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# Lead contamination and transfer in urban environmental compartments analyzed by lead levels and isotopic compositions

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Lead levels and isotopic compositions in atmospheric particles (TSP and $PM_{2.5}$), street dust and surface soil collected from Nanjing, a mega city in China, were analyzed to investigate the contamination and the transfer of lead in urban environmental compartments. The lead contents in TSP and $PM_{2.5}$ are significantly higher than them in the surface soil and street dust ($p < 0.05$). The enrichment factor using the mass ratio of lead to the major crustal elements (Al, Sr, Ti and Fe) indicates significant lead enrichment in atmospheric particles. The plots of $^{206}Pb/^{207}Pb$ *vs.* $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ *vs.* 1/Pb imply that the street dust and atmospheric particles (TSP and $PM_{2.5}$) have very similar lead sources. Coal emissions and smelting activities may be the important lead sources for street dust and atmospheric particles (TSP and $PM_{2.5}$), while the deposition of airborne lead is an important lead source for urban surface soil.

## 1. Introduction

Human exposure to lead occurs through inhalation and oral ingestion, which may pose potential adverse health effects to human, especially children. Therefore, lead contamination in urban soil, street dust and atmospheric particles have been well documented (Charlesworth et al., 2011; Cheng and Hu, 2010; Hu et al., 2010; Komarek et al., 2008; Laidlaw et al., 2012; Luo et al., 2012; Wei and Yang, 2010). However, most investigations have focused on a single urban environmental compartment to assess contamination, sources and human health risks of lead. Various natural and anthropogenic lead sources in urban environment include mining, smelting, industrial uses, waste incineration, coal burning and traffic emissions (vehicle exhaust particles), and suspension of soil particles (Charlesworth et al., 2011; Wei and Yang, 2010). It is also believed that long-range transport of airborne particles is an important external source (Hsu et al., 2006; Lee et al., 2007; Mukai et al., 1994). The dry and wet deposition of atmospheric particles is an important source for heavy metals in street dust and urban surface soil (Tanner et al., 2008). Street dust is easily re-suspended back into atmospheric aerosols by wind or the movement of vehicles. It can also be transfer to surface soil by urban runoff (Tanner et al., 2008). For example, re-suspended soil/road dust is a primary source accounting for 74% of the total suspended particulate (TSP) mass in Ho Chi Minh City, Vietnam (Hien et al., 1999). Therefore, interactions between urban soil, street dust and atmospheric particles may indicate the transfer of lead in the urban environment. Atmospheric particles and street dust have more lead loads due to anthropogenic activities, while the pedogenic lead from the weathering of parent rocks is an important origin of soilborne lead. A systematic investigation of lead in urban surface soil, street dust and atmospheric particles can help us to understand its environmental geochemical behavior. It also aids assessment of the health risks posed by lead in the urban environment.

Lead has four stable isotopes: $^{204}Pb$, $^{206}Pb$, $^{207}Pb$ and $^{208}Pb$. Generally, each Pb source has a distinct or sometimes overlapping isotopic ratio range. Physico-chemical and biological fractionation processes do not significantly alter these isotopic lead ratios (Komarek et al., 2008; Yip et al., 2008). Therefore, lead isotopic composition can be used as a "fingerprinting" to identify lead

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sources and to trace lead pollution in different environmental compartments such as soils, sediments and atmosphere particles (Bentahila et al., 2008; Chen et al., 2008; Cloquet et al., 2006; Margui et al., 2007; Prohaska et al., 2005; Renberg et al., 2002; Semlali et al., 2001; Soto-Jimenez and Flegal, 2009; Townsend et al., 2009; Wong and Li, 2004; Zhang et al., 2008). In the present study, atmospheric particles (TSP and $PM_{2.5}$) were collected monthly for a year from two sampling sites in Nanjing located on the lower reaches of the Yangtze River, one of the fastest developing areas in China. Urban surface soil and street dust samples were also collected from various urban and suburban areas in Nanjing. The lead content and isotopic composition and the crustal elements (Al, Sr, Ti and Fe) were analyzed to investigate the contamination and the transfer of lead in urban environmental compartments.

