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Identification of trace metal pollution in urban dust from kindergartens using magnetic, geochemical and lead isotopic analyses

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HIGHLIGHTS

- Magnetic measurements were combined with geochemical and Pb isotopic analyses.
- Magnetic properties showed more prominent values of I_{geo} than those of individual metals.
- Metal pollution sources were identified by Pb isotopes and PCA.
- Industrial emissions and coal combustion are major metal pollution sources in urban areas.

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ABSTRACT

In the present study, magnetic measurements were combined with geochemical analysis and stable Pb isotopic ratios to reveal the distribution and origination of trace metal pollutants in kindergarten dusts from a typical urban environment of Wuhan, central China. The geoaccumulation index (I_{geo}) of magnetic properties was more prominent than those of individual metals. The magnetic susceptibility (MS) and trace metals (Zn, Pb, and Cu) in this study together with published results from other Chinese cities formed a liner relationship, suggesting that metal contaminants in Chinese urban areas had similar MS to metal ratios, which could be used as an indicator for identification of pollution sources between Chinese cities and the other Asian cities. Stable Pb isotopic ratios (1.1125–1.1734 for $^{206}Pb/^{207}Pb$ and 2.4457–2.4679 for $^{208}Pb/^{207}Pb$) in the urban dusts from Wuhan were characterized by higher ^{208}Pb component in comparison with those from other Chinese cities. This result combined with principal component analysis (PCA) indicated that metal pollutants in the dusts were derived from industrial activities and coal combustion, whereas the traffic emissions were no longer a predominant pollution source in urban environment. Our study demonstrated that environmental magnetic methods could not only reveal the overall situation of trace metal contamination, but also prove evidence in the identification of pollution sources.

1. Introduction

Trace metal pollutants have received increasing attention in recent decades due to their potential adverse health effects to humans and widespread existence in urban environment as a result of rapid urban expansion. Atmospheric deposited dust in urban settings is an important carrier of trace metal contaminants. The intensified human activities such as industrial operations, traffic, fossil fuel combustion, and municipal waste disposal, have produced large quantities of metal particles, which could eventually settle down in urban dust. Through resuspension-inhalation, hand-mouth ingestion and dermal contact, trace metals contained in urban dust could enter human bodies and endanger human's health, especially children's (Roels et al., 1980; Ferreira-Baptisa and De Miguel, 2005; Zheng et al., 2010; Soto-Jiménez and Flegal, 2011). For example, many studies indicated that there is a significant correlation between the blood lead levels (BLLs) of children and Pb concentration in urban dust/soil (Laidlaw et al., 2005; Laidlaw and Taylor, 2011). A recent research from the Pearl River Delta region, China, demonstrated that lead contaminated residential dust could be the primary driving mechanism of child blood lead exposure in this area (Chen et al., 2012). Considering the

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high threat of dust metals to children, dusts deposited in kindergartens should deserve more attention since they can be easily contacted by children during their daily outdoor activities.

The contaminated extent and toxicity of trace metals are generally assessed by their total concentrations and speciation, which are usually determined by chemical analysis (e.g., AAS, ICP-AES, and ICP-MS). In addition to the direct but time-consuming chemical approaches, environmental magnetic methods (e.g., magnetic susceptibility and saturation isothermal remanence – SIRM) have also been used to rapidly reveal the overall status of trace metal contamination in various ecosystems, including soils (Jordanova et al., 2003; Spiteri et al., 2005; Yang et al., 2007a; Kapička et al., 2008; Blundell et al., 2009; Rosowiecka and Nawrocki, 2010), dusts (Kim et al., 2009; Yang et al., 2010; Bućko et al., 2010, 2011; Qiao et al., 2011; Wang et al., 2012; Zhang et al., 2012; Zhu et al., 2012), sediments/sludge (Chapparro et al., 2004; Yang et al., 2007b; Zhang et al., 2007, 2011; Rijal et al., 2010; Bijaksana and Huliselan, 2010), and plants (Matzka and Maher, 1999; Jordanova et al., 2003; Davila et al., 2006; Zhang et al., 2006; Maher et al., 2008; Salo et al., 2012). This use of magnetic techniques stems from the fact that heavy metal pollution in many cases is accompanied by emissions of ferromagnetic/ferrimagnetic particles because of the abundant presence of Fe in natural resource materials (Jordanova et al., 2003).

It is well known that stable Pb isotopes provide a useful means for identifying the origins of trace metals in the environment. This is because Pb derived from anthropogenic sources is less radiogenic than the geogenic Pb, and different sources of anthropogenic contaminants may contain Pb with characteristic isotopic compositions (Sangster et al., 2000).

