Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China during summertime


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Abstract:

Simultaneous measurements of particle number size distribution, particle hygroscopic properties, and size-resolved chemical composition were made during the summer of 2014 in Beijing, China. During the measurement period, the mean hygroscopicity parameters ($\kappa_s$) of 50, 100, 150, 200, and 250 nm particles were respectively 0.16±0.07, 0.19±0.06, 0.22±0.06, 0.26±0.07, and 0.28±0.10, showing an increasing trend with increasing particle size. Such size-dependency of particle hygroscopicity was similar to that of the inorganic mass fraction in PM$_1$. The hydrophilic mode (HGF>1.2) was more prominent in growth factor probability density distributions and its dominance of hydrophilic mode became more pronounced with increasing particle size. When PM$_{2.5}$ mass concentration is greater than 50 $\mu$g/m$^3$, the fractions of the hydrophilic mode for 150, 250, and 350 nm particles increased towards 1 as PM$_{2.5}$ mass concentration increased. This indicates that aged particles dominated during severe pollution periods in the atmosphere of Beijing. Particle hygroscopic growth can be well predicted using high time-resolution size-resolved chemical composition derived from AMS measurement using the ZSR mixing rule. The organic hygroscopicity parameter ($\kappa_{\text{org}}$) showed a positive correlation with oxygen to carbon ratio. During the new particle formation event associating with strongly active photochemistry, the hygroscopic growth factor or $\kappa$ of newly formed particles is greater than for particle with the same sizes during non-NPF periods. A quick transformation from external mixture to internal mixture for pre-existing particles (for example 250 nm particle) was observed. Such
transformations may modify the state of mixture of pre-exiting particles and thus modify properties such as the light absorption coefficient and cloud condensation nuclei activation.

1 Introduction

Hygroscopic growth of atmospheric particles is one of the important parameters controlling their direct and indirect climate effects (McFiggans et al., 2006; Haywood and Boucher, 2000). Due to water uptake, hydrophilic particles grow significantly in size at high relative humidity (RH), which influences the particle light scattering and extinction coefficients, thereby impairing visibility (Sloane and Wolff, 1985). In addition, the water content of atmospheric aerosol particles can serve as a site for heterogeneous nucleation and reactions that perturb local photochemistry (Kreidenweis and Asa-Awuku, 2014). Therefore, a better understanding of hygroscopic behavior of atmospheric aerosol particle is required to further elucidate the physicochemical processes in the atmosphere.

The association of the particle chemical composition with their size-dependent hygroscopic behavior is rather complex. In order to overcome such complexities, Petters and Kreidenweis (2007) proposed a single hygroscopicity parameter (κ), namely κ-Köhler theory. On the basis of the κ-Köhler theory and Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Stokes and Robinson, 1966; Zdanovskii, 1948), particle hygroscopic growth of a homogeneous chemical mixture can be predicted, knowing hygroscopic growth factors of pure chemical species. Aerosol mass spectrometers (AMS), which have been increasingly deployed in atmospheric aerosol studies, can provide a high time resolution of the size-resolved chemical composition of non-refractory particle material (DeCarlo et al., 2006). Therefore, coupled measurements of an AMS and a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) are able to capture highly variable changes in chemical particle composition and hygroscopicity in real time. Some studies highlighted the advantage of using size-selected AMS information over size-averaged
information from off-line chemical characterization (Medina et al., 2007; Gunthe et al., 2009; Cerully et al., 2011; Wu et al., 2013).

Another key product of AMS measurements is the oxidation level and chemical information of organic aerosols. Compared to inorganic species, which exhibit a well-characterized hygroscopic behavior, knowledge on the influence of the water uptake of the organic aerosols remains limited (Kanakidou et al., 2005; Hallquist et al., 2009). The hygroscopicity of organic material varies with its oxidation state (Jimenez et al., 2009), which may be highly variable in the real atmosphere, depending on the history of an air mass. Such variation may present a significant challenge when predicting hygroscopicity assuming a constant hygroscopic growth factor of the organic aerosol fraction at a given relative humidity, as has usually been done in closure studies.

Currently, some studies have been performed to investigate the relationship between particle hygroscopicity and chemical composition in both field measurements and laboratory experiments (Massoli et al., 2010; Wong et al., 2011; Lambe et al., 2011; Rickards et al., 2013; Moore et al., 2012b; Suda et al., 2014; Paramonov et al., 2013; Levin et al., 2012; Moore et al., 2012a). These works specially focused on parametrizing the empirical correlations between the atomic Oxygen : Carbon (O:C) ratio and organic hygroscopicity parameter ($\kappa$) derived from either hygroscopic growth factor (e.g. Wu et al., 2013; Rickards et al., 2013) or Cloud Condensation Nuclei (CCN) activity (e.g. Mei et al., 2013; Wong et al., 2011; Lambe et al., 2011; Chang et al., 2010). Typically, a linear parametrization of the correlation between $\kappa$ and O:C was presented. Rickards et al. (2013) recently summarized the literature data and pointed out the systematic variability in parametrizations between organic $\kappa$ and the O:C ratio determined from the different studies remains large. A recent work done by Suda et al. (2014) tested the influence of the number and location of molecular functional groups on the hygroscopicity of organic aerosols and may improve our understanding the mechanisms of organics hygroscopicity.

