



Thermodynamic properties of nanoparticles during new particle formation events in the atmosphere of North China Plain



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ABSTRACT

To better understand the sources, formation, and the transport of air pollutants over North China Plain (NCP), a four-week intensive campaign during summertime in 2014 was conducted in a central NCP rural site. In this study, particle hygroscopicity and volatility measurements were focused to characterize the thermodynamic properties of nanoparticles and gain insight into chemical composition of nanoparticles during the new particle formation (NPF) events. The water-soluble fractions of 30 and 50 nm newly formed particles were respectively 0.64 ± 0.06 and 0.61 ± 0.06 , indicating that the water-soluble chemical compounds, most likely ammonium sulfate, dominated the condensational growth of newly formed particles over the NCP. Due to containing higher water-soluble fraction, nanoparticles can be activated as cloud condensation nuclei (CCN) at lower supersaturation in the atmosphere of NCP in contrast to cleaner environments, such as Melpitz (Central European background) and Hyytiälä (boreal forest) during the NPF events. Our observations showed that the NPF and subsequent growth significantly resulted in an enhancement in CCN number concentration. The ranges of enhancement factors of CCN number concentration for supersaturation (SS) = 0.2, 0.4, 0.8% were respectively 1.9–7.0, 2.7–8.4, and 3.6–10.1. After being heated to 300 °C, the shrink factors for 30 and 50 nm particles were respectively 0.35 and 0.38. This indicated that non-volatile compounds could be produced during the growth process of newly formed particles.

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1. Introduction

Atmospheric new particle formation (NPF) and subsequent growth are of a great interest because it is an important source of cloud condensation nuclei (CCN) (Kazil et al., 2010; Kerminen et al., 2012; Laakso et al., 2012; Sotiropoulou et al., 2006; Spracklen et al., 2008; Wang and Penner, 2009; Wiedensohler et al., 2009). In addition, the newly formed particles may significantly deteriorate air quality via their rapid and long-term growth in the atmospheric environment with rich in gaseous precursors, like in a Mega-city, Beijing (Guo et al., 2014; Wiedensohler et al., 2009), Shanghai (Xiao et al., 2015), Nanjing (An et al., 2015), and suburban site of Yangtze River Delta of China (Qi et al., 2015). Freshly formed particles must grow tens of nanometers in order to serve as a CCN (Dusek et al., 2006; Kerminen et al., 2012). Therefore, it is important to understand the growth processes of newly formed particles for determining their roles in the atmosphere.

Detection of the chemical composition of newly formed particles is a key factor for quantitatively understanding the particle formation and

subsequent growth processes. The tandem differential mobility analyzer is often employed to measure the hygroscopicity and volatility of nanoparticles to provide indirect information on condensing vapor properties and chemical composition of newly formed particles (e.g. Ehn et al., 2007a; Hämeri et al., 2001; Ristovski et al., 2010). Over the past decades, the determination of particle hygroscopicity and volatility during the NPF events was deployed in various atmospheric environments, such as urban (Sakurai et al., 2005), rural (Wu et al., 2015), forest (Ehn et al., 2007a), and coastal areas (Väkevä et al., 2002). These observations show that the hygroscopicity and volatility of newly formed particles varied with the sampling atmospheres, indicating that condensed vapors driving the particle growth varied too. Up to now, no similar study was performed in the North China Plain (NCP). Such a scarcity of information on the nanoparticle thermodynamic properties during the NPF events in a polluted area has motivated the current study.

The NCP, including the Beijing City, often suffers from severe air pollution, especially due to long-range transport from southerly directions under calm weather conditions (Wehner et al., 2008). To better understand the sources, formation, and the transport of air pollutants, an intensive atmospheric field campaign during summertime 2014 was

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conducted near the city Wangdu located at about 150 km southwest of Beijing. During the four-week intensive study, NPF events occurred >50% of the sampling days. These frequent NPF events gave us the opportunity to investigate not only the hygroscopicity and volatility of nanoparticles but also the changes in chemical composition of newly formed particles during the NPF events. In this study, we will characterize the thermodynamic properties of nanoparticles during the NPF events to gain some insights into the particle growth processes in a sulfur-rich environment and make comparisons with other environments.

2. Experiment

The field campaign was conducted at Wangdu County (38.666N, 115.210E), located in the central NCP, as displayed in Fig. 1. Wangdu County is to the southwest and 150 km away from Beijing. The measurement site is located in an ecological park in the rural area of Wangdu County. The surrounding area was wheat field without significant traffic and industry emissions.

Table 1 summarizes the instruments and the parameters involved in this study. The core instruments are briefly described in the following sections. All aerosol instruments were installed in a temperature-controlled container (25 °C) and shared one sampling line with PM₁₀ cutoff. The relative humidity (RH) of the sampling air was kept below 30% using an automatic silica gel dryer system (Tuch et al., 2009).

2.1. Particle hygroscopic growth measurements

The particle hygroscopicity was investigated using a high humidity tandem differential mobility analyzer (HH-TDMA). The HH-TDMA was designed to measure the size-resolved particle hygroscopicity at RH up to 99% (Hennig et al., 2005). It consists of two DMAs connected in series with a humidity conditioning section between the two DMAs. The humidity conditioning section and the second DMA are placed in two different temperature controlled water baths to keep the fluctuation

Table 1

The summary of instrumentation and parameters.