Systematic assessment of trace metal contamination by the combined proxies (metal concentrations, magnetic parameters, and Pb isotopic ratios) has not been conducted before, which may provide detailed information about trace metal behaviors in urban environment. In the present study, atmospheric deposited dust samples were collected from kindergartens in a metropolis (Wuhan, China), and the concentrations of trace metals (i.e., Cd, Co, Cr, Cu, Ni, Pb, Zn, As, Sb, Ba, and Mo), magnetic parameters, and stable Pb isotopic compositions were fully investigated. The major objectives of this research are 1) to assess the contamination status and sources of trace metals in urban kindergarten dusts using magnetic, geochemical and lead isotopic analyses and 2) to explore the possible relationships between these different environmental proxies.

2. Materials and methods

2.1. Study area and sample collection

Wuhan (29°58′–31°22′N, 113°41′–115°05′E) is one of the biggest metropolises in China with an urban population of about 10.02 million in 2011. Its climate represents a typical subtropical humid monsoon with an average annual temperature of 17.7 °C and an average annual rainfall of 1300 mm. The prevailing wind is northeast wind in winter and south wind in summer. The number of kindergartens in this city is 638 with a total children population of 125,351 (WMBS, 2009).

Dust samples were collected from sixty-nine kindergartens in five districts, including Qingshan district (QS), Wuchang district (WC), Hankou district (HK), Hanyang district (HY), and Jiangxia district (JX) (Sun et al., 2013). QS is an industries concentrated area (including iron/steel smelters, machine manufacturing, and coal-power plants), WC is a commercial and education area, HK is a business and commercial area, HY is a residential area, and JX is a suburban district. Sampling was conducted in dry periods when no rain had occurred during the previous week. Approximately 50 g dust sample was collected using polyethylene brush on impervious surface (children activities equipment, pavement and windowsill) from five to eight points of each kindergarten. All dust samples were stored in sealed polyethylene bags, labeled and then transported to the laboratory. The samples were air-dried at room temperature, and passed through a 1 mm sieve to remove rocks, plants, hair and other impurities. The homogenized dust samples were ground to a fine powder texture with an agate mortar prior to chemical analyses.

2.2. Experimental methods

Magnetic susceptibility (MS) at low (χ_{lf}, 976 Hz) and high (χ_{hf}, 15,616 Hz) frequencies were measured with a kappabridge MFK1-FA (AGICO, Brno) at 200 Am^{-1} field intensity. Frequency-dependent susceptibility (χ_{fd}) was calculated and expressed as a percentage $\chi_{fd}\ \% = (\chi_{lf} - \chi_{hf})/\chi_{lf} \times 100\%$. An isothermal remanent magnetization (IRM) experiment was performed with an ASC Scientific (Model IM-10) impulse magnetizer and spinner magnetometer (Model SMD-88). The IRM acquired in a field of 1.0 T was regarded as saturation IRM (SIRM).

About 0.20 g of the prepared dust sample was digested with a concentrated HNO_3–$HClO_4$–HF–HCl mixture. The concentrations of trace metals of the digested solution were determined by an inductively coupled plasma–mass spectrometer (ICP–MS) (Finnigan MAT Element). For determination of As and Sb, the dust samples were digested with aqua regia (3:1, HCl:HNO_3) and determined by a hydride generation–atomic fluorescence spectrometer (HG–AFS) (AFS-920, Beijing Titan Instruments Co., Ltd.). QA/QC included reagent blanks, analytical duplicates, and analysis of the standard reference material (SRM) (SRM 2710). The recovery rates for the considered metals in the SRM were between 80 and 115%.

To determine the Pb isotopic composition, the solutions from the strong acid digestion were diluted to around 30 $\mu g\ g^{-1}\ Pb^{-1}$ with 5% (v/v) high-purity HNO_3 and measured by ICP–MS (Perkin–Elmer Elan 6100 DRC^{Plus}). The analytical parameters were sent as 190 sweeps/reading, one reading/replicate, and 10 replicates per sample solution. An international standard reference material (NIST SRM 981) was used for sample calibration and analytical control. The relative standard deviation (RSD) of the 10 replicates was generally below 0.5%. The measured $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of SRM 981 were 0.0645 ± 0.0001, 1.0930 ± 0.0025 and 2.3702 ± 0.0050, which were in close agreement with the standard reference values of 0.0645, 1.0933, 2.3704, respectively.

2.3. Statistical analysis

The data were statistically analyzed using the statistical package, SPSS v13.0 (SPSS Inc.). A one-way ANOVA test ($p < 0.05$) was used to analyze the difference in analytical results among different urban areas. The correlation analysis was conducted by a Pearson correlation, and the level of significance was set at $p < 0.05$ and $p < 0.01$ (two-tailed). Principal component analysis (PCA) was conducted using factor extraction with eigenvalues >1 after varimax rotation.

Pollution status of the studied area was assessed using geo-accumulation index (I_{geo}) introduced by Muller (1969), which is calculated using the following equation:

$$I_{geo} = \log_2\left[\frac{C_{m\ Sample}}{(1.5 \times C_{m\ Background})}\right]$$

Where $C_{m\ Sample}$ is the measured concentration of the magnetic parameters or metals in dust, $C_{m\ Background}$ is the geochemical