Over the past several decades, particle hygroscopicity measurements have been carried out world-wide, using the H-TDMA technique. Atmospheric environments, in
which those measurements were performed included marine, Antarctic, boreal forest, rural, and urban areas. Swietlicki et al. (2008) and Kreidenweis and Asa-Awu (2014) compiled the existing observations on particle hygroscopic growth in the literature. Throughout these compilations, measurements of particle hygroscopicity have been rarely performed in China, which is experiencing frequently severe haze pollution episodes. These few particle hygroscopicity measurements using the H-TDMA technique were deployed in Yangtze River Delta (Shanghai (Ye et al., 2013) and Hangzhou (Zhang et al., 2011)), Pearl River Delta (Xinken (Cheng et al., 2008) and Hong Kong (Lopez-Yglesias et al., 2014; Yeung et al., 2014)) and North China Plain (Beijing (Massling et al., 2009; Meier et al., 2009), Yufa (Achtert et al., 2009), and Wuqing (Liu et al., 2011)). Unfortunately, most of measurements lack a linkage between particle hygroscopicity and chemical composition with a high time resolution.

This study investigated the size-resolved particle hygroscopicity and chemical composition in Beijing, China, during summertime. Our work provided a general overview of particle hygroscopic behavior as well as a comparison of the observed hygroscopic particle growth and simulated one using AMS-based chemical particle composition, emphasizing on the organic mass fraction. Additionally, the evolution of particle hygroscopicity during the new particle formation event was investigated to understand the effects of strong photochemistry-driven atmospheric oxidation processes on particle hygroscopicity and the mixing state.

2 Measurements

2.1 The Sampling site

The sampling site is on the campus of Peking University, located in northwest Beijing. The laboratory was equipped with a suit of aerosol instruments sites on the roof of a building (30 m above the ground). The relative humidity (RH) of the sampled air was kept to below 30% using a silica gel dryer and a Nafion dryer in
series. The particle number size distribution, particle hygroscopicity, and aerosol mass spectrometric measurements were concurrently made. Particle number size distributions from 3 to 800 nm were measured by TSI-SMPS (Long-DMA3081+CPC3775 and Nano-DMA3085+UCPC3776). The multiple charge correction and particle loss correction were carried out. Other core instruments will be briefly described below.

2.2 Particle hygroscopicity measurements

The H-TDMA used in this study has been described in detail in previous publications (Wu et al., 2011; Massling et al., 2003), and complied to the instrumental standards and quality assurance prescribed in Massling et al. (2011). The H-TDMA consists of three main parts: (1) A Differential Mobility Analyzer (DMA1) that selects quasi-monodisperse particles, and a Condensation Particle Counter (CPC1) that measures the particle number concentration leaving the DMA1 at the selected particle size; (2) An aerosol humidifier conditioning the particles selected by DMA1 to a defined relative humidity (RH); (3) The second DMA (DMA2) coupled with another condensation particle counter (CPC2) to measure the number size distributions of the humidified particles. The second DMA and the aerosol humidification were placed in a temperature-controlled box. Hygroscopicity scans with 100 nm ammonium sulfate particles were performed every 3 hours to analyze the stability of the relative humidity of 90% in the second DMA. Hygroscopicity scan with a deviation of more than 3% in relative humidity to the set-point of 90% was not considered for further analysis.

The hygroscopic growth factor (HGF) is defined as the ratio of the particle mobility diameter, \(D_p(RH)\), at a given RH to the dry diameter, \(D_{pdry}\):

\[
\text{HGF}(RH) = \frac{D_p(RH)}{D_{pdry}}
\]  \[1\]

The TDMA\textsuperscript{inv} method developed by Gysel et al. (2009) was used to invert the H-TDMA data. Dry scans (under RH<10%) were used to calibrate a possible offset between DMA1 and DMA2 and define the width of the H-TDMA's transfer function.
Based on the ZSR method, the \( HGF \) of a mixture can be estimated from the \( HGF_i \) of the pure components and their respective volume fractions, \( \varepsilon_i \) (Malm and Kreidenweis, 1997):

\[
HGF_{\text{mixed}} = \left( \sum_i \varepsilon_i HGF_i^3 \right)^{1/3} \tag{2}
\]

Here, we assumed that two components including soluble and insoluble fractions consist of aerosols (also refer to Ehn et al., 2007; Swietlicki et al., 1999). The soluble fraction was assumed to be ammonium sulfate. Then, the water-soluble volume fraction \( \varepsilon_{\text{soluble}} \) can be calculated by:

\[
\varepsilon_{\text{soluble}} = \frac{HGF_{\text{measured}}^{-1} - HGF_{\text{(NH}_4\text{)}_2\text{SO}_4}^{-1}}{\varepsilon_{\text{soluble}}} \tag{3}
\]

where \( HGF_{\text{measured}} \) is the HGF of the particles measured by H-TDMA, and \( HGF_{\text{(NH}_4\text{)}_2\text{SO}_4} \) is the HGF of pure \( \text{(NH}_4\text{)}_2\text{SO}_4 \) particles with the same size. When calculating \( HGF_{\text{(NH}_4\text{)}_2\text{SO}_4} \) in different diameters, the parameterizations for \( \text{(NH}_4\text{)}_2\text{SO}_4 \) water activity developed by Potukuchi and Wexler (1995) and the density reported by Tang and Munkelwitz (1994) were used. The Kelvin term was considered in the calculation. In this study, the hygroscopic growth factors of 50, 100, 150, 250, and 350 nm particles were measured at RH=90%.

