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Contamination and source differentiation of Pb in park soils along an urban–rural gradient in Shanghai

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ABSTRACT

Urban soil Pb contamination is a great human health risk. Lead distribution and source in topsoils from 14 parks in Shanghai, China were investigated along an urban–rural gradient. Topsoils were contaminated averagely with 65 mg Pb kg^{-1}, 2.5 times higher than local soil background concentrations. HCl-extracts contained more anthropogenic Pb signatures than total sample digests as revealed by the higher $^{207/206}Pb$ and $^{208/206}Pb$ ratios in extracts (0.8613 ± 0.0094 and 2.1085 ± 0.0121 versus total digests 0.8575 ± 0.0098 and 2.0959 ± 0.0116). This suggests a higher sensitivity of HCl-extraction than total digestion in identifying anthropogenic Pb sources. Coal combustion emission was identified as the major anthropogenic Pb source (averagely 47%) while leaded gasoline emission contributed 12% overall. Urbanization effects were observed by total Pb content and anthropogenic Pb contribution. This study suggests that to reduce Pb contamination, Shanghai might have to change its energy composition to clean energy.

1. Introduction

Urban soil Pb contamination is of concern to the public due to Pb's adverse human health effects, especially with respect to damage of the nervous system. Since the Industrial Revolution, emissions of Pb to the atmosphere have been significantly elevated by various anthropogenic activities, such as leaded gasoline use, coal combustion, waste disposal and incineration, construction, metallurgy, and paint (Nriagu, 1979; Nriagu and Pacyna, 1988). Soils serve as one of the most important sinks for metals (Wong et al., 2006), receiving anthropogenic metals from atmospheric deposition and direct disposals. Located in the center of Pb production and consumption, urban soils are heavily exposed to anthropogenic Pb contamination. Lead in urban soils can be absorbed into the human body via ingestion of soil (Mielke et al., 1999; Rasmussen et al., 2001) and inhalation of re-suspended soil particles (Laidlaw and Filippelli, 2008), posing a great risk to public health. Children are more susceptible to the urban soil Pb contamination than adults due to their hand-to-mouth behavior, which has been regarded as an important pathway for children's nondietary ingestion exposure to Pb (Xue et al., 2007). Once excessively exposed to Pb contamination, children might suffer with elevated blood Pb levels (BLLs) > 10 μg dL^{-1}, which have been detected around the world, including in China (Wang and Zhang, 2006; He et al., 2009; Zhang et al., 2009). Severe physiological and neurological effects in children, such as a decrease in intelligence quotient (IQ) scores, deficits in verbal memory and attention, learning failure, reading disabilities, lower vocabulary, hyperactivity, increased risk for antisocial and delinquent behaviors, anemia, and coma, have been associated with elevated BLLs (Kaufman, 2001; Bellinger, 2004; Counter et al., 2008; Zahran et al., 2009). Further, neurobehavioral performances of children can be influenced even by low BLLs <10 μg dL^{-1} or <5 μg dL^{-1} (Chiodo et al., 2007; Min et al., 2007; Surkan et al., 2007; Ha et al., 2009).

Health risks, especially childhood health impairment, make studies on Pb distribution and source in urban soils of great importance. Parks are one of the limited playgrounds for urban dwellers, especially for children, who pay frequent visits. Numerous studies point out that urban park soils in large cities have considerably elevated Pb contents (Li et al., 2001; Madrid et al., 2002, 2006; Manta et al., 2002; Chen et al., 2005b). However, the majority of these studies focus on the distribution of Pb content and chemical fractions in the urban soils. The source apportionment of urban soil Pb is still not fully clear for cities in China. Komárek et al.

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(2008) used Pb isotope ratios ($^{208/206}$Pb and $^{207/206}$Pb) to identify sources of soil Pb. Several studies found that plotting $^{208/206}$Pb versus $^{207/206}$Pb or Pb isotopes versus soil Pb content could give some information related to Pb origins in soils (Ettler et al., 2004; Bacon and Dinev, 2005). Monna et al. (2000) developed Pb isotope ratio based models to calculate relative contributions of various Pb sources in sediments.

Isotope ratio analyses have been conducted for soil Pb with (pseudo-)total digestion (Duzgoren-Aydin et al., 2004; Wong and Li, 2004; Luo et al., 2011) or dilute acid extraction (Hou et al., 2006; Townsend et al., 2009; Hosono et al., 2010). Teutsch et al. (2001) pointed out the anthropogenic Pb was mainly associated with the labile phases and that Pb in the residual silicate fraction mainly occurred naturally. Chemically, the dilute acid attacks the labile fractions of soil Pb (Snape et al., 2004). Therefore, the source apportionments by the Pb isotope ratios from total digestion and dilute acid extraction do not indicate the same pool. The dilute acid extraction indicates Pb isotopic information of anthropogenic sources and total digestion contains isotopic information of both anthropogenic and natural sources. Hence, we hypothesize that the isotope ratio analysis by the dilute acid extraction could identify anthropogenic Pb sources in urban soils more accurately than by the total digestion.

