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# Wet and dry deposition fluxes of heavy metals in Pearl River Delta Region (China): Characteristics, ecological risk assessment, and source apportionment

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ABSTRACT

The atmospheric deposition of heavy metals poses serious risks to the ecological system and human health. To advance our knowledge of atmospheric dry/wet heavy metal deposition in the PRD region, monthly fluxes were examined based on soluble/insoluble fractions of five heavy metal elements (Cu, Pb, Cd, Cr and Zn) in samples collected from January 2014 to December 2015 at Guangzhou (urban) and Dinghushan (suburban) sites. The ratios of wet/dry deposition fluxes indicated that heavy metal deposition was governed by wet deposition rather than dry deposition in the PRD region. Affected by the shifting of the Asian monsoon, wet deposition fluxes exhibited significant seasonal variation between summer monsoon seasons (April to September) and winter monsoon seasons (October to February) in this region. Cd was classified as an extremely strong potential ecological risk based on solubility and the Hakanson ecological risk index. Source contributions to wet deposition were calculated by PMF, suggesting that dust, biomass burning, industries, vehicles, long-range transport and marine aerosol sources in Guangzhou, and Zn fertilizers, marine aerosol sources, agriculture, incense burning, biomass burning, vehicles and the ceramics industry in Dinghushan, were the potential sources of heavy metals.


## Introduction

With the rapid industrialization, agricultural modernization and urban expansion in China, the mining and smelting of metal minerals, thermal power, automobile exhaust and waste incineration emissions are the major sources of the atmospheric heavy metal pollutants. Recent research studies demonstrated that atmospheric heavy metal emissions have rapidly increased in a linear fashion during the past two decades (Tian et al., 2012a, 2012b). Heavy metals in the atmosphere eventually return to land and water surfaces by the processes of dry and wet deposition (in-cloud or below-cloud scavenging). The experimental results demonstrated that atmospheric deposition is the major source of heavy metals in soil (Gandois et al., 2010; Gray et al., 2003; Nicholson et al., 2003; Shen et al., 2016) and water environments (Sandroni and Migon, 2002;

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Wang et al., 2014), and causes persistent damage to these ecosystems. Public concern due to heavy metal transfer and accumulation in the food chain by atmospheric deposition into the ecosystem has increased rapidly with the substantial atmospheric emissions.

Since simultaneous measurements of atmospheric deposition to examine the relative importance of wet and dry deposition in removing airborne metals are lacking (Pan and Wang, 2015), monitoring observations have been performed, and wet deposition is considered to be the dominant removal mechanism for atmospheric pollutants, especially in monsoon areas with abundant rainfall (Sakata and Asakura, 2011). There are many studies focusing on the soluble fraction of the atmospheric heavy metal deposition (Avila and Rodrigo, 2004; Azimi et al., 2003; Hou et al., 2005; Moaref et al., 2014; Sakata et al., 2006), but recently researchers have paid more attention to the insoluble fraction (Baez et al., 2007; Fernandez-Olmo et al., 2014; Theodosi et al., 2010). Evaluation of the heavy metal soluble and particulate fractions is essential since the soluble and particulate forms have different fates in the environment, especially with respect to bioavailability (Theodosi et al., 2010).