## 2. Materials and methods

### 2.1. Sampling

Surface soil samples (0–15 cm depth) were collected from a total of 61 sites using a simple random sampling method (the sampling area is shown in Fig. S1 of the supplementary materials). They were 19 samples from urban parks and greenbelts, 34 samples from suburban greenbelts and sporadic vegetable fields, and 8 samples from mining vegetable fields near the suburban Qixia lead–zinc mining/smelting plant, the largest lead–zinc deposit in eastern China. Three sub-samples were collected at each sampling site using a stainless-steel hand auger and combined into one single soil sample. The soil samples were stored in polyethylene bags and brought back to the laboratory. After the removal of stones, coarse materials, and other debris, the soils were air-dried, ground and sieved through a 200 μm nylon sieve for further treatment. Street dust on road surfaces was collected using a commercial vacuum cleaner as described in the literature (Tanner et al., 2008). The detailed sampling scheme was the same as we outlined in an earlier report (Hu et al., 2011). Thirty samples were obtained (Fig. S1). In accordance with reports in the literature (Tanner et al., 2008), (McKenzie et al., 2008), particles less than 63 μm in size are considered to arise mainly from atmospheric deposition and transportation by re-suspension. Therefore, the air-dried street dust was sieved through a 63 μm nylon sieve and stored for analysis.

Atmospheric particles (TSP and $PM_{2.5}$) were collected from two sampling sites in Nanjing as our previous report (Fig. S1) (Hu et al., 2013). Briefly, four TSP samples and three $PM_{2.5}$ samples were collected per month from June 2010 to May 2011. Overall, 48 TSP samples and 35 $PM_{2.5}$ samples were obtained from each sampling site. All filter membranes were equilibrated in a desiccator for 48 h and then weighed before and after aerosol sampling to determine the aerosol mass. The filter membranes were subsequently placed into a clean glass vial with a Teflon-lined cap and stored at −20 °C until required for analysis. The field blank filter membranes were set at the same time.

### 2.2. Analysis of metal contents and lead isotope ratios

The metal content of the soil and street dust samples was analyzed using $HCl-HNO_3-HF-HClO_4$ mixture acid and a microwave sample preparation system (Milestone ETHOS 1) with temperature control, as in our previous report (Hu et al., 2011). Atmospheric particles (TSP and $PM_{2.5}$) were also digested using the Milestone ETHOS 1 as in our another report (Hu et al., 2013). Digestion solutions after microwave pretreatment were evaporated near to dryness, then dissolved with 65% $HNO_3$, and afterward brought to volume with Milli Q water. Solutions were stored in 25 ml high-density polyethylene vials at 4 °C prior to instrumental analysis. Precision and accuracy were verified using standard reference materials available at the National Research Center for Geoanalysis, China (GBW07405, Soil). The concentrations of Al, Sr, Ti, Fe and Pb in the digestion solutions were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin–Elmer SCIEX, Optima 5300). Detailed information on the ICP-OES operating parameters for measurement of elemental concentrations is described in Table S1 (the supplementary materials).

Although lead isotope ratios can be measured by using thermal ionization mass spectrometry (TIMS) and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), inductively coupled plasma quadruple mass spectrometry (ICP-QMS) is believed to be sufficient for lead isotope ratio measurement in most environmental examinations such as tracing lead sources and monitoring historical and environmental changes (Barbaste et al., 2001; Halicz et al., 1996; Komarek et al., 2008; Margui et al., 2007; Yip et al., 2008). In the present study, therefore, lead isotopic ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ were determined using ICP-QMS (ICP-MS, Perkin–Elmer SCIEX, Elan 9000) (the instrumental conditions are listed in Table S2 of the supplementary materials). During the measurement of the lead isotope ratios, the sample solutions were diluted to a concentration of approximately 30 ng $ml^{-1}$ Pb. The lead isotopic ratios reported in this work were corrected using standard reference material (SRM981, common lead isotopic material, National Institute of Standards and Technology, NIST, USA)). The NIST SRM 981 was analyzed repeatedly after every two real samples were measured to calculate the precision and the accuracy of the lead isotopic determination using normalization. The analytical precision of the lead isotope ratios in NIST SRM 981 at 30 ng $ml^{-1}$ Pb was 0.25% for $^{207}Pb/^{206}Pb$ and 0.36% for $^{208}Pb/^{206}Pb$.

### 2.3. Data analysis

One-way analysis of variance (ANOVA) was used to determine the differences in the lead content and isotopic ratio in surface soil, street dust and atmospheric particles (TSP and $PM_{2.5}$). Post-hoc multiple comparisons of means were conducted using the least significant difference (LSD) test. The criterion for statistical significance was taken to be $p < 0.05$. Statistical analysis was performed using Statistical Product and Service Solutions (SPSS) 13.0 software for Windows, and the figures were drawn using Origin 7.0.