Instruments	Parameters
High humidity tandem differential mobility analyzer (HH-TDMA)	Particle hygroscopic growth at RH = 98%
Volatility TDMA (V-TDMA)	Particle volatility at 300 °C
Twin differential scanning mobility particle sizer (TDSMPS)	Particle number size distribution (3–800 nm)
LIF	OH radical
Thermo Fisher Scientific	Sulfur dioxide (SO ₂) concentration
Weather station	Meteorological parameters

of the temperatures within ± 0.1 K in the HH-TDMA system. The final RH up to 98.5% is produced by decreasing the temperature of the second DMA relative to the humidity conditioning section. During the measurement, a constant temperature difference of approximately 2.5 K is maintained between the water bath for the second DMA (operated at 20 °C) and the water bath for the humidity conditioning section (operated at 22.5 °C). A dew point mirror (DPM) is located in the excess airline of the second DMA to measure the RH inside. Temperature and RH stability tests conducted by Hennig et al. (2005) showed that the absolute temperatures in HH-TDMA system can be maintained within ± 0.1 K with a stability of ± 0.02 K, and the RH in the second DMA reaches an absolute accuracy of $\pm 1.2\%$ for 98%. More detailed information regarding the HH-TDMA system is provided by Hennig et al. (2005) and Liu et al. (2011). Hygroscopicity scans with 100 nm standard ammonium sulfate particles were performed every late afternoon to calibrate the stability of the relative humidity of 98% in the second DMA. The TDMA_{inv} algorithm developed by Gysel et al. (2009) was used to process the HH-TDMA data and derive the probability density function of the hygroscopic growth factor at measured sizes. The hygroscopic growth factor (HGF) is defined as the ratio of the particle mobility diameter at a given RH ($D_p(RH)$) to the dry diameter ($D_{p,dry}$):

$$\text{HGF}(RH) = \frac{D_p(RH)}{D_{p,dry}} \quad (1)$$

Based on the Zdanovskii-Stokes-Robinson (ZSR) method (Stokes and Robinson, 1966; Zdanovskii, 1948), the HGF of a mixture can be estimated from the HGF of pure components and their respective volume fractions, ε_i (Malm and Kreidenweis, 1997):

$$\text{HGF}_{\text{mixed}} = \left(\sum_i \varepsilon_i \text{HGF}_i^3 \right)^{1/3} \quad (2)$$

Here, we assume that aerosol particles consist of two components including soluble and insoluble fractions (also refer to Ehn et al., 2007a; Swietlicki et al., 1999). The soluble fraction is assumed as ammonium sulfate. Then, ε of soluble fraction can be calculated by:

$$\varepsilon_{\text{soluble}} = \frac{\text{HGF}_{\text{measured}}^3 - 1}{\text{HGF}_{(\text{NH}_4)_2\text{SO}_4}^3 - 1} \quad (3)$$

where $\text{HGF}_{\text{measured}}$ is the HGF of particle measured by HH-TDMA, and $\text{HGF}_{(\text{NH}_4)_2\text{SO}_4}$ is the HGF of pure $(\text{NH}_4)_2\text{SO}_4$ particle with the same size. When calculating $\text{HGF}_{(\text{NH}_4)_2\text{SO}_4}$ in different diameters, the parameterizations for $(\text{NH}_4)_2\text{SO}_4$ water activity developed by Potukuchi and Wexler (1995) and the density reported by Tang and Munkelwitz (1994) are used. The Kelvin term was considered in the calculation.

One should keep in mind that the assumption of insoluble organic fraction may lead to overestimate the soluble fraction because atmospherically relevant secondary organics typically have a growth factor larger than 1 (e.g. Varutbangkul et al., 2006). This implies that in the presence of several classes of hygroscopic substances, ε derived from Eq. (3) is only an “equivalent” soluble fraction (i.e. assuming

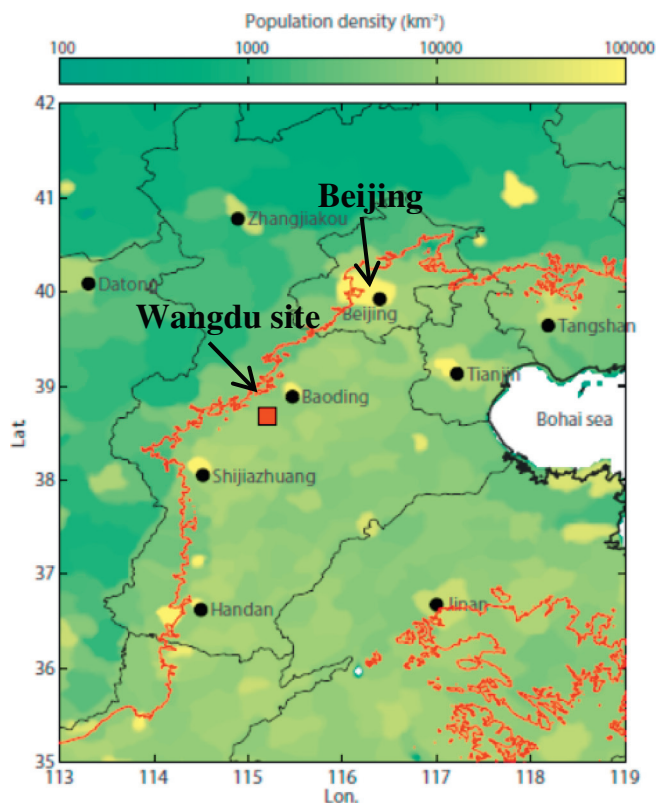


Fig. 1. The location of the measuring site (red square). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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