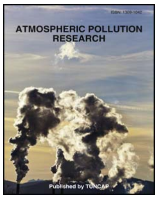
ARTICLE IN PRESS

Atmospheric Pollution Research xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: www.elsevier.com/locate/apr



Characteristics of airborne lead in Hangzhou, southeast China: Concentrations, species, and source contributions based on Pb isotope ratios and synchrotron X-ray fluorescence based factor analysis

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ARTICLE INFO

Keywords:
$PM_{2.5}$
Airborne lead
Chemical speciation
Bioavailability
Source contribution

ABSTRACT

$PM_{2.5}$ samples were simultaneously collected from three representative areas, the central city, industrial area, and clean district of Hangzhou, southeast China in October 2015. Aerosol Pb concentrations, species, and source contributions were investigated using chemical extraction, synchrotron X-ray fluorescence based factor analysis, and stable isotope fingerprinting technology. The results indicated that the airborne lead has been decreasing due to the stringent regulations on the emissions of trace metals from various sources. More than half the lead in $PM_{2.5}$ were associated with the F1(soluble and exchangeable metals) and F2 (carbonates, oxides and reducible metals) fractions, which are more bioavailable when inhaled by humans. Major contributors of aerosol Pb were coal combustion dust, metallurgic dust, and vehicle exhaust particles. Using a three endmember mixing model based on Pb isotope ratios, coal combustion contributed 45.4 ± 25.2%, industrial emission 28.9 ± 6.9%, and traffic exhaust 25.6 ± 18.3% to aerosol Pb in Hangzhou in October 2015.

1. Introduction

Recently, lead (Pb) associated with air-borne particulate matter (PM), primarily in urban areas, has received special attention (Berg and Steinnes, 1997; Callender and Rice, 2000; Anagnostopoulou and Day, 2006; Duzgorenaydin, 2007), especially the aerosol Pb. Due to the increased surface area of fine particulates, $PM_{2.5}$ has a high potential to absorb trace metals, and the toxic elements bound within fine particulates are easily absorbed by alveolus pulmoniscan, posing serious health hazards to residents (Mohanraj et al., 2004; Hu et al., 2012; Li et al., 2013; Zhai et al., 2014). Health problems, such as hearing loss, liver damage, and impaired cognitive functions occur once aerosol lead is inhaled to the human respiratory system. Young children (< 6 years old) are more vulnerable to Pb poisoning than adults (Nriagu et al., 1996; Millstone, 1997; Needleman, 2004).

Previous studies have shown that aerosol lead can be emitted from different sources, such as iron and steel manufacturing, coal combustion, diesel-powered motor vehicles, road re-suspension dust, and solid waste incineration (Begum et al., 2005; Zheng et al., 2005; Pancras et al., 2013). The contribution of vehicle exhaust fumes to air pollution has declined considerably since leaded gasoline was banned in 2000. Other anthropogenic actions, such as fossil fuel burning and industrial activities, have become the major sources of atmospheric lead pollution in China (Zheng et al., 2004; Chen et al., 2005; Wang et al., 2006; Schleicher et al., 2009).

In general, Pb from anthropogenic sources is more labile and bioavailable (Feng et al., 2009; Li et al., 2017). The bioavailability, or potential toxicity of aerosol lead, are closely related to the physical and chemical forms of lead. While investigating the mineralogical characteristics and leaching behavior of Pb in Rome, Tagliani et al. (2017) attributed Pb to oxides, hydroxides and alloys in the $PM_{2.5}$, which was primarily sourced from vehicular traffic; the undissolved fraction corresponded to the presence of alloys. Using X-ray absorption of fine structures (XAFS), Tan et al. (2006) showed that major chemical forms of aerosol Pb in the 2002–2003 winter in Shanghai were likely $PbCl_2$, $PbSO_4$, and PbO. The dominant contributor of aerosol Pb was coal combustion dust. Sakata et al. (2014) reported that lead species were different for the fine and coarse aerosol size fractions. The Pb species in