2.3 Particle chemical composition

The Aerodyne HR-ToF-AMS (here simply referred to as AMS) (DeCarlo et al., 2006) was operated with a time resolution of 5 minutes. Due to the 600°C surface temperature of the vaporizer, the AMS can only analyze the non-refractory chemical composition of the particles. Elemental carbon, crustal material, and sea-salt cannot be detected. Therefore, based on the transmission efficiency of the aerodynamic lenses and the detected compounds, the AMS can provide the size-resolved chemical composition of the submicrometer non-refractory aerosol particle fraction (NR-PM\(_1\)) (Canagaratna et al., 2007). Applying the method developed by Canagaratna et al. (2015) the high resolution organic particle mass spectra were used to determine the elemental composition and the Oxygen to Carbon atomic ratio (O:C). The vacuum
aerodynamic diameter for AMS measurements was converted to the particle mobility
diameter by division of AMS vacuum aerodynamic diameter by the estimated particle
density (1500 kg/m³). Here, the particle density is estimated by dividing the
AMS-measured PM₁ and black carbon mass concentrations by the SMPS-derived
particle volume concentration. Hereafter, the mobility diameter (assuming spherical
particles) was used for AMS data below.

AMS-positive matrix factor (PMF) analysis was performed to identify different
organic aerosols (OA) factors on the basis of the high resolution mass spectra of
organics (Ulbrich et al., 2009). Four OA components were resolved by PMF,
including low-volatility oxygenated organic aerosol (LV-OOA), semi-volatile
oxygenated OA (SV-OOA), hydrocarbon-like OA (HOA) and cooking OA (COA).
LV-OOA and SV-OOA typically represented aged SOA and freshly formed SOA,
respectively (Ulbrich et al., 2009). HOA and COA were both anthropogenic primary
organic aerosol (POA) components (Lanz et al., 2007).

Black carbon (BC) mass concentration in μg/m³ is derived from Photoacoustic
Extinctiometer (PAX) measurements (DMT Company) (Arnott et al., 1999) equipped
with PM₁ cut-off inlet. In this study, PAX measurements were performed at
wavelength 532 nm.

2.4 Meteorological parameters

Additionally, a weather station (Met One Instruments Inc.) provided the
meteorological parameters. The wind speed, wind direction, ambient temperature, and
relative humidity (RH) were detected.

Air mass backward trajectories arriving at the sampling site were calculated
using the NOAA “HYSPLIT-4” (Hybrid Single-Particle Lagrangian Integrated
Trajectory) model (Draxler and Hess, 1998). The 48 h trajectories terminated on a
height of 200 m above the ground at 00:00, 06:00, 12:00 and 18:00 local time
(UTC+08). In total, 100 air mass backward trajectories were grouped by assigning to
five clusters using a k-means clustering algorithm. The number of clusters was
identified according to the changes of total spatial variance (TSV) (cf. HYSPLIT4
user’s guide). Five was chosen as the final number of clusters considering optimum
separation of trajectories (larger number of clusters) and simplicity of display (lower
number of cluster).

3 Theory

3.1 Hygroscopicity parameter

The hygroscopicity parameter, κ, can be calculated from the hygroscopic growth
factor (HGF) measured by H-TDMA (Petters and Kreidenweis, 2007):

\[ \kappa_{HTDMA} = (HGF^3 - 1) \left( \frac{\exp\left( \frac{A}{D_{P,dry}HGF} \right)}{RH} - 1 \right) \]  

Where \( A = \frac{4\sigma_{s/a}M_w}{RT_{\rho_w}} \)  

Where \( D_{P,dry} \) and \( HGF \) are the initial dry particle diameter and the hygroscopic growth
factor at 90% RH measured by H-TDMA, respectively. \( \sigma_{s/a} \) is the droplet surface
tension (assumed to be that of pure water, \( \sigma_{s/a} = 0.0728 \text{ N m}^{-2} \)), \( M_w \) the molecular
weight of water, \( \rho_w \) the density of liquid water, \( R \) the universal gas constant, and \( T \) the
absolute temperature.

For a given internal mixture, κ can also be predicted by a simple mixing rule on
the basis of chemical volume fractions \( \varepsilon_i \) (Petters and Kreidenweis, 2007):

\[ \kappa_{chem} = \sum_i \varepsilon_i \kappa_i \]  

Here, \( \kappa_i \) and \( \varepsilon_i \) are the hygroscopicity parameters and volume fraction for the
individual (dry) component in the mixture with \( i \) the number of components in the
mixture. We derived \( \varepsilon_i \) from the particle chemical composition measured by AMS and
PAX. The detailed description of how to calculate volume fraction is given in section
3.2. In the following discussions, \( \kappa_{HTDMA} \) and \( \kappa_{chem} \) denote respectively the values
derived from H-TDMA and predicted using the ZSR mixing rule.
3.2 Hygroscopicity-chemical composition closure

