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High time-resolved elemental components in fine and coarse particles in the Pearl River Delta region of Southern China: Dynamic variations and effects of meteorology

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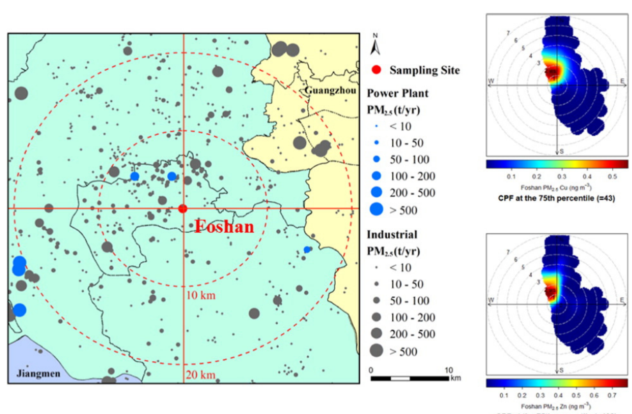
HIGHLIGHTS

- Hourly resolution $PM_{2.5}$ and $PM_{10-2.5}$ samples were collected at a subtropics urban agglomeration.
- Elemental compositions in size-resolved aerosols were measured.
- Key factors were identified contributing to the extreme events of $PM_{2.5}$ and selected elements.
- Industries, coal burning and soil dust contributed to PM elements pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Hourly-resolved $PM_{2.5}$ and $PM_{10-2.5}$ samples were collected in the industrial city Foshan in the Pearl River Delta region, China. The samples were subsequently analyzed for elemental components and black carbon (BC). A key purpose of the study was to understand the composition of particulate matter (PM) at high-time resolution in a polluted urban atmosphere to identify key components contributing to extreme PM concentration events and examine the diurnal chemical concentration patterns for air quality management purposes. It was found that BC and S concentrations dominated in the fine mode, while elements with mostly crustal and oceanic origins such as Si, Ca, Al and Cl were found in the coarse size fraction. Most of the elements showed strong diurnal variations. S did not show clear diurnal variations, suggesting regional rather than local origin. Based on empirical orthogonal functions (EOF) method, 3 forcing factors were identified contributing to the extreme events of $PM_{2.5}$ and selected elements, i.e., urban direct emissions, wet deposition and a combination of coarse mode sources. Conditional probability functions (CPF) were performed using wind profiles and elemental concentrations. The

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Potential sources
The PRD region
Foshan city

CPF results showed that BC and elemental Cl, K, Fe, Cu and Zn in the fine mode were mostly from the northwest, indicating that industrial emissions and combustion were the main sources. For elements in the coarse mode, Si, Al, K, Ca, Fe and Ti showed similar patterns, suggesting same sources such as local soil dust/construction activities. Coarse elemental Cl was mostly from the south and southeast, implying the influence of marine aerosol sources. For other trace elements, we found vanadium (V) in fine PM was mainly from the sources located to the southeast of the measuring site. Combined with CPF results of S and V in fine PM, we concluded shipping emissions were likely an important elemental emission source.

1. Introduction

Particulate matter (PM) is well-known to have adverse effects on human health and a range of other environmental effects, including local reductions in visibility and effects on the Earth's radiative balance (Nel, 2005; Seinfeld and Pandis, 2006; Huang et al, 2014; Wang et al., 2015). Elevated PM concentrations have been related to increased human mortality and morbidity (Schwartz and Dockery, 1992; Kan et al., 2012). Though low in concentrations, elements are ubiquitous in urban atmospheres and are highly concerning because of their health impacts. Moreover, elemental components are useful tracers for PM source identification due to their atmospheric stability and source specificity (Taiwo et al., 2014; Visser et al., 2015b). Many studies have been conducted to investigate their spatial and temporal distributions, sources and health implication (Niu et al., 2015; Chen et al., 2015; Tan et al., 2014; Visser et al., 2015a; Gao et al., 2014; Moreno et al., 2011; Richard et al., 2011; Järup, 2003). Natural emissions, traffic and industrial emissions were identified as major sources of elements (Duan and Tan, 2013; Zhou et al., 2014). However, the vast majorities of previous studies were based on long time periods, typically 24-h, and integrated one size-fraction filter sampling method, which cannot capture the dynamic variations of elemental concentrations caused by short-term source emissions and meteorological changes within one day. Therefore, to learn more about elements and their further health implications, higher time resolutions (hourly) with size-resolved PM monitoring are required.

