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Characteristics of new particle formation events in Nanjing, China: Effect of water-soluble ions

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HIGHLIGHTS

- The characteristics of NPF events are examined in the YRD region.
- Aerosol size distributions from 10 nm to 10 μm are measured in Nanjing.
- The water-soluble ions of aerosol from 10 nm to 18 μm are determined in Nanjing.
- Interaction mechanisms between NPF events and water-soluble ions are investigated.

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ABSTRACT

New particle formation (NPF) events and water-soluble ions were studied at the meteorological building on the campus of the Nanjing University of Information Science and Technology (NUIST), which is located in the western part of the Yangtze River Delta (YRD). A wide-range particle spectrometer (WPS) provided particle number size distributions between 10 nm and 10 μm, whereas water-soluble ions for particles with diameters between 10 nm and 18 μm were measured using a 13-stage Nano-MOUDI aerosol sampler and 850 professional Ion Chromatography (IC). Additionally, meteorological data, trace gas concentrations and mass concentration were recorded. Ten NPF days were captured during the measurement period from 08 July to 02 August 2012. The mean aerosol number concentration, which was primarily composed of Aitken-mode particles, i.e., with diameters of 20–100 nm, was 13,664 cm^{-3}, which was 1.9 times larger than that on non-NPF days. The results suggest that the NPF events were only slightly affected by O_3, SO_2, and NO_2; the primary factors affecting NPF events were meteorological factors and air mass directions. NPF events were found to be favorable during the summer in the presence of high temperatures, strong radiation, low humidity, strong winds and clean air masses originating from the southeastern coast. The mean growth rate (GR), formation rate (J_{10}), condensational sink (CS), condensing vapor rate (Q), and condensation vapor (C) were determined to be 7.6 nm h^{-1}, 3.7 cm^{-3} s^{-1}, 2.8 × 10^{-2} s^{-1}, 2.9 × 10^{6} cm^{-3} s^{-1}, and 10.5 × 10^{7} cm^{-3}, respectively, on NPF days. The largest effects of the studied NPF events were on the mass and water-soluble ion concentrations of Aitken-mode particles, followed by nuclei-mode particles; few contributions to accumulation- and coarse-mode particles were observed. Different water-soluble ions were observed to have distinct interactions with the NPF events. The proportions of NH_4^+, SO_4^{2-}, NO_3^-, K^+ and Mg^{2+} in nuclei- and Aitken-mode particles to the total concentrations on NPF days were substantially higher than on non-NPF days.

1. Introduction

Atmospheric aerosol particles play an important role in Earth's radiative balance, atmospheric composition and human health (Davidson et al., 2005; Fan et al., 2012; Lohmann and Feichter, 2005). A central phenomenon related to atmospheric aerosols is the formation of new particles (nucleation) and their subsequent growth to larger sizes (Herrmann et al., 2014; Kulmala, 2003), e.g., to the size of Cloud Condensation Nuclei (CCN) (Dusek et al., 2010). Moreover, NPF events have be observed under different atmospheric conditions (Kulmala et al., 2004b, Kulmala and Kerminen,

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2008; Wang et al., 2014; Wu et al., 2007), including nighttime studies (Lee et al., 2008).

Aitken (1917) was the first to report evidence of new particle formation (NPF) in the atmosphere. However, research regarding new particle formation did not progress substantially until recent decades due to the limitation of observation instruments. Currently, particles can be detected at sizes as small as 1 nm (Kulmala et al., 2013), which is crucial for studying the mechanisms related to NPF events. Previous studies have shown that NPF events are closely related to SO_2 and H_2SO_4. The H_2SO_4–H_2O binary nucleation and H_2SO_4–NH_3–H_2O ternary nucleation theories were developed as a result of these relationships (Kulmala et al., 2002; Weber et al., 1999; Yue et al., 2010). Although organic species have been shown to be vital for NPF events in older studies (Odum et al., 1997), Zhang et al. (2004, 2009) demonstrated that the existence of organic species can substantially increase the nucleation rate of H_2SO_4, further promoting new particle formation; however, the mechanism for this process remains unknown. For example, isoprene oxidation products can be important for aerosol growth based on laboratory (Claeys et al., 2004) and field (Zhang et al., 2009) observations. However, Kiendler-Scharr et al. (2009) and Kanawade et al. (2011) demonstrated that isoprene has inhibition effects on the formation of new particles in forest districts.

The growth of new particles is also important for the nucleation process, primarily with respect to initial growth and subsequent growth (Kulmala et al., 2004a). Initial growth can occur via vapor condensation, the activation of soluble vapor, heterogeneous nucleation, the growth of molecular clusters via ions, the self-coagulation of molecular clusters, and multiphase chemical reactions (Kulmala et al., 2004a). Subsequent growth is relatively simple, including such processes as the condensational growth of precursors and the coagulation of individual particles. The evaluation method for condensational growth and the volatilization of soluble vapor on particle surfaces is primarily based on the condensational growth of H_2SO_4 (Pirjola and Kulmala, 2001). Therefore, the growth rate is typically determined according to the coagulation of H_2SO_4 with individual particles.

