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# Source apportionment of Pb-containing particles in Beijing during January 2013

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ABSTRACT

Although leaded gasoline has been banned in some megacities in China since 1997 and nationally since 2000, atmospheric lead (Pb) pollution is still an important issue in China, as its concentration in megacities such as Beijing remains high. To measure the Pb concentration and identify sources of Pb-containing particles in Beijing during January 2013, both an online Single Particle Aerosol Mass Spectrometer (SPAMS) and offline filters analyzed by inductively coupled plasma-mass spectrometer (ICP-MS) were used at a monitoring site on the Peking University (PKU) campus. The average Pb concentration in $PM_{2.5}$ was 370 ng/m$^3$ in January 2013 and the highest daily concentration was as high as 1.3 μg/m$^3$ during our sampling period. Based on the mass spectra from the SPAMS, these particles were classified into 4 major types, including $NO_3$-rich (61%), ECOC-rich (18%), Fe-rich (14%), and $SO_4$-rich (7%). Results from this study suggest that combustion processes and the iron/steel industry were the major primary sources of Pb in Beijing. On clean days, the importance of the primary combustion particle type (ECOC-rich) increased, while during severe haze episodes, Pb-containing particles mixed with secondary ions and Fe were dominant. Based on estimates from the CMAQ model, on average 45% of Pb in $PM_{2.5}$ in urban Beijing was transported in January 2013, with a much higher percent transported during the haze episodes. The percentage of transported Pb increased with the concentration of Pb and $PM_{2.5}$, indicating that emissions from the surrounding areas need to be controlled during high Pb episodes in Beijing in winter.


## 1. Introduction

Lead has been widely used for thousands of years in human history and its adverse health effects, such as neurological and kidney diseases, even under low exposure levels, have been gradually understood (He et al., 2012). Due to concerns about severe effects of Pb pollution and the resulting ban of leaded gasoline, atmospheric Pb concentrations in developed countries such as the U.S. have shown a continuous and significant decreasing trend over recent decades (Cho et al., 2011). However, even though leaded gasoline has been banned since 2000 nationally, and since 1997 in megacities such as Beijing, Shanghai and Guangzhou, the atmospheric Pb concentration has not decreased correspondingly (Duan and Tan, 2013; Sun et al., 2006; Xu et al., 2012; Zheng et al., 2004). According to a recent review, the average concentration of atmospheric Pb was 261.0 ± 275.7 ng/m$^3$ in 44 major cities in China after the year 2000 (Duan and Tan, 2013). Though its concentration did not exceed the current national ambient air quality standard in China (500 ng/m$^3$ annually (MEP, 2012)), it is far beyond the three-month rolling average of the U.S. ambient air quality standard (150 ng/m$^3$ (EPA, 2006)).

In Beijing, leaded gasoline has been banned since 1997 and most metal smelting facilities and coal-fired power plants were gradually removed from Beijing city before and after the 2008 Olympic Games. However, the Pb concentration has not shown a significant steady decrease; instead, the annual Pb concentration in total suspended particulate matter (TSP) was still around 300–400 ng/

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$m^3$ in downtown Beijing during the 2000–2010 period (Wang and Li, 2010), very close to the level when leaded gasoline was still widely used (Chen et al., 1994; He et al., 2001; Li et al., 2012). Surprisingly, Okuda et al. (2008) found that the Pb concentration in $PM_{2.5}$ in Beijing increased by 20% per year after leaded gasoline was banned. In recent years, increased Pb concentrations have also been found in Dingling, a rural area located to the northwest of Beijing city (Wang and Li, 2010). The difference between the Pb concentration in downtown and background sites was reported to be decreasing, indicating that atmospheric Pb pollution is becoming a regional problem for Beijing. However, a detailed study of Pb sources and the level of regional transport in Beijing is still lacking.

Although there have been some source apportionment studies of Pb particles in a few Chinese megacities (Zhang et al., 2017), such as Beijing (Sun et al., 2006), Shanghai (Zheng et al., 2004), Guangzhou (Widory et al., 2010) and Xi'an (Xu et al., 2012), these studies were usually based on filter-based isotopic tracers and receptor models (such as Positive Matrix Factorization, PMF) (Bian, 2009; Mukai et al., 1993, 2001). Although there have been some emission inventory studies focused on Pb emissions in China, and a few studies on Pb transport from China to other countries (Li et al., 2012; Niisoe et al., 2010; Tian et al., 2011, 2012b, 2013, 2015), the Pb emission inventory has not been integrated with an air quality model to distinguish local versus regional transport to megacities in China such as Beijing.

The traditional source apportionment method using isotope ratios has its limitations for studying sources of Pb in China. Since the naturally occurring Pb isotopes $^{206}Pb$, $^{207}Pb$, and $^{208}Pb$ are formed through radioactive decay processes, the isotope ratios of Pb depend on geological conditions (Cheng and Hu, 2010). Since the 1990s, the Pb-containing anti-knocking gasoline additive used in leaded gasoline in China was imported from Australia (Cheng and Hu, 2010), which has isotope ratios very different from those of domestic Pb ores and sources in China. While leaded gasoline was in use, the isotope ratio method was effective to distinguish between gasoline and other domestic Pb sources. However, since leaded gasoline was banned, using Pb isotope ratios to identify gasoline emissions is no longer as effective.