The Pearl River Delta (PRD) region is located in the central Guangdong province in southern China, and has experienced remarkable economic development and urbanization during the past three decades (Lai et al., 2016). The PRD region is one of main industrial centers in China, and covers $4.17 \times 10^4$ $km^2$ land surface but hosts more than 5.8% of the Chinese population, and contributed more than 10.7% of the national GDP in 2015 (Bereau of Statistics of Guangdong Province, 2016; National Bureau of statistics of China, 2016). With rapid development, the PRD region is becoming a major atmospheric emission region for heavy metals (Cu, Zn, Cd and Cr) in China (Duan and Tan, 2013). Although many measurements have been performed to analyze the characteristics of heavy metals in the airborne particles *i.e.*, TSP, $PM_{10}$ and $PM_{2.5}$ (Lee et al., 2007; Tan et al., 2014, 2016; Zhu et al., 2015), atmospheric heavy metal deposition has yet to receive much attention. So far, there have been only a few research studies on atmospheric deposition in this region. Wong et al. (2003) and Huang et al. (2014) observed the bulk deposition of heavy metals. Huang et al. (2016) recorded the soluble mercury in atmospheric deposition from 2010 to 2012 in both Guangzhou and Dinghushan. To our knowledge, these published works have not examined the relative importance of the atmospheric input to the PRD region in either wet or dry deposition in soluble and particulate fractions. Moreover, source apportionment of atmospheric wet deposition of this region has not been well performed. The Pearl River Delta region is a typical region suffering from serious atmospheric pollution, and is located in the subtropical monsoon climate zone with abundant rainfall from April to September. Hence, we carried out this study: (1) to investigate the characteristics of atmospheric deposition for heavy metals (Cu, Pb, Cd, Cr and Zn) over two different underlying surfaces, *i.e.*, suburban and urban; (2) to determine the ecological risks of heavy metals induced by atmospheric deposition using the Hakanson potential ecological risk index; and (3) to identify the possible sources of typical heavy metals in wet deposition using positive matrix factorization (PMF).

## 1. Methodology

### 1.1. Site description

Two sites in the PRD region were selected for collecting atmospheric heavy metal deposition. The Guangzhou site is representative of urban areas, whereas the Dinghushan site, in the northwest of the PRD region, represents suburban areas. Both sites are shown in Fig. 1.

In Guangzhou (GZ), the south campus of Sun Yat-sen University (113°17′E, 23°06′N) was selected as the representative urban site. Guangzhou is in the center of the PRD region. The sampling site is located on the seventh floor (about 20 m above the ground) of the Geography and Environment Building in Sun Yat-sen University, and is surrounded by three main roads, which represents a typical urban surface.

The site in Dinghushan (DHS), on the third floor (about 10 m above the ground) of the Dinghushan Ecosystem Research Building (112°33′E, 23°10′N) at the foot of Dinghu Mountain, was also selected in this study, about 78 km away from Guangzhou. Dinghushan is 1132.2 ha in area, encompassing 132 ha of virgin forest landscape (approximately 12%). Dinghushan is located in the downwind area of Qingyuan City and Foshan City, which are in the heavy industrial area of Guangdong Province. The area around the Dinghushan site is an open terrain surrounding, and it is an excellent representative for a typical suburban surface.

### 1.2. Sampling and analytical method

An automated wet and dry sampler was used to collect the wet and dry deposition. The sampler consisted of two dishes (22 cm inner diameter with 11.5 cm height in DHS and 26 cm with 30 cm height in GZ, respectively), each equipped with a movable polyethylene cover which automatically covers the dry or wet sampler port depending on the rain. The dish collecting dry deposition is an aqueous surface with the water level kept at about 2 cm. The same sampler was also applied by Wang et al. (2013).

Atmospheric wet and dry deposition samples were collected from January 2014 to December 2015 at both the GZ and DHS sites. Wet deposition samples were collected after the rain stopped and dry samples were collected biweekly. In total, 106 wet samples and 41 dry samples were collected at the GZ site, while 82 wet samples and 45 dry samples were collected at the DHS site during the study period.

The samples were filtered by a 0.45 μm mixed cellulose ester membrane (MCEM, ADVANTEC, Japan) with 47 mm diameter, and the filtrate was acidified to a pH of less than 2.0 by adding 1% $HNO_3$. The filter residue membrane was processed based on EPA Method 3051 (US EPA, 2007) and the microwave-assisted method with nitric acid ($HNO_3$) was applied. A CEM Mars 6 microwave sample preparation system with temperature control was used to digest the filter residue membrane. Briefly, the filter was digested using 65% $HNO_3$ for the extraction of heavy metals. The preparation procedure for sample digestion is as follows: the temperature of each sample was increased from room temperature to 150°C in approximately 10 min and remained constant for 2 min, and then was raised to 190°C in approximately 5 min and remained constant for 30 min. After



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