Water-soluble ions, especially for the secondary species of sulfate, nitrate, and ammonium salt, may have a surface activator that alters particle morphology and hygroscopicity, which further influences heterogeneous reactions of pollutants on the surface of aerosol (Hu et al., 2008; Zhu et al., 2011). However, there have only been a few studies regarding the interaction effects of NPF events with water-soluble ions, which are the dominant aerosol component in the YRD region (Fu et al., 2008; Yao et al., 2002). In this study, aerosol number concentrations for particles with sizes between 10 nm and 10 μm, mass concentration for particles with sizes between 10 nm and 18 μm, trace gases, and water-soluble ions were measured using WPS, DOAS, MOUDI-125a, and IC chromatography in July 2012 in Nanjing. The characteristics and formation conditions of the studied NPF events were obtained by integrating the meteorological factors and a backward trajectory model. The interaction mechanisms of NPF events with water-soluble ions are also discussed in this study.

2. Instruments and experiments

2.1. Instrumentation

The primary instrument used in this study to measure aerosol number concentrations was a wide-range particle spectrometer (WPS) produced by MSP (USA). Similar instrument combinations have been successfully used in previous studies of atmospheric nucleation (e.g., Gao et al., 2009; Wang et al., 2014). The instrument combines a differential mobility analyzer (DMA), a condensation particle counter (CPC) and a laser light scattering (LPS). The DMA and CPC are used to measure particles in the diameter range of 10–500 nm, whereas the LPS is used to measure particles in the diameter range of 0.35–10 μm. In this study, 48 channels were used for sampling with the DMA; 24 channels were used for the LPS. Therefore, 5 min were required for one complete scan of the entire size range with a 3 s scanning period for each channel. The WPS sample flow was set to 1 L min^{-1}, the DMA sample flow was set to 0.3 L min^{-1}, the LPS sample flow was set to 0.7 L min^{-1}, and the laboratory temperature was approximately 25 °C.

Mass concentration was measured using a 13-stage Nano-MOUDI aerosol sampler (Nano-MOUDI^{TM}, 125A, MSP, Inc., USA) with a diameter range of 0.01–18 μm for water-soluble ionic components. The flow rate required by the Nano-MOUDI is 10 L min^{-1}. The sampler was operated with a 47 mm Teflon filter (Whatman, Clifton, England) for water-soluble ionic components; the membranes were weighed using a Mettler Toledo MX- 5 microbalance at a constant temperature and humidity both before and after sampling. The microbalance was calibrated using a standard weight. The weight difference before and after the sampling is the particle weight. The size-segregated aerosol samples were continuously collected for 23 h from 08:00 to 07:00 in the next day.

Water-soluble ions were measured using 850 professional Ion Chromatography (IC) (Metrohm, Switzerland); NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, F^- and NO_2^- were analyzed in this study. Chromatography includes the use of a column oven, a conductivity detector, an 858 auto-injector and a MagIC net chromatography workstation (Metrohm, Switzerland). The column oven consists of a Metrosep C 4 150/4.0 separation column and a Metrosep A Supp 5 150/4.0 separation column. Moreover, the eluant was set at 3.2 mmol L^{-1} Na_2CO_3+1.0 mmol L^{-1} $NaHCO_3$ or anions and 1.7 mmol L^{-1} HNO_3+0.7 mmol L^{-1} pyridine carboxylic acid for cations. The column temperature was maintained at 30 °C. The flow-rate was 1.0 mL min^{-1}; the inject volume was 20 μL. Ultrapure water with a resistivity of 18.2 MΩ was used to prepare and dilute the solution. Changes in the primary meteorological factors were recorded using an automatic weather station.

Meteorological data, including wind speed/direction, temperature, pressure, relative humidity, radiation, and precipitation, were obtained from a CSI-CR1000 automatic weather station. Ozone, NO_2 and SO_2 concentrations were measured using differential optical absorption spectroscopy (DOAS). Specifically, an AR500 system produced by OPSIS AB (Sweden; Opsis) was used in this study. More detailed descriptions of the instruments are provided in Zhu et al. (2013).

2.2. Observation sites and experiment descriptions

This study was conducted at the meteorological building on the campus of the Nanjing University of Information Science and Technology (NUIST) (32.21°N, 118.72°E, 62 m a.s.l.) in the northern suburbs of Nanjing. The locations of the individual sites are shown in Fig. 1. Nanjing City is located in the center of the middle and lower reaches of the Yangtze River, which has a mean altitude of 26 m. The city is located to the north of the Jianghuai Plain and to the east of the Yangtze River Delta. The NUIST is approximately 3 km southwest of the Nanjing Chemical Industry area. WPS DOAS and meteorological factor observations were obtained from 08 July to 02 August 2012. Moreover, Nano-MOUDI^{TM} observations were collected from 19 July to 02 August 2012.

2.3. New particle formation event characteristics

The growth rate (GR) of NPF events was calculated according to Herrmann et al. (2014) and Kulmala et al. (2012):