Source identification and apportionment of heavy metals in urban soil profiles

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HIGHLIGHTS

- Discriminating contaminant's sources is crucial for pollution control.
- Receptor model (APCS-MLR) can quantify sources of heavy metals (HMs) in soil.
- Isotopic component model can differentiate contributions of specific sources for Pb.
- Primary anthropic source of HMs in urban soil of southeast China is coal combustion.
- Leaching and historic traffic input lead to HM contamination in deep soil layer.

ARTICLE INFO

ABSTRACT

Because heavy metals (HMs) occurring naturally in soils accumulate continuously due to human activities, identifying and apportioning their sources becomes a challenging task for pollution prevention in urban environments. Besides the enrichment factors (EFs) and principal component analysis (PCA) for source classification, the receptor model (Absolute Principal Component Scores-Multiple Linear Regression, APCS-MLR) and Pb isotopic mixing model were also developed to quantify the source contribution for typical HMs (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in urban park soils of Xiamen, a representative megacity in southeast China. Furthermore, distribution patterns of their concentrations and sources in 13 soil profiles (top 20 cm) were investigated by different depths (0–5, 5–10, 10–20 cm). Currently the principal anthropogenic source for HMs in urban soil of China is atmospheric deposition from coal combustion rather than vehicle exhaust. Specifically for Pb source by isotopic model ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$), the average contributions were natural (49%) > coal combustion (45%) ≫ traffic emissions (6%). Although the urban surface soils are usually more contaminated owing to recent and current human sources, leaching effects and historic vehicle emissions can also make deep soil layer contaminated by HMs.

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1. Introduction

Among various types of environmental pollutants, heavy metals (HMs) are particularly hazardous due to their ubiquity, toxicity, and persistence (Guney et al., 2010; Burges et al., 2015). Long term industrialization (mining, metallurgy, fossil fuel combustion) and rapid urbanization (traffic, municipal solid waste) have resulted in elevated amounts of HMs in urban environments (Luo et al., 2012b; Szolnoki et al., 2013), which pollution will pose significant risks to humans and ecosystem (Siciliano et al., 2009). The major differences between urban and natural soils result from the accumulation of anthropogenic materials, that form a cultural layer with specific properties and composition (Puskás and Farsang, 2008; Luo et al., 2012b). The HM contaminants in urban soils often originate from multiple sources (Wong et al., 2006), including natural (pedogenic processes) and various anthropogenic sources (atmospheric deposition of industrial and vehicle emissions, and direct input by human activities). Therefore, serving directed pollution control, it is crucial to discriminate pollution sources, that has become a significant environmental issue (Hu and Cheng, 2013; Szolnoki et al., 2013; Luo et al., 2014). Furthermore, besides spatial

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variation, the concentration levels and source contributions of HMs in urban soils may also vary with depth, due to the temporal input characteristics and leaching transport of pollutants (Zhang et al., 2007). In order to identify the detailed sources for soil HMs and to better understand their fate and sink, it is necessary to investigate their patterns relating to urban soil profiles.

However, most studies in the past only focused on pollution levels and risk assessments of HMs in soil environments (Luo et al., 2012b; Cheng et al., 2014), few were conducted for qualitative source identification and much less for quantitative source apportionment. Compared with atmospheric research (Belis et al., 2013; Luo et al., 2014), it was extremely limited by the effective methods available. Currently, the source studies about soil pollution are mainly source identification, including the enrichment factors (EFs) classifying natural and anthropogenic origins (Ye et al., 2011), multivariate analyses (principal component analysis, PCA; cluster analysis, CA) for grouping natural and key anthropogenic input types (Zhang, 2006; Davis et al., 2009) and associate with geostatistics for large scale investigations (Nanos and Rodríguez Martín, 2012; Sun et al., 2013), and using stable isotopic signatures such as $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ to distinguish specific Pb contributors (Cloquet et al., 2006; Luo et al., 2011). But for the aerosol study (Li et al., 2013; Nguyen et al., 2013), many approaches have been applied to both identify and apportion pollution sources, including receptor models such as Chemical Mass Balance (CMB) model, PCA related methods (Absolute Principal Component Scores, APCS; Multiple Linear Regression, PCA-MLR; UNMIX model), and Positive Matrix Factorization (PMF). Recently, APCS-MLR was also developed to estimate the source contribution of airborne particulate HMs (Luo et al., 2014). Nonetheless, such methods for assessing soil HM pollution are still absent. Accordingly, several methodologies will be extended to solve the difficulties in soil environmental science.