The AMS provided the particle mass size distribution of sulfate ($SO_4^{2-}$), nitrate ($NO_3^{-}$), and ammonium ($NH_4^+$) ions as well as that of organic compounds. We used a simplified ion pairing scheme as presented in Gysel et al. (2007) to convert the ion mass concentrations to the mass concentrations of their corresponding inorganic salts as listed in Table 1. Unlike inorganic salts, the hygroscopicity of organic aerosols is not well-recognized. In the literature, there were different approaches in representing $\kappa_{\text{org}}$ in the closure studies. Typically, $\kappa_{\text{org}}$ is assumed as a constant value. Chang et al., (2010) represented $\kappa_{\text{org}}$ by using the factors from the PMF analysis to group organics measured by AMS into two components: a non-hygroscopic, unoxygenated component consisting of the hydrocarbon-like organic aerosol (HOA) factor and a hygroscopic component, consisting of the oxygenated factors LV-OOA, SV-OOA, and biomass burning organic aerosol (BBOA). In our study, organic materials derived from AMS measurements were grouped into two components including secondary organic aerosols (SOA) and primary organic aerosols (POA) based on AMS-PMF analysis. SOA, including LV-OOA and SV-OOA factors, is a more oxygenated organic aerosol, thereby more hygroscopic and has a $\kappa_{\text{SOA}}$ of 0.1, which was calculated from the hygroscopic growth factor of organics at RH=90% as given in Gysel et al. (2007) using Eq. (4) in section 3.1. By taking $\kappa_{\text{SOA}}$=0.1, the best fit between $\kappa_{\text{HTDMA}}$ and $\kappa_{\text{chem}}$ was obtained in this study. One should note that kappa of SOA may varied with its oxidation state (Jimenez et al., 2009). The usage of a constant kappa value may introduce uncertainty in the closure of particle hygroscopicity and chemical composition. POA is the unoxygenated component consisting of the HOA and COA factors and is treated as hydrophobic material with $\kappa_{\text{POA}}$=0. Then, $\kappa_{\text{org}}$ can be calculated as:

$$\kappa_{\text{org}} = f_{\text{POA}} \ast k_{\text{POA}} + f_{\text{SOA}} \ast k_{\text{SOA}} \quad [7]$$

Here, $\kappa_{\text{org}}$ is overall $\kappa$ for organic aerosols. $f_{\text{POA}}$ and $f_{\text{SOA}}$ are volume fraction of POA and SOA in total organic aerosols measured by AMS. One should note that Sun et al. (2012b) found that the contributions of POA and SOA to OA showed a
size-dependency. The relative contribution of POA to OA significantly increased with decreasing particle sizes. In this study, the closure studies were performed for particles with the mobility diameters of 150, 250, and 350 nm (larger than 200 nm in vacuum aerodynamic diameter). Using the relative contribution of POA to OA in PM$_1$ tended to overestimate percentage of POA for the size range focused in this study, thus underestimate the $\kappa$. In our case, the POA/OA and SOA/OA were respectively 0.39 and 0.61. According to equation [7], the $\kappa_{\text{org}}$ can be calculated as 0.06 assuming $\kappa_{\text{SOA}}=0.1$. On the basis of Sun et al.’s study, the POA/OAs for 150, 250, and 350 nm particles were 0.30, 0.23, and 0.19, respectively. Using these ratios and equation [7], the calculated $\kappa_{\text{org}}$s were 0.07, 0.08, and 0.08, respectively, which were slightly higher than the one ($\kappa_{\text{org}}=0.06$) in our case. This minor difference can be negligible.

The volume fraction of each species was calculated from the particle mass concentration divided by its density as given in Table 1. The densities for inorganic salts were well defined. By summarizing the articles published (Park et al., 2004; McMurry et al., 2002; Kondo et al., 2011; Kiselev et al., 2010), 1700 kg/m$^3$ was selected as BC density. The hygroscopicity parameter $\kappa$ of the hydrophobic black carbon was considered to be zero. The density of organic particle mass fraction including both SOA and POA was taken to be 1400 kg/m$^3$ (Gysel et al., 2007; Alfarra et al., 2006; Dinar et al., 2006). The $\kappa_{\text{HTDMA}}$ values for the individual compounds listed in the Table 1 were calculated from the hygroscopic growth factor at 90% RH as given in Gysel et al. (2007) using equation [4] in the section 3.1.

4 Results and discussion

4.1 Meteorological condition during the sampling period

Fig. 1 showed the mean air mass backward trajectories for five clusters arriving at the sampling site from May 31 to June 24, 2014. The mean backward trajectories in five cluster showed the significant differences in direction and length. The air masses from the east (45%) and the south (26%) were the dominate trajectories. The
short-length air mass backward trajectories in cluster 1 and 2 indicated that air parcels moved slowly and spent much more time over the industrialized regions south and east of Beijing. As a result, the southerly and easterly air masses may be heavily polluted once they arrived at Beijing (Wehner et al., 2008). Cluster 3 spent much more time over the sea and may be associated with humid air masses. Northerly (8%) and north-westerly (10%) air masses, as represented by clusters 4–5, typically lead to the advection of dry and continental air into the Beijing area.

Fig. 2 displays the time series of wind speed, wind direction, ambient temperature, and RH during the sampling period. There was a clear diurnal cycle for all meteorological parameters. During nighttime, the wind speed was usually very low (around 1 m/s) and started to increase around noon on each day. The nighttime static wind may lead to very poor dilution with clean air and dispersion of pollutants and result in the local emissions were trapped in the urban atmosphere. The ambient temperature usually was above 30 °C during daytime and around 20 °C during nighttime. The average temperature and RH were respectively 24±7 °C and 45±20%. It rained several times during the measuring period, as indicated in the Fig. 2 (a). The heaviest wet deposition occurred on 17, June. The wet deposition obviously removed the atmospheric particles, as can be seen from the particle number size distribution shown in Fig. 3 (a).

