Science of the Total Environment 639 (2018) 793–803

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Seasonal variation and size distributions of water-soluble inorganic ions and carbonaceous aerosols at a coastal site in Ningbo, China

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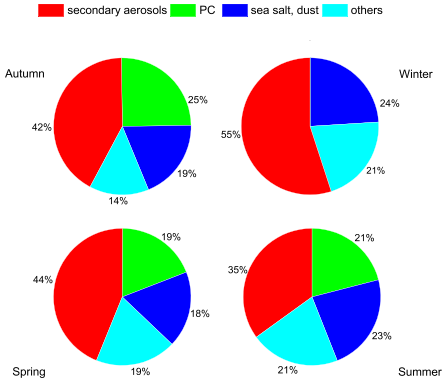
HIGHLIGHTS

- Size-segregated aerosols were collected throughout four seasons.
- Size distributions of eight carbon fractions were studied for the first time.
- OC4 and OP were closely associated with secondary aerosols.
- Higher temperature carbon fractions trend to focus on fine mode.
- Primary carbonaceous aerosols also contribute to air pollution.

GRAPHICAL ABSTRACT



PC: primary carbonaceous aerosols

ARTICLE INFO

Article history:
Received 6 April 2018
Received in revised form 13 May 2018
Accepted 15 May 2018
Available online xxxx

Editor: Jianmin Chen

Keywords:
Size distribution
Water-soluble ions
Carbonaceous aerosol
Coastal city

ABSTRACT

Size-fractioned aerosol samples were collected by an eight-stage Anderson sampler for four seasons from November 2014 to August 2015 at a coastal and suburban site in Ningbo, China, with a total of 270 samples were obtained. The seasonal variations and size distributions of water-soluble inorganic ions (WSIIs), carbonaceous aerosols (OC and EC), which consist of four organic carbon (OC1-OC4), pyrolyzed carbon (OP) and three elemental carbon fraction (EC1-EC3), were investigated. For the sampling periods, the average total concentration of WSIIs, OC and EC in $PM_{1.1}$, $PM_{1.1-2.1}$ and $PM_{2.1-9.0}$ were 21.3 ± 7 μg/m^3, 6.7 ± 2.7 μg/m^3 and 12.8 ± 1.9 μg/m^3, constituting 75.5%, 62.7% and 43.2% of the different size particle mass, respectively. The predominant chemical species were SO_4^{2-}, NO_3^-, and OC. WSIIs, OC and EC all exhibited significant difference between $PM_{2.1}$ and $PM_{2.1-9.0}$, reflecting their different sources. Ion balance calculations showed that the acidity of aerosols increased with a decrease in size, with the maximum of 1.07 in 1.1–2.1 μm and the minimum of 0.47 in 2.1–9 μm. It showed that size distributions of high-temperature carbon fraction such as OC4, OP and EC1 were almost unimodal during all seasons as well as SO_4^{2-} and NH_4^+, in contrast, that of lower temperature carbon fraction (OC1-OC3), Mg^{2+}, and Ca^{2+} appear like bimodal. Furthermore, the high consistency between the size distribution of OC4, OP and SO_4^{2-}, NH_4^+ in all seasons suggests that the similar or related generation process for the secondary organic and inorganic/ionic species, which contribute the most significant component of the particulate matter. Besides the

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https://doi.org/10.1016/j.scitotenv.2018.05.183
0048-9697/

secondary aerosols, primary carbonaceous aerosols (PC), which may originate in emissions from mixed combustion or natural source, also contributed a significant fraction of haze pollution, especially in autumn, spring and summer.

1. Introduction

The Yangtze River Delta (YRD) region with its highly dense population and vibrant economy, is one of the most prosperous urban agglomerations in the world. Lied in the south of YRD area, Ningbo is the second largest city of Zhejiang Province, which covers an area of 9816 km^2 and has a population of 7.8 million. It had 1.7 million vehicles by the end of September 2016, almost twice as published five years ago. The comprehensive energy consumption has increased incessantly from 31.4 million tonnes standard coal in 2010 to 38.3 million tonnes in 2015 with an increase rate of 4.34% annually (Ningbo Statistical Yearbook, 2016). Consequently, a mixture of local emissions, secondary formation, long-range transport and pollutants from marine sources cause severe air pollution in Ningbo, and aerosol particles have become the major harmful pollutants (Li et al., 2017). Aerosol particles, especially fine particulate matter ($PM_{2.5}$, with aerodynamic diameter not larger than 2.5 μm), can directly or indirectly impact the global climate by their radiation effects, impair visibility and endanger human health as well (Zhang et al., 2015; Kang et al., 2013; Zhou et al., 2010; Tie et al., 2009; Tie and Cao, 2009; Ramanathan and Carmichael, 2008; Bellouin et al., 2005). Specifically, fine particles can change the lifetime and albedo of cloud droplets, affect precipitation and lighting, regulate photochemistry, advance multiphase chemistry, and eventually impact earth energy budget (Lin et al., 2014; Zhao et al., 2005). Fine particles can impair visibility due to its scattering effect and dominate over other contributions to the extinction coefficient (Huang et al., 2016). In addition, fine particles are more likely to induce various diseases than larger ones, and have higher possibility to settle in the lungs after inhalation (Schlesinger et al., 2006). And ultrafine PM can even penetrate extrapulmonary organ (e.g. the heart, reproductive tract, and intestine) circularly through blood to bring inflammation, cause DNA damage or inhibit the anti-inflammatory ability of plasma high-density lipoprotein (Oberdörster et al., 2004; Kreyling et al., 2004).

