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Size distribution and source of heavy metals in particulate matter on the lead and zinc smelting affected area

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ABSTRACT

In order to understand the size distribution and the main kind of heavy metals in particulate matter on the lead and zinc smelting affected area, particulate matter (PM) and the source samples were collected in Zhuzhou, Hunan Province from December 2011 to January 2012 and the results were discussed and interpreted. Atmospheric particles were collected with different sizes by a cascade impactor. The concentrations of heavy metals in atmospheric particles of different sizes, collected from the air and from factories, were measured using an inductively coupled plasma mass spectrometry (ICP-MS). The results indicated that the average concentration of PM, chromium (Cr), arsenic (As), cadmium (Cd) and lead (Pb) in PM was 177.3 ± 33.2 μg/m^3, 37.3 ± 8.8 ng/m^3, 17.3 ± 8.1 ng/m^3, 4.8 ± 3.1 ng/m^3 and 141.6 ± 49.1 ng/m^3, respectively. The size distribution of PM displayed a bimodal distribution; the maximum PM size distribution was at 1.1–2.1 μm, followed by 9–10 μm. The size distribution of As, Cd and Pb in PM was similar to the distribution of the PM mass, with peaks observed at the range of 1.1–2.1 μm and 9–10 μm ranges while for Cr, only a single-mode at 4.7–5.8 μm was observed. PM (64.7%), As (72.5%), Cd (72.2%) and Pb (75.8%) were associated with the fine mode below 2.1 μm, respectively, while Cr (46.6%) was associated with the coarse mode. The size distribution characteristics, enrichment factor, correlation coefficient values, source information and the analysis of source samples showed that As, Cd and Pb in PM were the typical heavy metal in lead and zinc smelting affected areas, which originated mainly from lead and zinc smelting sources. Q4

Introduction

Most heavy metals in the atmosphere are found in almost all aerosol size fractions, and their concentration and size distribution are controlled by natural (crustal minerals, forest fires and oceans) and anthropogenic emissions (such as fossil fuel combustion and industrial processes) into the atmosphere as reported by many investigators (Shao et al., 2013; Duan and

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Tan, 2013; Pan and Wang, 2015). Particulate matters (PMs) are a mixture of primary and secondary aerosols and usually have bimodal mass distribution, which appears in both fine particulates (aerodynamic diameter less than 2.5 μm in) and coarse particulates (aerodynamic diameter between 2.5 and 10 μm), separately (Karanasiou et al., 2007). In general, fine particles carry higher concentrations of toxic metals than coarse particles (Fang and Huang, 2011). As particle size decreases, the specific surface (the surface area per unit volume (or mass)) increases, which makes harmful heavy metals to be easier absorbed by PM (Kaupp and McLachlan, 2000). Heavy metals associated with inhalable particulates have also been shown to increase numerous diseases such as lung or cardiopulmonary injuries (Hu et al., 2012; Pandey et al., 2013; Xie et al., 2016). Fine particles are able to penetrate into the lung, and consequently impair human health. Thus, much attention has been focused on the relationship between the heavy metal content and size of PM (Wilson et al., 2002; Liu et al., 2015; Masiol et al., 2015; Rogula-Kozlowska et al., 2013). Mohanral et al. (2004) indicated that about 70%–90% of heavy metals are contained by PM_{10}, and the smaller the particles size, the higher the concentration of heavy metals. Brook et al. (1997) showed that heavy metals in $PM_{2.5}$ were potentially harmful to the human body. Cyrys et al. (2003) and Duan and Tan (2013) hold that the content of heavy metals was higher in fine PM than that in coarse PM; poisonous and harmful heavy metals, such as Pb, Cd, Ni, Mn, V, Zn *etc.*, were mainly adsorbed by fine particles.