In summer, the new particle formation and traffic emissions are the major sources of ultrafine particles in the atmosphere of Beijing (Wu et al., 2008; Wu et al., 2007). In addition, air masses across the industrialized regions in the south and east typically bring the high concentrations of accumulation mode particles to urban areas of Beijing (Wehner et al., 2008).

4.2 Overview of particle hygroscopic growth and the mixing state

Fig. 3 provides an overview of the particle number size distribution (a), hygroscopicity parameters (κ) (b), and chemical composition of PM$_1$ (c) during the entire field campaign. The trajectory clusters were marked as black circles in the Fig.
As shown in the Fig. 3 (a), new particle formation (NPF) events were observed frequently. During the sampling period, the inorganic species and SOA were dominated in NR-PM$_1$ when air masses came from south and east of Beijing (trajectory cluster 1 and 2 as indicated by black circles in Fig.3 (a)). SOA was usually dominated in the organic compounds during the sampling period. Differently, the POA was a major fraction on June 7, 8, and 9, on which the BC mass fraction increased too. During this time period, the northerly air masses (trajectory cluster 5 marked in Fig. 3 (a)) arriving at the measurement site may be influenced by the wheat straw burning, which usually takes place from late May to early June over North China Plain. Several previous studies showed that wheat straw burning significantly contributes to degradation of air quality in Beijing during the harvest season in the summer (Li et al., 2008; Zheng et al., 2005).

Fig. 3 (b) displays the time series of hygroscopicity parameters for 50 nm ($\kappa_{50\text{nm}}$) and 250 nm ($\kappa_{250\text{nm}}$) particles. Both $\kappa_{50\text{nm}}$ and $\kappa_{250\text{nm}}$ had an obvious temporal variability. Their variations were similar to that of inorganic mass fraction in PM$_1$ displayed in Fig. 3 (c). An in-depth analysis of the relationship between particle hygroscopicity and chemical composition will be given in section 4.3. Fig. 4 gives an overview of growth factor probability density distributions (GF-PDF) for 50 and 250 nm particles during the entire field campaign. The GF-PDFs of both 50 and 250 nm showed two distinct modes, which are identified as hydrophobic mode (GF<1.2) and hydrophilic mode (GF>1.2). This implied that the particles were usually externally mixed. The hydrophilic mode of 250 nm particles is more prominent most of the time. Differently, the hydrophobic mode was dominated in 50 nm particles. As marked in the Fig. 4 (a) by the square with dashed line, the hydrophobic mode disappeared occasionally, indicating that the vast majority of particles in this size range can be fully hygroscopic. This phenomenon took place during the NPF events. A case study of particle hygroscopic behavior during the NPF event will be given in section 4.4.

Fig. 5 (left) shows the size-dependent particle hygroscopicity parameters and inorganic mass fraction of NR-PM$_1$ derived from averaging over the entire measuring period. The particle hygroscopicity increased with increasing particle size, displaying
the same size-dependency with the mass fraction of inorganic composition in
NR-PM$_1$. This is because inorganics including ammonium sulfate and ammonium
nitrate are major water-soluble chemical compounds in the atmospheric particles.
Compared to inorganic components, the hygroscopicity parameter of organic aerosols
are typically lower than 0.1 (Varutbangkul et al., 2006; Virkkula et al., 1999). The
similar size-dependency of particle hygroscopicity was observed in various
environments. For examples, Levin et al. (2012; 2014) and Paramonov et al. (2013)
reported that particle hygroscopicity increased with particle size at a forested site in
Colorado and a boreal environment of southern Finland at the SMEAR station,
respectively. Jurányi et al. (2013) observed that particle hygroscopic growth increased
with increasing dry diameter in the urban areas of Paris. Swietlicki et al. (2008)
compiled worldwide H-TDMA data and found that the particle hygroscopicity showed
a pronounced size-dependency, with hygroscopicity increasing with particle diameter.

Fig. 5 (right) shows the size-dependency of the fraction of the hydrophilic mode.
It can be seen that the hydrophilic mode was more prominent, no matter what particle
size was considered. With increasing particle size, the dominance of hydrophilic mode
became more pronounced. Above 150 nm, the number fraction of hydrophilic mode
was around 0.8, and its size-dependency was insignificant. Below 150 nm, the number
fraction of hydrophilic mode increases significantly with increasing particle size. The
median number fraction of hydrophilic mode for 50 nm particles was 0.6, which was
smaller than those of larger particles. Fors et al. (2011) also reported that smaller
particles had a higher fraction of less hygroscopic particles in southern Sweden.
Larger particles (here, above 150 nm) constituting a larger fraction of the hydrophilic
mode can be explained as such: In the urban area, traffic emissions are major sources
for particles below 100 nm. Typically, freshly emitted particles, such as soot, are
initially hydrophobic and externally mixed. In contrast, larger particles have
undergone atmospheric aging processes during transport (such as coagulation,
condensation, chemical reaction) (Pöschl, 2005) for a longer time. These aging
processes enhance the particle’s water solubility (Pöschl, 2005; Jimenez et al., 2009)
and result in more internally mixed particles.
Over the entire study, the mean $\kappa$s of 50, 100, 150, 250, and 350 nm particles were $0.16\pm0.07$, $0.19\pm0.06$, $0.22\pm0.06$, $0.26\pm0.07$, and $0.28\pm0.10$, respectively. These values were similar to the hygroscopicity parameter $\kappa = 0.12-0.27$ (measured at RH=90%) for 35–265 nm determined in the urban atmosphere of Paris (Jurányi et al., 2013). Yeung et al. (2014) observed that hygroscopicity $\kappa$s of particles with sizes of 75, 100, 150, and 200 nm were respectively 0.28, 0.29, 0.26, and 0.27 when Hong Kong experienced a continental airstream. In their study, the particle hygroscopicity showed no obvious size-dependency and was higher than our observation in Beijing.