Since the concentration of particulate matter in China can vary significantly within a very short time period (e.g., a few hours), it is hard to identify quick changes in the sources of particulate matter using traditional 24-h offline filter samples. For example, the $PM_{2.5}$ concentration in Beijing can increase from 50 $\mu g/m^3$ to 600 $\mu g/m^3$ within just 8 h (Wang et al., 2013b), necessitating a high-time resolution method for source apportionment.

In January 2013, the East China region experienced very severe fine particulate pollution episodes with hourly $PM_{2.5}$ concentration as high as 791 $\mu g/m^3$ and a daily average of 500 $\mu g/m^3$ measured on the Peking University (PKU) campus in Beijing. It was also a regional issue as a monthly average $PM_{2.5}$ concentration over 200 $\mu g/m^3$ was seen in many cities in the North China Plain (NCP) during the same month (Li and Han, 2016; Wang et al., 2013b). Some studies indicated that secondary species such as sulfate and nitrate increased significantly, suggesting that aging processes were very important in this period (Huang et al., 2014; Liu et al., 2016b). However, there are very few studies related to source apportionment of primary components such as hazardous metals during January 2013. From our measurements at the PKU site in Beijing, it was found that the monthly average concentration of Pb in January ($369 \pm 288$ $ng/m^3$) was much higher than those in other seasons in 2013 ($55 \pm 46$ $ng/m^3$, $115 \pm 77$ $ng/m^3$ and $99 \pm 97$ $ng/m^3$ for April, June and October, respectively). To better understand the extremely high Pb pollution in Beijing in January 2013, both field observations (online Single Particle Aerosol Mass Spectrometer (SPAMS)) and model simulations (the Weather Research and Forecasting (WRF) - Community Multi-scale Air Quality Modeling System (CMAQ)) were used to study sources and transport of Pb in fine particles in downtown Beijing.

## 2. Methods

### 2.1. Online SPAMS measurement

Our sampling site is located in the Air Quality Monitoring Station on the PKU campus in the northwest of Beijing, on the rooftop of a 6-story building (39.99° N, 116.31° E; 20 m a.s.l.). There are no major emission sources near the sampling site, with the exception of two major roads (150 m to the east and 200 m to the south). The PKU campus is a residential and teaching area without obvious Pb sources. The concentration of $PM_{2.5}$ was measured by a tapered element oscillating microbalance (TEOM). The concentration of $SO_2$, as well as meteorological parameters, was also measured at the same site. As in previous studies, the site is assumed to be representative of a typical urban site in Beijing (Lin et al., 2009; Wang et al., 2013a, 2015a; Wu et al., 2008; Yue et al., 2009).

A SPAMS (Hexin Analytical Instrument Co., Ltd., China) can provide information about particle size, chemical composition, and mixing state of single fine particles (from 200 to 2000 nm) with high-time resolution (normally 30 min or 1 h). Details of the instrument are available elsewhere (Cai et al., 2015; Li et al., 2011) and are briefly described here. Ambient fine particles are collected at a flow rate of 0.1 L/min. Particles are first accelerated and focused into a very narrow beam by an aerodynamic lens. As particles travel through two continuous lasers (532 nm) separated by 6 cm, the time and light-scattering signals are recorded by two photomultiplier tubes. The velocity and aerodynamic diameter of each particle are calculated (Li et al., 2011). Particles are then ionized by a pulsed Nd:YAG laser (266 nm). The mass spectra of the single particles are obtained using a dual polarity time-of-flight mass spectrometer. A SPAMS is a high-time resolution instrument which can provide large datasets and catch the rapid variations of fine particle composition. Since single particles are continuously ionized and measured by the time-of-flight mass spectrometer, this instrument can provide detailed information about the mixing state of single particles, especially for episodes in which the particle population changes quickly.

SPAMS measurements were carried out continuously from January 1–10 and 12–31, 2013. In this study, 1,056,759 individual particles were collected and analyzed (sampled time, particle diameter, and mass spectra) during our sampling period. Pb-containing particles were defined as particles with a relative peak area of $m/z$ 208 higher than 0.5%, which is the same criterion that has been used in another online Pb single-particle study (Zhang et al., 2009). According to our definition of Pb-containing particles, we measured 11,377 Pb-containing particles during our sampling period in January 2013.

The adaptive resonance algorithm known as ART-2a, a clustering method was used to cluster the Pb-containing particles based on spectral similarity. The ART-2a analysis was carried out with a vigilance factor of 0.9 and a learning rate of 0.05. Through ART-2a analysis, information about the sources of Pb-containing particles can be inferred.

### 2.2. Offline filter-based measurement

One of the limitations of the single particle instrument is that it is less quantitative due to matrix effects during ionization (Cai et al., 2015). In contrast, offline filters analyzed by ICP-MS can measure the concentration of Pb quantitatively and provide precise concentrations for CMAQ simulations, though with much lower time