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Source of atmospheric heavy metals in winter in Foshan, China

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HIGHLIGHTS

- Foshan city is the most air polluted city in Pearl rivel Delta.
- Atmospheric Zn, Pb and As were significantly high in this area.
- Two special sources were identified during the sampling period.
- Ceramic industry is the most important source of atmospheric heavy metal.
- EFs analysis indicated that local emissions were the main sources.

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ABSTRACT

Foshan is a ceramics manufacturing center in the world and the most polluted city in the Pearl River Delta (PRD) in southern China measured by the levels of atmospheric heavy metals. $PM_{2.5}$ samples were collected in Foshan in winter 2008. Among the 22 elements and ions analyzed, 7 heavy metals (Zn, V, Mn, Cu, As, Cd and Pb) were studied in depth for their levels, spatiotemporal variations and sources. The ambient concentrations of the heavy metals were much higher than the reported average concentrations in China. The levels of Pb (675.7 ± 378.5 ng/m^3), As (76.6 ± 49.1 ng/m^3) and Cd (42.6 ± 45.2 ng/m^3) exceeded the reference values of NAAQS (GB3095-2012) and the health guidelines of the World Health Organization. Generally, the levels of atmospheric heavy metals showed spatial distribution as: downtown site (CC, Chancheng District) > urban sites (NH and SD, Nanhai and Shunde Districts) > rural site (SS, Shanshui District). Two sources of heavy metals, the ceramic and aluminum industries, were identified during the sampling period. The large number of ceramic manufactures was responsible for the high levels of atmospheric Zn, Pb and As in Chancheng District. Transport from an aluminum industry park under light north-west winds contributed high levels of Cd to the SS site (Shanshui District). The average concentration of Cd under north-west wind was 220 ng/m^3, 20.5times higher than those under other wind directions. The high daily maximum enrichment factors (EFs) of Cd, Pb, Zn, As and Cu at all four sites indicated extremely high contamination by local emissions. Back trajectory analysis showed that the heavy metals were also closely associated with the pathway of air mass. A positive matrix factorization (PMF) method was applied to determine the source apportionment of these heavy metals. Five factors (industry including the ceramic industry and coal combustion, vehicle emissions, dust, transportation and sea salt) were identified and industry was the most important source of atmospheric heavy metals. The present paper suggests a control policy on the four heavy metals Cd, Pb, Zn, and Cu, and suggests the inclusion of As in the ceramic industry emission standard in the future.

1. Introduction

The association of airborne particulate matter (PM) with adverse health effects has been recognized for a long time (Fang et al., 2005, 2010; Gao et al., 2005; Yang et al., 2011; Franck et al., 2011; Steinle et al., 2013). Heavy metals are part of PM and pose serious risks to human health, resulting in a variety of human dysfunction (Pineiro-Iglesias et al., 2003) and various diseases. Atmospheric heavy metals are removed by wet and dry deposition which can then cause negative effects on the biogeochemical cycling (Wong et al., 2003). Natural emissions, traffic and industrial emissions are the principal sources of heavy

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metals in the ambient air (Lee and Hieu, 2011; Park et al., 2008). Studies showed that most heavy metals were enriched in $PM_{2.5}$ (Duan et al., 2012b; Lu et al., 2012). For example, the ratios of heavy metals in $PM_{2.5}$ to those in PM_{10} in Beijing, China ranked as Pb (88.5%) > Cd (81.8%) > Zn (81.5%) > As (77.1%) > Cu (75.9%) > Cr (71.7%) > Ni (67.9%) > Mn (63.3%) > V (46.8%) (Duan and Tan, 2013). Foshan is one of the most important manufacturing bases not only for China, but also for the world (Guo et al., 2011). The city is characterized by a high density of ceramics plants, accounting for around 30% world production of ceramics and consuming about 40% coal in Foshan in 2008 (Shen and Wei, 2012). With the substantial economic development, large amounts of pollutants were emitted into the atmosphere, which led to a rapid deterioration of air quality in and around this region. According to the Pearl River Delta Regional Air Quality Monitoring Network, the average concentrations of SO_2, NO_x and PM_{10} in Foshan city were significantly higher than those in other areas of Pearl River Delta (PRD). Many studies (Nie et al., 2010; Chen et al., 2012; He et al., 2009) showed that heavy metal pollution was a serious problem in Foshan. Heavy metal (Cd, Pb, Zn, and Cu) level invegetable soil in Foshan were significantly higher than those in the other areas throughout Guangdong Province and the whole country (Nie et al., 2010). Child blood lead levels (BLLs) in Foshan city were much higher than those in the developed countries (Chen et al., 2012; He et al., 2009). Several studies have been conducted on atmospheric heavy metals in the PRD region (Li et al., 2003; Wang et al., 2006a); however, no literature on characteristics and sources of atmospheric heavy metals has been investigated in Foshan.