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

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https://doi.org/10.1016/j.apr.2017.12.009
Received 25 September 2017; Received in revised form 18 December 2017; Accepted 18 December 2017

Please cite this article as: Fang, J., Atmospheric Pollution Research (2018), https://doi.org/10.1016/j.apr.2017.12.009

fine aerosol particles were PbC_2O_4, $PbSO_4$, and $Pb(NO_3)_2$. The major Pb sources were fly ash, derived from municipal solid waste incinerator, and heavy oil combustion. That is, the Pb species in aerosol particles varied from different sources, which affected the toxicity and health effects. Therefore, it is important to monitor both the concentrations, and the species and sources of Pb in aerosol particles.

Enrichment factors (EF), principle component analyses (PCA), and lead isotopic fingerprinting have been widely used to identify sources of Pb in the atmosphere (Querol et al., 2001; Banerjee, 2003; Yatkin and Bayram, 2007; Sen et al., 2016; Li et al., 2016). Due to the complexity of environmental samples, multi proxies are suggested to provide more accurate information than a single proxy when tracing anthropogenic inputs of Pb (Zhu et al., 2013; Sen et al., 2016). Using stable Pb isotopic ratios combined with PCA, Zhu et al. (2013) revealed that Pb in the kindergarten dust from Wuhan, central China, can be classified into two major sources: non-ferrous metal related industries and coal combustion. In addition to the direct, but time-consuming chemical approaches, spectra analyses such as energy dispersive electron probe X-ray microanalysis, confocal microprobe Raman imaging, X-ray diffraction (XRD), and XAFS, have proven especially powerful techniques for a more comprehensive understanding of the sources, reactivity, transport, and removal of atmospheric chemical species (Batonneau et al., 2006; Yue et al., 2006; Tagliani et al., 2017). Unfortunately, because Pb is a minor component in aerosol particles, specific Pb species cannot be identified in most cases. Synchrotron radiation micro-X-ray fluorescence (SR-μXRF), however, with high sensitivity (Fittschen and Falkenberg, 2011; Wu et al., 2013), might be capable of characterizing the origins of aerosol Pb. Based on PCA of a set of SR-μXRF spectra, Schreck et al. (2012) observed three representations in ryegrass leaves, which illustrated the foliar uptake of Pb resulting from the emissions of a battery-recycling factory. Here, we hypothesized that Pb isotope ratios coupled with synchrotron X-ray fluorescence based factor analysis could successfully determine the provenance of aerosol Pb.

Hangzhou, the capital of Zhejiang province, is one of the most highly-developed cities in China. With rapid economic development over the past 20 years, the air quality has correspondingly declined (Qi et al., 2005; Ming et al., 2017). The Pb concentration in $PM_{2.5}$ was 122.0 ng/m^3 over the 2013–2014 year (Ming et al., 2017). To improve air quality, the local government implemented a series of pollution controls, including traffic restriction and banning coal. It was expected that aerosol Pb in Hangzhou would be reduced as a result. The objectives of this study were (1) to determine the concentration of aerosol Pb and its bioavailability in an urban area of Hangzhou; (2) to identify the potential Pb sources using the stable isotope ratios coupled with SR-μXRF based factor analyses. The results should provide useful information for both pollution control and risk assessment.

2. Method and material

2.1. Sampling sites

Hangzhou (120.19°N, 30.26°E) is a coastal city located in the Yangtze River delta region, with a total area of 16,596 km^2 and a population of > 9 million. The prevailing wind directions are SSW and N, with an average wind speed of 1.91 $m\ s^{-1}$. $PM_{2.5}$ samples were collected from three different locations within the city (Fig. 1). Xiasha is in the eastern industrial zone of Hangzhou. Rubber manufacturing, textile, and mechanical manufacturing industries are the main sources of air pollution. The Hemu sampling site, located in a densely populated areas, is affected by high levels of traffic emissions. Xixi is in the National Wetland Park, west of Hangzhou city, ~6 km away from the Wulin Square, the urban center. Local important enterprises with large air pollution emissions at the time of sampling were the Hanggang Steel Corporation and thermal power plants, which are also indicated in Fig. 1.