## 3. Results and discussion

### 3.1. Lead levels in atmospheric particles, street dust and surface soil

The descriptive statistics of the lead contents of the atmospheric particles (TSP and $PM_{2.5}$), street dust and surface soil are summarized in Table 1. Lead contents of the studied atmospheric particles (TSP and $PM_{2.5}$) were significantly higher than that in the surface soil and street dust ($p < 0.05$). The lead contents in $PM_{2.5}$ were significantly higher than them in TSP at $p < 0.05$. The pervious study reported that average TSP-Pb concentrations were 1135 mg $kg^{-1}$ in January and 1874 mg $kg^{-1}$ in August in 2007 in Nanjing (Zhang, 2009), which were in the similar range of our study. It is also similar to the report that lead contents varied between 70 and 2940 mg $kg^{-1}$ (average of 1364 ± 620 mg $kg^{-1}$) in $PM_{2.5}$, and between 32 and 2188 mg $kg^{-1}$ (average of 920 ± 638 mg $kg^{-1}$) in TSP in Beijing, China (Widory et al., 2010). The lead contents of the suburban soil samples showed the lowest average contents among the studied urban surface soil, mining surface soil, street dust and atmospheric particles (TSP and $PM_{2.5}$) (Table 1). The average coefficient of variation (CV) for lead contents in urban and suburban surface soil samples (157%) was apparently higher than that for street dust (44.0%), TSP (73.7%) and $PM_{2.5}$ (67.9%). The lead content of the 8 surface soil samples from the Qixia mining district ranged from 356 to 578 mg $kg^{-1}$, which was significantly higher than them in street dust and other surface soils (Table 1). Therefore, the mining/smelting may be an important lead source for soil pollution near the mining/smelting plant. The lead content of the 19 urban soil samples (47.1 ± 27.7 mg $kg^{-1}$) was significantly higher than that of the 34 suburban soil samples

**Table 1**
The descriptive statistics of Pb contents and isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) of the studied soil, street dust and atmospheric particles (TSP and $PM_{2.5}$).

| | Pb (mg $kg^{-1}$) | $^{206}Pb/^{207}Pb$ | $^{208}Pb/^{206}Pb$ | Pb (mg $kg^{-1}$) | $^{206}Pb/^{207}Pb$ | $^{208}Pb/^{206}Pb$ |
|---|---|---|---|---|---|---|
| TSP ($n = 96$) | | | | Urban surface soil ($n = 19$) | | |
| Min | 266 | 1.151 | 2.075 | 22.4 | 1.162 | 2.090 |
| Max | 3969 | 1.185 | 2.124 | 126 | 1.186 | 2.115 |
| Median | 936 | 1.165 | 2.103 | 37.0 | 1.176 | 2.102 |
| Mean | 1117 | 1.165 | 2.103 | 47.1 | 1.175 | 2.103 |
| S.D. | 688 | 0.006 | 0.009 | 27.7 | 0.007 | 0.006 |
| $PM_{2.5}$ ($n = 72$) | | | | Suburban surface soil ($n = 34$) | | |
| Min | 391 | 1.150 | 2.079 | 19.3 | 1.172 | 2.084 |
| Max | 9840 | 1.175 | 2.118 | 43.4 | 1.194 | 2.114 |
| Median | 1826 | 1.166 | 2.102 | 29.2 | 1.185 | 2.098 |
| Mean | 2122 | 1.165 | 2.102 | 30.1 | 1.184 | 2.098 |
| S.D. | 1459 | 0.005 | 0.007 | 6.5 | 0.006 | 0.009 |
| Street dust ($n = 30$) | | | | Mining surface soil ($n = 8$) | | |
| Min | 37.2 | 1.160 | 2.093 | 356 | 1.125 | 2.158 |
| Max | 203 | 1.172 | 2.115 | 578 | 1.132 | 2.171 |
| Median | 97.3 | 1.164 | 2.105 | 417 | 1.128 | 2.167 |
| Mean | 109 | 1.164 | 2.105 | 431 | 1.128 | 2.166 |
| S.D. | 48 | 0.003 | 0.006 | 73 | 0.002 | 0.004 |