Heavy metals are released into the atmosphere by the combustion of fossil fuels, vehicle emission, high temperature industrial activities, metal mining and smelting, waste incineration and other human activities. Heavy metals in the atmosphere are frequently associated with specific pollutant sources, and these are often used as tracers to identify the source of atmospheric particles (Duan and Tan, 2013; Chen et al., 2013). Many studies have been undertaken to reveal PM and its associated heavy metal concentrations in the atmosphere surrounding industrial areas (Chen, 2007; Lim et al., 2010). Toscano et al. (2011) revealed that the coarse particles were thought to be formed by low temperature combustion, crustal erosion and road dust resuspension, while fine particles were believed to be principally emitted from anthropogenic sources including combustion, high-temperature industrial activities and automotive traffic. Wei et al. (2009) found that metal mining and smelting activities were the major sources of heavy metals entering the environment. Waste gas pollutants from non-ferrous metal smelting are one of the main sources of heavy metal pollution in atmospheric particles (Davis et al., 1995).

From recent report, the most severe polluted areas locate in northern China (Zhang and Cao, 2015). But the concentrations of Pb, Cr and Cd in PM in southern cities were 12.3%, 7.3% and 171%, higher respectively than those in northern cities, while the concentration of As in PM in northern cities was higher 65.5% than those in southerner cities according to the data obtained in 44 major cities in China during the last 10 years (Tan and Duan, 2013). Non-ferrous metal mining and smelting plants are one of the main sources of atmospheric heavy metals and are widely distributed in China (Wei et al., 2009). Lead and zinc smelting belong to non-ferrous smelting. There are five lead and zinc production bases: the northeast, the northwest, Yunnan and Sichuan, the Hunan, and the Guangdong and Guangxi. These five Pb and zinc mining and processing bases account for more than 85% of total Pb output, and 95% of total Zn output in China, respectively. Hunan Province is famous as the "hometown of non-ferrous metal smelting". The emissions from non-ferrous smelting in Hunan have been one of the main sources of heavy metals in the environment (Wei et al., 2009; Duan and Tan, 2013; Xie et al., 2016). Non-ferrous smelting activity has caused serious heavy metal pollution in surrounding districts, which has caused significant health and ecological risks (Lyu et al., 2017). Previous studies have not been able to provide a clear illustration of heavy metal variation in areas where intensive non-ferrous smelting activities have occurred, nor have been able to interpret the possible contamination-source relationship. Knowledge on the size of the atmospheric particles and their relationship to heavy metals is vital for understanding the characteristics of atmospheric heavy metals of the lead and zinc smelting affected regions.

Chang-Zhu-Tan city clusters is a new urban agglomeration in central China, which is the first two-type social demonstration city group, *i.e.*, environment-friendly and resource-saving. Zhuzhou, the second largest city in Hunan province, is an important part of Chang-Zhu-Tan city clusters. It is one of the industrial regions in South China where non-ferrous smelting activities have developed rapidly since the 1950s (Ye et al., 2015), but many non-ferrous factories have closed in recent years due to the high demands required for environmental protection. Therefore the heavy metal pollution was very serious around the environment (Long et al., 2012). Wang and Stuanes (2003) studied the heavy metal pollution in air–water–soil–plant system of Zhuzhou city. Few studies on source identification and size distribution of heavy metals in atmospheric particles have been carried out in Zhuzhou. To understand the typical components of heavy metals in the atmosphere, we collected and analyzed the samplings in the atmospheric environment and from two non-ferrous smelting factories (lead and zinc smelting factories). The data obtained are important to understand the level of pollution and the type of heavy metals affected by the lead and zinc smelting factory. These results can be used to provide scientific evidence for setting up an air pollution control strategy.

The first batch of elements identified in the "12^{th} Five Year Plan on Heavy Metal's Comprehensive Prevention and Control" approved by the State Council were lead (Pb), mercury (Hg), chromium (Cr), cadmium (Cd) and arsenic (As). Mercury usually exists in a gaseous form in the atmosphere so that the concentration of mercury in PM is low. Although As is not a heavy metal (metalloid element), considering its negative health impacts it was regarded as a heavy metal and discussed as part of the study. Based on above, this study focused on the these four heavy metals.

1. Experimental methods

1.1. *Experimental methods of environment sampling*

1.1.1. *Study area and sampling site*

The weather of Zhuzhou is influenced by the prevalence of a subtropical humid monsoon climate. Northwesterly winds are