Some of the high resolution and size-resolved PM elements studies were carried out in Europe (Bukowiecki et al., 2005; Dall'Osto et al., 2013; Moreno et al., 2011; Visser et al., 2015b) and U.S. (Pancras et al., 2011), while these were limited in China, with 2-h resolution in PM_{10} previously reported (Niu et al., 2015; Ye et al., 2014). As the world's second largest economy, China is facing severe air pollution problems. The Pearl River Delta region (PRD) is one of the most polluted areas (Zhang et al., 2008). This area is one of the major economic growth areas of China, comprising >57 million people over roughly 55,000 km^2 of area, having significant local emissions of both industrial and residential nature representing a significant exposure profile (Guangdong-Statistical-Yearbook, 2015). Over the past several years, researchers have tried to find out the sources of PM and associated elements in the PRD region (Tan et al., 2014; Wang et al., 2006; Lee et al., 2007). Their results revealed that industry, traffic emission, soil dust and regional transport were the main elements sources. However, there is still lack of short-term dynamic of ambient elements concentration level in the PRD, which will allow for a better understanding of the complex urban PM sources and their detrimental health effects. High-temporal resolution compositional analysis of PM can provide unique and highly relevant information for the implementation of PM mitigation strategies and as a result have experienced more attention recently (Moreno et al., 2011; Pancras et al., 2011).

For this study we collected hourly samples of fine ($PM_{2.5}$) and coarse ($PM_{10–2.5}$) particulate matter from October to December 2014, during the peak autumn air pollution period at a monitoring site in a PRD industrial city, Foshan. The samples were analyzed for black carbon and elemental composition. Peak PM and element events were mathematically evaluated. Correlations with meteorological data and the nature of the diurnal variations in the composition of fine and coarse particulate matter were explained, leading to potential elemental source locations being identified. Compared with the previous work, our study was unique in that (1) we demonstrate the added value of hourly measurements, especially with respect to the extreme PM concentration events and identification of diurnal chemical concentration patterns which is of particular importance for air quality management purposes, and (2) based on the empirical orthogonal functions (EOF) and conditional probability functions (CPF) methods, we have focused on the elemental dataset to extract as much information as possible, particularly with respect to the trace elements to highlight the presence of these PM components, their potential source locations and the associations with other species. Often these trace species can be overlooked in studies that involve factor analyses (receptor modeling, such as PMF and PCA), which are data reduction processes aiming to best describe the mean or typical conditions and variables, often leading to some information being lost, such as minor source contributors and trace (or analytically 'noisy') variables. It is for this reason we wanted to explore the full data-space and bring to the attention of the research and air quality management community of the presence of these trace elements, their likely source locations and associations. For policy makers, a comprehensive and accurate description of PM composition and relative contributions of component chemical species to the ambient PM concentrations is critical for the assessment of population exposure and potential health impacts as well as the design of the corresponding treatment measures and control strategies. The findings of this work add significantly to the literature in this field.

2. Sampling and methodology

2.1. Description of the sampling site

The monitoring station was located in Foshan, Guangdong Province, China (Fig. 1), on top of the Foshan Environmental Monitoring Center (Foshan EMC) (latitude 23.0025°; longitude 113.1035°, approximately 35 m above ground level). Foshan is one of the most important manufacturing hubs in China, characterized by the ceramics industry and household appliance industry, and produces ~15% of China's home appliance and ~30% of the world's ceramics (Guo et al., 2011). Adjacent to the monitoring site is a continuous sampling system measuring NO_x (Advanced Pollution Instrumentation (API), model 200E), CO (API, Model 300E), SO_2 (API, model 100E), O_3 (API, Model 300E), and $PM_{2.5}$ and PM_{10} (Thermo Scientific, model FH62C14), operated by the Foshan Environmental Monitoring Center. The station is surrounded by residential buildings and business offices on flat terrain.

2.2. Aerosol sampling

Hourly time-integrated samples of size-segregated coarse ($PM_{10–2.5}$) and fine ($PM_{2.5}$) PM samples were collected using a modified Streaker sampler (PIXE International Corporation, USA). The Streaker sampler has previously been described in detail (Annegarn et al., 1988), and used in a number of studies (Annegarn et al., 1992; Annegarn et al.,