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Temporal and spatial variation in major ion chemistry and source identification of secondary inorganic aerosols in Northern Zhejiang Province, China

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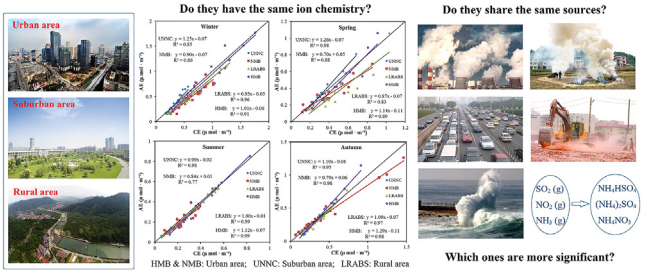
HIGHLIGHTS

- One year-long field measurement at four representative sites.
- Both $PM_{2.5}$ and water soluble inorganic ions (WSII) showed apparent seasonal variations.
- Non-sea salt chloride employed for the quantification of neutralization factors.
- The seasonal patterns of sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) values were opposite to each other.
- Contribution of various sources to WSII was of distinctive temporal and spatial characteristics.

GRAPHICAL ABSTRACT



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ABSTRACT

To investigate the seasonal and spatial variations of ion chemistry of fine particles in Northern Zhejiang Province (NZP), China, one year-long field sampling was conducted at four representative sites (two urban, one suburb, and one rural sites) in both cities of Hangzhou and Ningbo from December 2014 to November 2015. Twelve water soluble inorganic ions (WSII) were characterized in this comprehensive

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study. The annual average of $PM_{2.5}$ concentration in NZP as overall was 66.2 ± 37.7 μg m^{-3}, and urban sites in NZP were observed with more severe $PM_{2.5}$ pollution than the suburban and rural sites. The annual average concentration of total WSII at four sampling sites in NZP was 29.1 ± 19.9 μg m^{-3}, dominated by SO_4^{2-} (10.3 μg m^{-3}), and followed by NO_3^- (8.9 μg m^{-3}), NH_4^+ (6.6 μg m^{-3}), Cl^- (1.3 μg m^{-3}) and K^+ (0.7 μg m^{-3}). Among all cations, NH_4^+ was the predominant neutralizing ion with the highest neutralization factor (NF), while the remaining cations showed limited neutralization capacity. The highest and lowest sulfur oxidation ratio (SOR) values in this region were found in summer and winter, respectively; while the seasonal patterns for nitrogen oxidation ratio (NOR) were opposite to that of SOR. Principal component analysis (PCA) showed that the significant sources of WSII in NZP were industrial emissions, biomass burning, and formation of secondary inorganic aerosols. In addition, contribution from transboundary transport of polluted aerosols was also confirmed from the assessment through air mass backward trajectory analysis.

1. Introduction

Atmospheric aerosols, especially fine particles (aerodynamic diameter of ≤2.5 μm: $PM_{2.5}$), comprising of a complex mixture of solid particles and liquid droplets have received a significant attention over the recent decades due to their important roles, which affect ecology, climate change, visibility, and public health, such as respiratory diseases, cardiopulmonary mortality and lung cancer (Pope et al., 2002; Pope and Dockery, 2006; Fang et al., 2011; He et al., 2011; Xu et al., 2016a). In terms of the source origins and formation processes, they are classified as primary and secondary aerosols. The former aerosols are emitted directly from various sources, while the latter aerosols are formed through gas-to-particle transformation mechanisms with conducive meteorological conditions. For example, gaseous SO_2 and NO_2 are emitted mostly from coal-fired power plants and vehicles, and these two atmospheric gases are oxidized and subsequently converted to particulate SO_4^{2-} and NO_3^-, respectively through various heterogeneous and homogeneous reaction pathways (Kang et al., 2010; Lin et al., 2009). These inorganic species are successively converted to secondary aerosol particles such as $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3 through neutralization reactions with NH_4^+, which are originated from gas-phase NH_3. It was reported that secondary inorganic aerosols (sulfate, nitrate and ammonium: SNA) are among the most significant contributors to particulate matters (Waldman et al., 1991; He and Balasubramanian, 2008), accounting for more than one third of fine particle mass (Meng et al., 2016; Tsai and Chen, 2006); and they were also reported as important factors, which cause visibility impairment in urban environment (Kang et al., 2004; Tian et al., 2014). Their formation greatly depends on the characteristics of pre-existing aerosols, occurrence levels of the gaseous precursors, meteorological conditions including relative humidity (RH) and temperature, and atmospheric oxidants. (Baek et al., 2004; Deng et al., 2016; Pathak et al., 2009).

In China, due to significant deterioration of ambient air quality during recent decades across the country, the pollution characteristics of aerosols have been widely studied and the possible sources are being apportioned rigorously through various measurement campaigns. Among various components of atmospheric aerosols, water-soluble components are of great interest in urban atmosphere due to their impact on controlling aerosol acidity and environmental acidification (Deng et al., 2016). The earliest studies on WSII can be traced back to 1990s in China (Waldman et al., 1991), and after that a number of researches have been conducted in many cities to investigate the characteristics of water-soluble inorganic ions, such as Xiamen (Zhao et al., 2011), Handan (Meng et al., 2016), Guangzhou (Hu et al., 2008), Jinan (Gao et al., 2011) and Beijing (Hu et al., 2014; Huang et al., 2016). Yangtze River Delta (YRD) is one of the largest city-clusters and economically well-developed region in China, and WSII characteristics of severe aerosol pollutions in this region have also been reported to some extent. However, most of the studies of ion chemistry in fine aerosols in this region have been either based on a particular haze episode or a particular sampling site (Hua et al., 2015; Kong et al., 2014; Qiao et al., 2015; Wang et al., 2016b). Hence those past studies may not represent the seasonal ionic characteristics of the YRD region well. Due to absence of long-term observation of atmospheric inorganic ions in this region, Wang et al. (2015a) investigated the seasonal variations and sources of water-soluble inorganic ions in size-fractionated aerosols from 5 urban sites in YRD. However the results from Wang et al. (2015a) lack to explain the insights into ion chemistry occurring at urban, suburban and rural areas in YRD in a comparative way. In this respect, the investigation into seasonal varied ion chemistry, and assessing source attributions of fine particles at urban, suburban and rural sites in YRD should be valuable to filling such gaps, and gain further knowledge on how ion chemistry of fine particle formations of various representative sites in this region might differ from one another.

To fill such literature gaps,, twelve WSII species (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) in fine aerosols in Northern Zhejiang Province (NZP) were characterized at four different representative sampling sites (two urban, one suburban and one rural)in this study area located in the Southern YRD were investigated. The main objectives of this comprehensive study with experimental results from one year measurement field campaign were to characterize the temporal and spatial variations of fine aerosols and aforementioned ionic species profiles in NZP, intercomparison insights into the ionic chemistry at sampling sites with different urbanization gradients, and to explore the potential sources of these fine inorganic aerosols in the study domain (NZP region).

2. Experimental

2.1. Characteristics of sampling site

In order to investigate the ion chemistry of $PM_{2.5}$ and their possible sources in NZP, different types of representative sampling sites have been selected in both cities of Hangzhou and Ningbo, which are presented in Fig. 1 and briefly introduced, as explained below.

1) The University of Nottingham Ningbo, China (UNNC; suburban site; 29.80°N, 121.56°E) is located at the University Park in the south of Ningbo city, less than 10 km away from the central business district (CBD). It can be characterized as an