The damaging effects of PM discussed above are primarily due to aerosol properties, such as the mass concentration, size distribution, and chemical constituents. PM is a combination of various chemical components (i.e. water-soluble ions, crustal materials, elemental carbon, and organic matters, etc.), which can enter straightly into the air (primary) or develop through gas-to-particle transformation and chemical reaction (secondary) (Sun et al., 2004). Among these species, water-soluble inorganic ions (WSIIs) and carbonaceous species are the dominant contributors to $PM_{2.5}$ (Tian et al., 2016; Bougiatioti et al., 2013). Yang et al. (2011) found that organic matter (OM) had a continuous and meaningful contribution to $PM_{2.5}$ across China, and secondary inorganic aerosol (SIA) normally composed 40–57% of the average $PM_{2.5}$ in eastern China. Previous research found that the proportion of secondary inorganic ions significantly increased during sever pollution events, which indicates their key role in the formation of haze (Tian et al., 2016; Sudheer et al., 2014; Sun et al., 2004). Some studies described that concentrations of sulfates and nitrates displayed an increasement in the droplet mode during pollution period and the peak moved to a larger size (Tian et al., 2014; Sun et al., 2013; Wang et al., 2012). In addition, the environmental and climate impacts of organic carbon (OC) and elemental carbon (EC) are largely depend on the particle size (Huang and Yu, 2008). Knowing of size distribution of different chemical compositions is vital to recognize how the physical and chemical development affect aerosol properties during haze (Zhang et al., 2013). However, many relevant researches focused on the concentrations in $PM_{2.5}$ or PM_{10}, or studied one or two haze episodes in several cities. The typical pollution characteristics and size contribution of WSIIs and carbonaceous aerosols over four different seasons have not been analyzed or compared thoroughly in YRD area (Li et al., 2017; Xu et al., 2016; Wang et al., 2015).

To better know the development and characteristics of particles during different seasons, size-segregated aerosols were obtained throughout four seasons at a coastal site in Ningbo. Size distribution and seasonal variations of water-soluble ions and carbonaceous compositions were investigated in this study. The goals of this study are to characterize the temporal variation and size distribution of WSIIs, OC and EC, to uncover the potential patterns and possible sources of PM pollution in Ningbo.

2. Material and methods

2.1. Site description

The sampling for atmospheric aerosols was launched at Ningbo Urban Environment Observation and Research Station (NUEORS), Chinese Academy of Sciences (CAS) (29.75°N, 121.9°E). This site is located in a coastal suburb (Chunxiao county, Ningbo) and is 37 km away from the city center. There are mountains from southwest to northeast and about 3 km away from NUEORS, while in the south the East China Sea is about 0.6 km away. There are several industries around this site: an automobile factory, a natural gas plant, a clothing factory and the mechanical fittings factories. As a new coastal town, Chunxiao has experienced great changes in the past four years, with more and more people, vehicles and houses. The climate of Chunxiao is influenced by the subtropical monsoon, which prevail northwest wind in winter and southeast wind in summer. The air temperature has its highest (28.0 °C) in July and lowest (4.7 °C) in January with the annual mean of 16.4 °C. The annual mean precipitation is 1480 mm with 60% occurring from May to September. The average wind velocity is 2–3 m/s in urban region and >5 m/s in coastland.

2.2. Collection of size-segregated particles

30 batches of aerosol samples were gathered across four seasons in Ningbo: autumn sampling from November 1–November 23, 2014; winter sampling from December 24, 2014–January 22, 2015; spring sampling from March 23–April 21, 2015; and summer sampling from June 26–August 6, 2015. In autumn 6 sets of samples were collected, named as a1–a6. In winter, spring and summer 8 sets of samples were collected, numbered as w1–w8, sp1–sp8, s1–s8, respectively. The sampling was conducted on the rooftop of a four-story labs building of the NUEORS, which was approximately 20 m above ground.

Three-day size-fractioned PM samples were taken continuously for one month (begin at 9:30 am the first day and end at 08:30 the third day) with a cascade impact sampler (Anderson Series 20–800, Franklin, MA, USA) at the flow rate of 28.3 L/min. The particle size range of the nine stages are <0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and >9.0 μm, respectively. Quartz filters (81 mm in diameter) were used to gather the particles. All quartz filters were prebaked at 450 °C for 5 h and then stocked in aluminum foils previous to sampling. Before and after sampling, all the filters were weighed using a microbalance with a precision of 10 μg after 24 h equilibration inside a temperature (25 °C) and relative humidity (50% RH) controlled chamber. After sampling, the filters were immediately fetched back and