Since few studies were about distribution of HMs in urban soil profiles, and no attempt was made to determine their sources, it is essential to get a good understanding not only about the content and variability of HMs in soil profiles, but also about the contribution of both parent rocks and various principal human activities. The primary objectives of this study were: (1) to investigate the concentration distribution of cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in urban soil profiles; and (2) to differentiate and quantify the natural or anthropic contributions of these typical HMs using new multivariable statistic receptor model and Pb isotopic mixing model.

2. Materials and methods

2.1. Study area and soil profile sampling

Thirteen urban topsoil profiles were collected in 2011 from exposed lawns of 6 public parks in Xiamen island, the downtown of the mega-city located in coastal southeast China, which region had undergone three decades of intense industrialization and urbanization. In the study areas, there were no specific point-sources of HMs, thus soil metal contamination is derived from continuous urbanization and development. For each profile, soils from different depths were sectioned as layers of surface 5 cm (D5), 5–10 cm (D10), and 10–20 cm (D20). At each sampling site, 9 replicate samples for each layer were collected within a 2 m × 2 m grid using a stainless steel column sampler, and thoroughly mixed to obtain a bulk composite sample. These sampling points were at least 30 m away from the roads, and based on the park history information, these soil profiles were not disturbed

recent years. In total, 39 representative urban soil samples were collected for the contaminant source study.

The collected soil samples were air-dried, gently disaggregated, and sieved through a 2-mm nylon sieve to remove stones and coarse materials, and then stored in polyethylene bags before analysis. Portions of each sample were ground (<150 μm) by an agate grinder for metal analysis.

2.2. Analysis of metal contents in soil

Concentrations of HMs (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) in soil were analyzed using a strong acid (HNO_3–$HClO_4$) pseudo-total digestion method (Luo et al., 2012a), determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Optima 7000 DV, PerkinElmer, USA) and assisted by Graphite Furnace-Atomic Absorption Spectrometry (GFAAS; Thermo Elemental M6, USA) for low concentration of Cd. Reagent blanks, analytical duplicates, and standard reference materials (GBW07429, GBW07317) were used for the quality assurance (QA) and quality control (QC). The recovery rates for investigated metals in the standard reference materials were around 75–100%.

2.3. Lead isotopic composition analysis

For Pb source identification, Pb isotope ratios in soil digests were measured with an ICP-Mass Spectrometer (ICP-MS, Agilent 7500 CX, USA) (Luo et al., 2011). To optimize the analytical performance of the instrument, the acid digests above were diluted with 5% high-purity HNO_3 to a Pb concentration of about 10 μg L^{-1}. The peak pattern of maximum (20 points) was chosen, and integration times of 1 and 0.3 s per point were set for ^{204}Pb, and for ^{206}Pb, ^{207}Pb, ^{208}Pb, respectively. Solutions of standard reference material (SRM, NIST 981 Common Lead Isotope, National Institute of Standards and Technology, Gaithersburg, MD) were measured after every five samples for calibration and QC. The relative standard deviations (RSD) of the Pb isotopic ratios of 10 replicate sample readings were generally lower than 1%. The average measured ratios of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ for SRM were 1.0934 ± 0.0031 and 2.3702 ± 0.0057, and in good agreement with the certified standard values (1.0933 and 2.3704, respectively).

2.4. Data processes and statistical analysis for source identification and apportionment

2.4.1. Three end-member mixing model for Pb source

In the past, the binary model of Pb isotopic fingerprint was mostly used for two-end-member (natural and anthropogenic) source apportionment (Bird, 2011). In this study, a three-end-member model (Cheng and Hu, 2010) was used to calculate the relative contribution of natural source and two key anthropogenic sources to total Pb in urban park soils. The equations for trinary mixing of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios were written as follows:

$$(^{206}Pb/^{207}Pb)_{Sample} = f_{Coal} * (^{206}Pb/^{207}Pb)_{Coal} + f_{Traffic} * (^{206}Pb/^{207}Pb)_{Traffic} + f_{Nature} * (^{206}Pb/^{207}Pb)_{Nature} \quad (1)$$

$$(^{208}Pb/^{207}Pb)_{Sample} = f_{Coal} * (^{208}Pb/^{207}Pb)_{Coal} + f_{Traffic} * (^{208}Pb/^{207}Pb)_{Traffic} + f_{Nature} * (^{208}Pb/^{207}Pb)_{Nature} \quad (2)$$

$$f_{Coal} + f_{Traffic} + f_{Nature} = 100\% \quad (3)$$