In contrast, $\kappa$s measured were relatively low at a forested site in Colorado ($\kappa = 0.16\pm0.08$ detected by CCNc), a boreal forest in Finland ($\kappa = 0.18$ at RH=90%) (Sihto et al., 2011), and a tropical forest site in the Amazon ($\kappa = 0.16\pm0.06$ detected by CCNc) (Gunthe et al., 2009). At these forested locations, organic species were predominance in particles. Differently, in the atmosphere of Beijing, the inorganic fraction was relatively dominated, as shown in the Fig.3 (c).

The haze issue caused by high aerosol loadings over the northern plain of China is a major concern, for both air quality and climate effects. Here, the PM$_{2.5}$ mass concentration which measured by TEOM® Monitor (Series 1400ab), a key factor characterizing air pollution, vs. the fraction of the hydrophilic mode is plotted (Fig. 6) to analyze the relationship between the particle mixing state and air pollution. There was no obvious dependency between the PM$_{2.5}$ mass concentration and the number fraction of hydrophilic mode for 50 nm particles, which can be expected due to the low mass fraction of ultrafine particles. This was however also true for 150, 250, and 350 nm particles, if PM$_{2.5}$ mass concentration is lower than 50 $\mu$g/m$^3$. The reason for this is that the particle mass concentration is dominated by local sources and less by secondary aerosol particles formed during long-range transport. Conversely, when PM$_{2.5}$ mass concentration was larger than 50 $\mu$g/m$^3$, the fraction of the hydrophilic mode was larger than 0.7. With the increasing PM$_{2.5}$ mass concentration, the fraction rose towards to 1, indicating that the aged aerosols were dominant. This means that secondary aerosol particles were dominant during severe particulate pollution episodes, occurring frequently in Beijing. Our results were consistent to recent
scientific findings (Guo et al., 2014; Huang et al., 2014), which pointed out that the 
haze pollution events were mainly attributable to secondary aerosol formation.

4.3 Closure between particle hygroscopicity and chemical components

The AMS-derived particle mass concentrations for different chemical compounds 
were used to perform a closure study. The particle mass concentrations for individual 
species were integrated over the size interval of $D_{\text{Pdry}} \pm 50$ nm. Here, $D_{\text{Pdry}}$ is the dry 
particle diameter selected by H-TDMA. Considering the limited signal statistics in 
this narrow size range, AMS data were used to carry out the closure only if the sum of 
sulfate, nitrate, ammonium, and organics mass concentrations derived from 
integrating size range of $D_{\text{Pdry}} \pm 50$ nm was greater than 1 $\mu$g/m$^3$.

The BC particle mass concentration within the size range of $D_{\text{Pdry}} \pm 50$ nm was 
estimated as follows: First, the ratio ($R_{\text{BC/PM1}}$) of BC particle mass concentration 
(derived from PAX) to bulk particle mass concentration (derived from AMS 
measurement) was calculated, assuming this ratio was independent on the particle size. 
Afterwards, the BC particle mass concentration in a certain size range, e.g., 150±50 
nm was estimated by multiplying the mass concentration derived from integrating 
particle size range of 150±50 nm (AMS data) and $R_{\text{BC/PM1}}$. One should note that this 
assumption may give an uncertainty in the closure, because the BC mass 
concentration has a dependency with particle size (Huang et al., 2006). Sun et al. 
(2012a) reported that the average mass size distribution of BC had one mode peaking 
at a volume-equivalent diameter of 207 nm. The sizes of 150, 250, 350 nm covered 
the peak of BC mass size distribution. As a result, the BC mass concentration for 
particles in diameter of 150, 250, and 350 nm should be higher than that estimated 
with the assumption of uniformly distributed BC across the whole particle size range.

The SOA and POA mass fractions within the size range of $D_{\text{Pdry}} \pm 50$ nm were 
estimated using a similar method as the calculation of BC mass concentration given 
above. The POA ($MF_{\text{POA}}$) and SOA ($MF_{\text{SOA}}$) mass fractions in total organic aerosols 
in NR-PM1 are calculated on a basis of the AMS-PMF analysis results. Assuming
$MF_{POA}$ and $MF_{SOA}$ were independent of the particle diameter, the POA or SOA mass concentration in the size range $D_{\text{Pdry}} \pm 50$ nm can be calculated by multiplying the organic mass concentration derived from integrating particle size range of 150±50 nm (AMS data) and $MF_{POA}$ or $MF_{SOA}$. Fig. 7 shows the scattering plots of $\kappa_{\text{chem}}$ calculated from the size-resolved chemical composition against $\kappa_{\text{HTDMA}}$. The fitted slopes for 150, 250, and 350 nm particles were 1.02, 0.99, and 0.97, respectively, which is close to unit. The root mean square errors (RMSE) of these linear fits were 0.04. This indicates that the measured $\kappa$ can be well predicted on a basis of AMS data and the ZSR mixing rule. While, one should note that the assumption of BC mass size distribution and $\kappa_{\text{org}}$ value in the closure as well as the measurement uncertainties for both H-TDMA and AMS could introduce the biases in the closure. This may lead to a scatter of data point around the fitting line.