This study was supported by the Foshan City Government to investigate the sources of serious pollution in winter in Foshan, and to put forward suggestions on control policies. Among the 22 elements and ions measured during the study, 7 heavy metals (Zn, V, Mn, Cu, As, Cd and Pb) were studied in-depth for their levels, spatiotemporal variations and sources. The objectives of the present study are to: (1) investigate the levels and their sources of atmospheric heavy metals (Pb, As, Zn and Cd) in Foshan; (2) put forward emission control policy suggestions for atmospheric heavy metals in Foshan.

2. Materials and methods

2.1. Sample collection

$PM_{2.5}$ samples were collected simultaneously by high volume (1.13 m^3/min) samplers (Thermo fisher instruments, USA) from 2th to 31th Dec 2008 at three urban sites (CC, NH and SD) and a rural site (SS) (Fig. 1). The CC site is situated in Chancheng district, the metropolitan center of Foshan city, which is surrounded by main traffic roads, residential buildings and factories. Most of the ceramic factories in Foshan city area round this site. The NH site is located in Nanhai district, which is only 2 km from the neighboring Guangzhou city and is surrounded by main traffic roads and residential buildings. The SD site is located in Shunde district, which is China's leading home appliance production base. Finally, the SS site is located in Shanshui forest park in Shanshui district with fewer nearby anthropogenic sources.

The sampler trapped $PM_{2.5}$ on quartz filters (Whatman QM-A, 20.3 × 25.4 cm) for 24 h and a total of 112 samples were collected. All quartz filters were annealed at 500 °C for 4 h to remove trace organics before usage. Before and after collection, filters were wrapped in baked aluminum foil. Prior to weighing, the filters were stored under a constant temperature and humidity condition of 25 °C and 50% for 24 hours. After sampling, each filter was wrapped in aluminum foil, then placed in an airtight bag, and taken to the laboratory at the local Environmental Protection Bureau (EPB) for storage at −30 °C. Upon the completion of sampling periods, the samples were transported in an ice box to the Key Joint Laboratory of Environment Simulation and Pollution Control at the School of Environment, Tsinghua University, for analysis. The lag period between sampling and analysis was about 2 months. Two types of blank samples were prepared: exposure blanks and filter blanks. The exposure blank filters were placed in the sampler for 24 h but had no air was drawn through them; hence, they were subjected to the same handling procedures as the actual samples. The filter blank samples were used to check for the contamination of the filters without going through the sampling procedures. On average, an exposure blank and a filter blank were taken for every 10 actual samples.

Meteorology data (Fig. 2) were recorded at the CC site by the equipment of "Davis Complete Weather Wizard III Cable Basic Weather Monitor" which provided ambient temperature, humidity, pressure, wind speed, wind direction at the CC site every 15 min during the sampling days. Visibility was measured by Belfort Model 6000 Visibility Sensor (Belfort Instrument, USA).

2.2. Sample analysis

A small portion of each filter was cut using stainless steel scissors and placed in Teflon tubes with a 4 ml mixture of concentrated high-

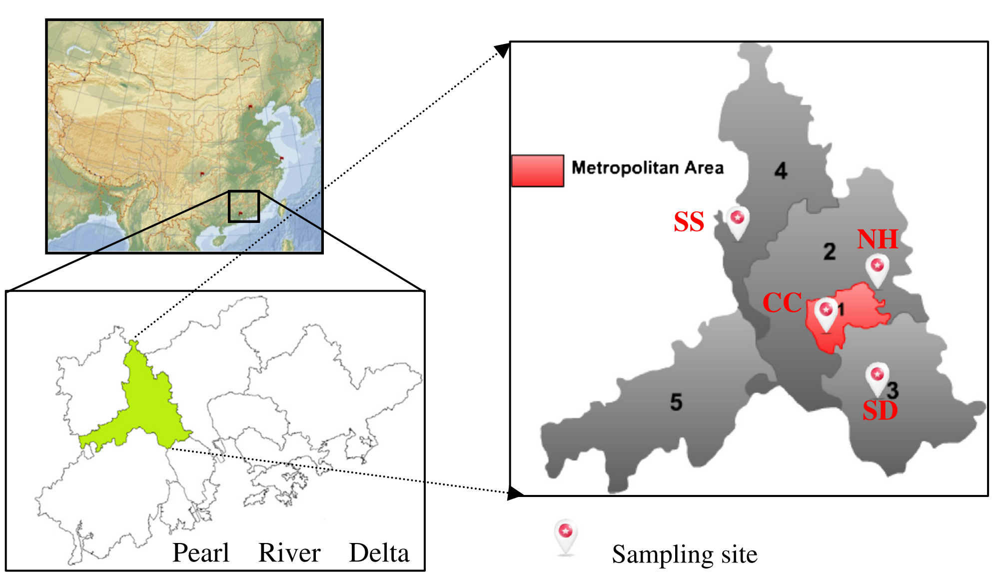

Fig. 1. Map of sampling sites.