization, and irrigation) using flux observation methods, and calculation of the contribution rate for each source type. Isotope ratio analysis (IRA) is an alternative method for detecting the fingerprint of heavy metal pollution. Comparison of the isotope ratios in the potential sources (environmental samples) with those in affected soils enables the contribution of each source to soil pollution to be estimated (Rosman et al., 1993; Hansmann and Koppel, 2000; Duzgoren-Aydin, 2007; Foucher et al., 2009; Huang et al., 2015). For technical reasons not all isotope ratios are easy to determine, and only Pb isotope ratio analysis has been widely used (Duzgoren-Aydn and Weiss, 2008; Foucher et al., 2009).

Methods for quantitative source apportionment, particularly emission inventory methods, have rarely been applied in research, and the methods for source apportionment have commonly been used in isolation. Generally, only one quantitative method has been used in each study (Phillips and Gregg, 2003; Huang et al., 2015). Therefore, the present study intends to integrate and apply two quantitative analytical methods (an emission inventory method and IRA) at a study site in a verification process, with the aim of obtaining more accurate and reliable results. This study also addresses the issue that agricultural soils merit more attention, because contamination of these soils with heavy metals poses long-term threats to food safety and human health. In addition, ecosystem health may be compromised and result in lower agricultural outputs. These issues highlight that agricultural soils are a priority research area related to source apportionment.

The study aimed to develop a combined approach to providing more accurate and reliable source apportionment data. First, heavy metal input fluxes to the agro-ecosystem from atmospheric deposition, fertilization, and irrigation were monitored, and the input rate for each source type was calculated using GIS spatial analysis of raster data. Second, IRA of Pb was used to quantify the source contributions of individual heavy metals using IsoSource, which is a contribution calculation software (Phillips and Gregg, 2003); this was also used to validate the results obtained using the emission inventory method. Third, the advantages and disadvantages of the two methods were assessed, and cost-effective methods proposed for analysis of source apportionment.

2. Material and methods

2.1. Study area

The study area, in the Lihe River watershed, is located to the west of Taihu Lake, in the city of Yixing, Jiangsu Province, China (31°09′00″–31°20′31″N, 119°42′00″–119°56′20″E); it includes the towns of Hufu and Dingshu. Taihu Lake is the largest lake in the China Eastern Coastal Area. It is located in the lower reaches of the Yangzi River Basin, which is one of the most developed areas and the most populous regions in China.

The watershed has a surface area of approximately 260 km^2 (Li et al., 2006). The total area of agricultural land is 57.8 km^2, of which the dry land is 21.4 km^2, and the paddy land is 36.4 km^2. Many types of industrial activities occur densely throughout the area, amongst which are ceramics factories, refractory materials plants, and chemical plants. Rice and wheat are cultivated in the agricultural zone.

Increasing heavy metal concentrations were observed in the soil of the lower Yangzi River plain in 2004–2014. In particular, the ratio between the median concentrations of Cd (18.2%) and Pb (6.9%) increased during this period (Xia et al., 2017). In addition, previous studies that undertook biomonitoring of heavy metal pollution in soils in the river estuaries of the 24 main rivers flowing into and out of Taihu Lake revealed that the Lihe River estuary was the most strongly contaminated. Moreover, the potential ecological hazard index (RI) for the Lihe River estuary was greater than 220, which indicates that the pollution in this area had reached a serious level and presented a very high ecological risk (Jiao et al., 2010). However, there has been little research into the source apportionment of heavy metals in this high-risk area.

2.2. Sample collection and preparation

2.2.1. Soil

Soils in crop fields were sampled at 0–10 cm depth at 32 randomly selected sites throughout the study area during 17–21 May 2016 (Fig. S1, Supplementary Materials). Each sample (0.5–1.0 kg) was divided into 5–9 subsamples. Following collection the samples were air dried at room temperature, ground, and passed through a 2 mm nylon sieve to remove stones and plant roots (Lin et al., 2016). The resulting fine soil powders were stored in polythene zip bags (Li et al., 2012; Lin et al., 2018).

2.2.2. Atmospheric deposition

According to the type of land use and urban layout of the study area, 10 wet/dry deposition monitoring points were set up in the form of a cross. One axis incorporated (sequentially) woodland, farmland, suburban area, a town center, suburban area, and farmland from the northwest to the southeast, and the other axis incorporated farmland, a town center, suburban area, and woodland from the northeast to the southwest. Monitoring was performed between 1 September 2016 and 1 September 2017 using a custom-made collecting device (Fig. S2) Three replicate samples were collected at each sampling point. Following collection the