Assuming the inorganic fraction was fully explained by the ZSR mixing rule, $\kappa_{\text{org}}$ can be calculated by subtracting $\kappa$ of inorganic fraction and BC from $\kappa_{\text{HTDMA}}$. Here, $\kappa_{\text{org}}$ for 150 nm particles was calculated because it provided a better closure result and higher organic fraction in contrast to other particle sizes. Duplissy et al. (2011) pointed out that the uncertainty in the estimation of $\kappa_{\text{org}}$ decreases with increasing organic fraction, thereby, only data featuring organic fractions larger than 50% were used in this calculation. In addition, the evaporation of NH$_4$NO$_3$ could occur in the DMAs and the humidification section. This leads to a positive prediction bias because the volatile NH$_4$NO$_3$, which is fully detected by AMS, can evaporate in the H-TDMA system (Gysel et al., 2007). Here, only data with NH$_4$NO$_3$ volume fraction below 20% were considered in order to reduce the evaporation artifact of NH$_4$NO$_3$. Restricting data to times when ammonium nitrate is below 20% and organics were greater than 50% may lead to a bias in data points between daytime and nighttime. The statistics showed that nighttime data points (204 data points) were more than those during daytime (160 data points). This is because that the organic mass fraction during nighttime was higher than that during daytime. This bias could make the fit between $\kappa_{\text{org}}$ and O:C ratio more representative for nighttime situation than daytime.
Fig. 8 shows $\kappa_{\text{org}}$ as a function of O:C ratio. From the degree of scatter point of view, $\kappa_{\text{org}}$ was not correlated to the O:C ratio. Several previous studies reported the similar plots of $\kappa_{\text{org}}$ values as a function of O:C ratios (Chang et al., 2010; Bhattu and Tripathi, 2015; Rickards et al., 2013). In order to derive an empirical relationship between $\kappa_{\text{org}}$ and O:C ratios, $\kappa_{\text{org}}$ values were usually binned by O:C in increments of 0.1. As displayed in Fig. 8, a linear fitting function 

$$\kappa_{\text{org}} = (0.08 \pm 0.02) \times \text{O:C} + (0.02 \pm 0.01))$$

was obtained. Some empirical functions reported by other previous studies were also shown in Fig. 8. In these previous studies (Wu et al., 2013; Jimenez et al., 2009; Rickards et al., 2013; Duplissy et al., 2011), the $\kappa_{\text{org}}$ were derived from the measurements performed in the sub-saturation regime. In Massoli et al.’s study (2010) (not shown in the Fig. 8 due to the linear fitting using HGF, not $\kappa_{\text{org}}$), they reported a linear relationship (HGF$_{90\%}$ = (0.58 ± 0.15)×O:C + (0.85 ± 0.08)) between HGF$_{90\%}$ and O:C for the laboratory-generated SOA particles. Both results displayed in Fig. 8 and Massoli’s study showed a positive correlation between $\kappa_{\text{org}}$ and O:C. Such positive correlation was also reported by those studies based on CCNc measurements, for examples, Chang et al. (2010) and Mei et al. (2013). We note that the slopes of the linear fitting varied with different studies, indicating there was no a simple parametrization to describe the relationship between organic hygroscopicity and its oxidation state though the various atmospheric environments. Recently, Richards et al. (2013) had undertaken an extensive review of $\kappa$ values published in the literature and showed that $\kappa_{\text{org}}$ vs. O:C plot has a large degree of scatter. This indicates that other factors, such as phase state (Pajunoja et al., 2015) and molecular structures (Suda et al., 2014) of organic aerosols (OA) other than oxidation state may also play a role in the determination of the OA hygroscopicity.

### 4.4 Case study: particle hygroscopicity during a NPF event

As shown in Fig. 3 (a), the NPF events frequently took place during the sampling period. In order to understand the effects of NPF on particle hygroscopic behavior, this section will exemplify the evolution of particle hygroscopicity during a NPF
event. As an example, Fig. 9 displays the time series of particle number size
distribution, GF-PDFs and water soluble fraction of 50 and 250 nm particles, and
chemical composition of PM$_1$ during a NPF event occurred on 5$^{th}$ June, 2014. Here,
the particles with 50 nm in diameter represented the newly formed particles, and
particles with 250 nm in diameter represented the pre-existing particles.

The NPF event started at around 10:30 am and ended at 5:30 am the next day.
After the starting of new particle formation, the number fraction of the hydrophilic
mode for 50 nm particles increased from 0.5 to around 1, showing the conversion of
externally to more internally mixed particles, as marked by the black dashed lines in
Fig. 9 (b). Around 8:30 pm, the fraction of the hydrophilic mode particles dropped to
0.6, and the hydrophobic mode appeared again. This is attributed to the intensive
traffic emissions at the time of rush hour, which can clearly be seen from the particle
number size distribution. During nighttime, the growth factor of hydrophilic mode
particles decreased. This can be explained by sulfuric acid condensation playing a
minor role in particle growth during nighttime. Simultaneously, ambient temperature
decreased from 27 to 20 °C. Lower temperature facilitated the condensation of
semi-volatile organic vapors onto the newly formed particles. The chemical
composition of PM1 also (Fig. 9 (d)) showed that the inorganic species and SOA were
dominated before 8:30 pm, while mass fraction of organic compounds, especially
POA increased significantly afterwards.