2.2. Sample collection

$PM_{2.5}$ samples were collected on quartz microfiber filters using PM samplers equipped with a 2.5 μm inlet at a flow rate of 1 m^3/h. The collection duration per sampler was 8 h, from 0:00 to 8:00, 8:00 to 16:00, and 16:00 to 24:00. Sampling was conducted in October 2015, yielding a total of 35, 39, and 63 samples at Xiasha, Hemu and Xixi, respectively. Filters, 25 mm in diameter, were weighed at least three times before and after sampling with a micro-balance after stabilizing at constant temperature (25 ± 1 °C) and humidity (40 ± 1%) for 48 h. All samples were stored in a refrigerator at 4 °C prior to chemical analysis.

2.3. Chemical analysis

2.3.1. Sequential extraction procedure (SEP)

A total of thirty-three aerosol samples were used for SEP. The four-step SEP used in this study separated the particulate-bound lead into four fractions, including soluble and exchangeable metals (F1); carbonates, oxides and reducible metals (F2); bound to organic matter, oxidisable and sulfidic metals (F3); and residual metals (F4). The reagents and operational conditions used in each step are summarized in Table 1. Following each extraction step, separation was performed by centrifugation for 15 min at 4500 rpm. The extraction solution was filtered through a 0.45 μm filter and stored in a polyethylene bottle at 4 °C for analysis. Pb concentrations in the filtrates were determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES).

2.3.2. Procedures for lead concentration and isotopic analysis

The total Pb concentration was analyzed in each $PM_{2.5}$ sample. Half the filter was digested with a mixture of HNO_3-H_2O_2 (4:1). Quality control assessed by analyzing reagent blanks, replicates, spiked samplers, and standard reference materials (GSS-8). Lead concentrations were determined using an inductively coupled plasma mass spectrometer (ICP-MS), with the internal standard added online, 10 μg/L ^{115}In in 2% HNO_3. The contamination during the analysis was negligible, and the precision of the analysis was within 10% for all samples.

Lead stable isotope ratios of $^{207/206}Pb$ and $^{208/206}Pb$ were determined using ICP-MS (ThermoFisher Series 2). Prior to analysis, Pb concentrations were diluted to 20 μg/L using 2% HNO_3. The precision and accuracy of Pb isotopic measurements were verified using certified reference material (SRM 981, common lead isotopic material) from the National Institute of Standards and Technology (NIST), USA. Differences in isotope ratios were generally < 5%. The analytic precision of lead isotope ratio in NIST SRM 981 at 20 μg/L Pb was 0.21% for $^{207}Pb/^{206}Pb$ and 0.33% for $^{208}Pb/^{206}Pb$. Because of the small quantity of ^{204}Pb, only the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios were determined. The Pb isotope ratios reported in this work were corrected using the SRM 981, which was repeatedly analyzed every two samples.

2.3.3. Synchrotron-based μXRF analysis procedure

Synchrotron radiation micro-X-ray fluorescence (SR-μXRF) analysis was performed in a normal air environment at beamline 4W1B of the Beijing Synchrotron Radiation Facility (BSRF), China. The electron storage ring was operated at 2.5 GeV with the current ranging from 150 to 250 mA during the experiment. The incident X-ray energy was monochromatized using a W/B4C Double-Multilayer-Monochromator (DMM) at 15 keV and focused down to 50 μm in diameter with a polycapillary lens. The sample profile was adjusted to 45° with respect to the beam direction by adjusting the vertical and horizontal slits, and a fluorescent detector was located 30 mm away from the sample according to the signal intensity of the elements. The fluorescent radiation was detected using a PGT Si (Li) solid detector with a 7.5 μm thick beryllium window, and a resolution of 134 eV at 5.89 keV. A total of 137 aerosol samples were analyzed using the SR-μXRF analysis with