Shanghai, one of the world's largest cities, has a population of over 18 million, as well as 2 million vehicles. Lead free gasoline was introduced in the early 1990s and use of leaded gasoline was totally banned in Shanghai by 1997. After the phase-out of leaded gasoline, air Pb concentrations and child BLLs gradually dropped, but Pb concentrations remained high in the air (Zheng et al., 2004; Chen et al., 2005a), and 25% of the children had considerable high BBLs (Yan et al., 2002). On the other hand, coal is a main fossil fuel for electricity generation and other uses in Shanghai, and the city consumed 41.5 million tons (16.7 million tons for electricity) in 1995 and 51.4 million tons (27.4 million tons for electricity) in 2006 (Guo et al., 2009). Coal combustion dust was detected as the major source of Pb using Pb isotope analysis of atmospheric suspended particles (Chen et al., 2005a, 2008; Tan et al., 2006), and in children's blood before the leaded gasoline phase-out (Liang et al., 2010). Although little is known about the distribution and sources of Pb in Shanghai urban soils (Shi et al., 2008), we hypothesize that Pb in Shanghai park soils might also derive from coal combustion via atmospheric deposition.

Given the abundant literature and great significance of Pb contamination in air and children in Shanghai, in this study, Shanghai was selected as a model city to study Pb contamination and source differentiation in park soils along an urbanization gradient that ran from rural to urban. The main objectives of this study were: (i) to investigate Pb contamination in park soils along the urbanization gradient; (ii) to affirm the hypothesis that the dilute acid extraction might be more sensitive than the total digestion in differentiating anthropogenic sources of urban soil Pb via isotope ratio analysis; and (iii) to identify whether coal combustion is the major anthropogenic source of Pb to Shanghai park soils.

2. Materials and methods

2.1. Soil sampling and preparation

Fourteen parks located in the central urban core (CUC), the developed urban area (DDU), the developing urban area (DIU), and the suburban area (SU) of Shanghai, respectively, were selected (Fig. 1; Table 1). The four areas represented a steep gradient in population density. As the traditional center for residence and commerce (inside the Inner-ring Highway), the CUC area is the most highly urbanized area with a population density of 33,900 individuals km^{-2}. The DDU area is located between the Inner- and Middle-ring Highways with a population density of 17,500 individuals km^{-2}. There were some former industrial activities in the DDU area. The DIU area is on the urban development front between the Middle- and Outer-ring Highways with a population density of 7000 individuals km^{-2}. The SU area, including the area outside the Outer-ring Highway and Pudong district, is less urbanized with the lowest population density of 1400 individuals km^{-2}.

Three topsoil (0–5 cm) samples were collected from both the central and peripheral zones in each park using a stainless steel hand auger. Disturbed soil sites were avoided. Before sampling, the vegetation was removed by hand. Samples were sealed in separate polyethylene bags and air-dried in the laboratory. The air-dried soil samples were slightly hammered to pass through a 2-mm polyethylene sieve to remove stones, roots, leaves and other debris. After homogenization, a subsample (~20 g) was ground in a mortar to pass through a mesh-100 polyethylene sieve. The prepared samples were kept in desiccators prior to chemical analyses.

2.2. Soil analysis

The 100-mesh soil samples were subject to both pseudo-total digestion with HNO_3 and $HClO_4$ (Lee et al., 2006) and partial extraction with 1 mol L^{-1} HCl

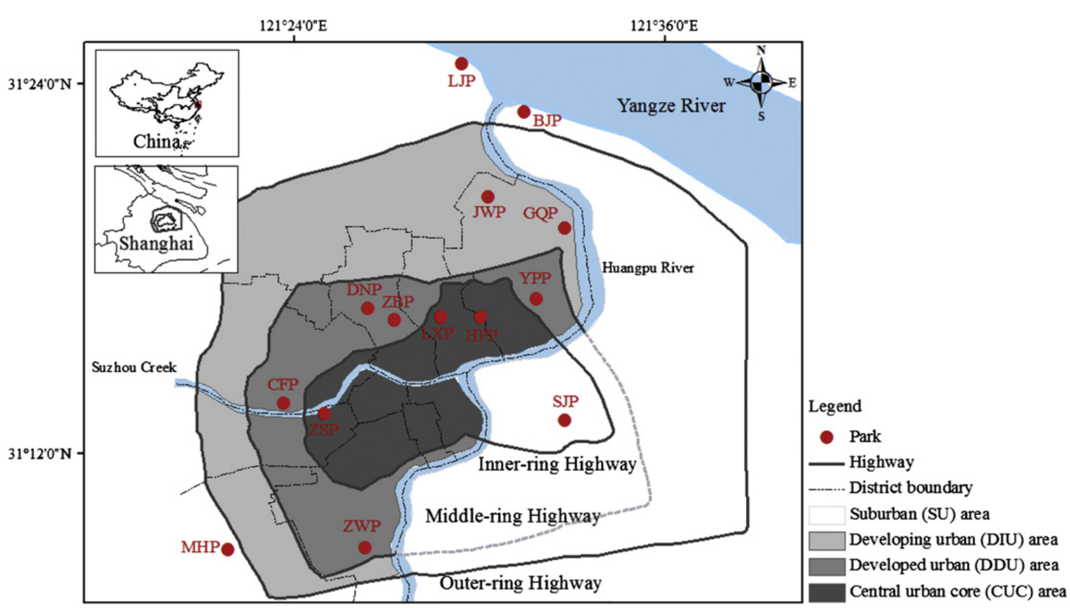

Fig. 1. Location of the 14 parks investigated in Shanghai, China. Parks were selected along an urbanization gradient from urban-to-rural, i.e. the central urban core (CUC), developed urban (DDU), developing urban (DIU), and suburban (SU) areas of Shanghai. The brief descriptions of the four areas and the investigated parks are shown in Table 1.