Clearly, an obvious enhancement in the water soluble fraction of 50 nm particles
took place after the NPF event started. Similar phenomenon was also observed by
Shantz et al. (2012), which showed that the 36 nm particles became increasingly CCN
active within 1-4 h after the nucleation during the NPF events. They hypothesized that
the condensation of sulphate on these small particles enhanced their CCN activity.
The water soluble fraction accounted for 42% in 50 nm newly formed particles. The
water soluble fraction was most likely ammonium sulfate formed from neutralization
reaction between ammonia and sulfuric acid. In contrast, the newly formed particles
consisted a minor fraction of water soluble fraction (16%) in Hyytiälä, Finland (Ehn
et al., 2007). Other observations in the clean atmospheric environments (relative to
Beijing), such as a forested site in Colorado (Levin et al., 2012), Mace Head, Ireland (Väkevä et al., 2002), Melpitz, Germany (Wu et al., 2015) also showed that low water soluble compounds, most likely secondary organic species mainly contributed to new particle growth. Differently, in urban Atlanta (Sakurai et al., 2005), the water soluble fraction was dominated in the newly formed particles, which was similar to our observation in this study.

As shown in Figure 9 (c), the fraction of the hydrophilic mode of 250 nm particles increased significantly and approached 1 after the NPF event started. This can be explained as such: during the particle formation, a large amount of condensable vapors, such as sulfuric acid and secondary organic species produced because of the strongly active photochemistry. These condensable vapors can condense onto the pre-existing particle and result in the transformation of external mixture to internal mixture. Such transformation may alter the atmospheric behaviors of pre-existing particles, such as optical property and cloud condensation nuclei activation during the new particle formation events.

5 Conclusions

Particle number size distribution, particle hygroscopicity, and size-resolved chemical composition were measured concurrently during summertime 2014 in Beijing, China. The particle hygroscopicity showed a pronounced size-dependency. It increased with increasing particle size. During the measurement period, the mean $κ_{250}$ of 50, 100, 150, 200, and 250 nm particles are 0.16±0.07, 0.19±0.06, 0.22±0.06, 0.26±0.07, and 0.28±0.10, respectively. The size-dependency behavior of particle hygroscopicity was similar to that of inorganic compounds in PM$_1$. The hydrophilic mode (HGF>1.2) was more prominent, no matter what particle size was considered. With increasing particle size, the dominance of hydrophilic mode became more pronounced. When PM$_{2.5}$ mass concentration was below 50μg/m$^3$, no dependency between PM$_{2.5}$ mass concentration and the number fraction of hydrophilic mode was found. Above 50 μg/m$^3$, the number fraction of hydrophilic mode for 150, 250, 350
nm particles increased and rose towards to 1 with the increasing PM$_{2.5}$ mass concentration. This means that aged particles was dominated the particle mass concentration, especially during severe particulate pollution events in Beijing. Based on the size-resolved AMS data, the particle hygroscopic growth can be well predicted using the ZSR method. The organic hygroscopicity parameter showed a positive correlation with O:C ratio.

Frequent new particle formation events took place during the measuring period. The hygroscopic growth factor or $\kappa$ of newly formed particles was greater than the hygroscopic growth factor of particles with the same sizes during non-NPF periods. During the new particle formation, fast transformations of external mixture to internal mixture for existing particles (for example 250 nm particle) have been observed. This was a strong indication that secondary aerosol material such as organics and sulfates were produced due to the strongly active photochemistry during NPF events, and subsequently condensed onto the particles. Such transformation may modify the atmospheric behaviors of pre-existing particles, such as optical property and cloud condensation nuclei activation.

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Table and figures

Table 1: Gravimetric densities ($\rho$) and hygroscopicity parameters ($\kappa$) used in this study.

<table>
<thead>
<tr>
<th>Species</th>
<th>NH$_4$NO$_3$</th>
<th>NH$_4$HSO$_4$</th>
<th>(NH$_4$)$_2$SO$_4$</th>
<th>SOA</th>
<th>POA</th>
<th>BC</th>
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<td>[kg/m$^3$]</td>
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<td>1769</td>
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<td>0.56</td>
<td>0.48</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1: Mean air mass backward trajectories for five clusters arriving at the sampling site.
Figure 2: The time series of wind speed, wind direction, wet deposition (a) and temperature and RH (b) during the sampling period.

Figure 3: Time series of particle number size distribution (a), hygroscopicity parameters ($\kappa$) (b), and chemical composition of PM1 (c) during the measuring period. The black circles in the upper panel (a) indicate the trajectory clusters. The smallest circle means cluster 1, and the biggest one is cluster 5.
Figure 4: The time series of the GF-PDFs for 50 and 250 nm particles.

Figure 5: Size-resolved particle hygroscopicity and inorganic mass fraction (left) in NR-PM1 and Size-dependent number fraction of hydrophilic mode (right).
Figure 6: Number fraction of hydrophilic mode vs PM$_{2.5}$ mass concentration

Figure 7: $\kappa_{\text{HTDMA}}$ vs. $\kappa_{\text{chem}}$ using size-resolved chemical composition data. All the root mean square errors (RMSE) of the linear fits were 0.04.
Figure 8: The relationship between organic hygroscopicity parameter ($\kappa_{\text{org}}$) and oxygen to carbon ratio (O: C).
Figure 9: The variation in particle number size distribution (a), GF-PDF (b, c), water soluble volume fraction (b, c), and chemical composition of PM$_1$ (d) during a NPF event.