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### Key Points:

- Remarkably-enhanced water uptake capacity of organic aerosol (OA) occurs on nucleation days
- A correlation between the hygroscopicity and oxidation state of OA is presented on new particle formation (NPF) days, and the correlation is absent on non-NPF days
- The photooxidation of volatile organic compounds to produce organic acids may dominate on NPF days, and the aqueous oligomerization might occur on non-NPF days

### Supporting Information:

- Supporting Information S1

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## Hygroscopicity of Organic Aerosols Linked to Formation Mechanisms

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**Abstract** Organic aerosols (OAs) account for a large fraction of tropospheric fine particulate matter, but the hygroscopicity of OA is poorly understood. Here, we show remarkably-enhanced water uptake capacity of OA due to formation of highly-oxidized oxygenated OA on new particle formation (NPF) events in Beijing. While non-nucleation processes also produce oxidized OA, their hygroscopicity exhibits little enhancement. As a result, a correlation between the hygroscopicity and oxidation state is absent for OA on non-NPF days. Further analysis reveals that the highly-oxidized oxygenated OA is 2.5 and 5-fold as hygroscopic as the oxidized primary OA and less-oxidized oxygenated OA, respectively. Our results suggest that nucleation-initiated photooxidation of volatile organic compounds to produce water-soluble organic acids may dominate on NPF days, and the aqueous oligomerization to yield less water-soluble products might occur on non-NPF days.

**Plain Language Summary** While organic aerosols (OAs) account for a large proportion of tropospheric fine particles, the water uptake capacity of OA is poorly understood. Here, we show distinct effects of different atmospheric processes on its hygroscopicity in polluted urban atmosphere. Remarkably-enhanced hygroscopicity is identified for OA formed from nucleation. Our results reveal that it is critical to account for the formation mechanisms in evaluating the impacts of OA on air quality and climate.

## 1. Introduction

The water uptake capacity of atmospheric aerosol particles impacts air quality and climate, by affecting the radiative forcing, visibility, and the ability to serve as cloud condensation nuclei (CCN; Hudson & Clarke, 1992; Qi et al., 2018). Organic compounds account for a large fraction (20% ~ 90%) of the total fine aerosol mass in the troposphere, but the water uptake capacity of organic aerosol (OA) is poorly known because of the presence of diverse organic species (Zhang et al., 2015). Some field studies estimated the water uptake capacity of OA using overall hygroscopicity of particles obtained from cloud condensation nuclei counter measurements and chemical composition based on  $\kappa$ -Köhler theory (Petters & Kreidenweis, 2007), showing that the hygroscopicity parameter ( $\kappa$ ) of OA varies considerably from 0.03 to 0.3 because of the presence of different OA constituents (Chang et al., 2010; Deng et al., 2018; Mei et al., 2013). The hygroscopicity of OA varies largely depending on the chemical composition, types and emissions of gas precursors under different environmental conditions (Fan et al., 2020; Zhang et al., 2015). While OA with a higher degree of oxidation (e.g., highly-oxidized oxygenated OA) is typically hygroscopic (Qiu et al., 2020), there is large uncertainty about the hygroscopicity of OA with a lower degree of oxidation (e.g., less-oxidized oxygenated OA). Specifically, Xiao et al. (2011) found that 61% of the less-oxidized oxygenated OA in Guangzhou, China, is water-soluble, while Timonen et al. (2013) estimated that only 14% of less-oxidized oxygenated OA is water-soluble in Helsinki, Finland, using a similar method. The water solubility of primary sources of OA, such as the biomass burning and coal combustion OA, or aqueous-oxygenated OA, were investigated in urban Beijing (Hu et al., 2020; Qiu et al., 2019). However, a more quantitative investigation of the OA from different sources has been lacking.

OAs are produced both from primary emissions (e.g., primary OA or POA) and secondary formation (e.g., secondary OA or SOA). There exist two distinct growth mechanisms for OA formation, that is,

condensation/partitioning of low-to-intermediate products from volatile organic compounds (VOCs) photooxidation (Shrivastava et al., 2017) and aqueous processes including hydration, oligomerization, and acid-catalyzed reactions (Gomez et al., 2015; Xu et al., 2014; Zhang et al., 2015; Zhao et al., 2006). Laboratory experimental studies revealed that photooxidation products of VOCs enhance the particles hygroscopicity in varying degrees depending on the VOC types (e.g., Khalizov et al., 2013; Qiu et al., 2012; Guo et al., 2016), but oligomerization from aqueous reactions decreases the hygroscopicity (Xu et al., 2014). The studies suggest that, while photooxidation and oligomerization both increase the oxidation degree (i.e., an increasing O:C ratio), the two processes may lead to distinct hygroscopicity of OA. In addition, acid-base reactions, such as those between organic acids and amines, also enhance hygroscopicity (Gomez-Hernandez et al., 2016). In the atmosphere, VOCs oxidation from natural and anthropogenic sources leads to distinct product distributions (Zhang et al., 2015), and hygroscopicity of the products with multifunctional groups (i.e., with the carboxylic and hydroxyl functionalities, or glyoxal and methylglyoxal) are expected to be variable. For example, previous field study suggested that a decrease in hygroscopicity of OA due to the formation of biogenic SOA (formed from photooxidation of biogenic VOCs) during new particle formation (NPF) in forest region (Deng et al., 2018); Several other observations in urban atmosphere showed an enhanced aerosols water uptake capacity and CCN activity correlates with NPF events (Lance et al., 2013; Wu et al., 2016), but these studies discussed only the particles overall hygroscopicity, have not focused on the OA hygroscopicity yet. Currently, there is still a lack of understanding of the water uptake capacity for OA from multiple anthropogenic sources in polluted urban atmosphere. The OA dominates ambient fine composition in Beijing, with a mass fraction of 40–51% (Guo et al., 2014; Sun et al., 2015; Wang et al., 2016), and the composition of aerosol is complex due to both primary sources and secondary gas-to-particle conversion (Guo et al., 2014; Li et al., 2020; Ren et al., 2018; Zhang et al., 2015, 2019, 2020). With the aim of obtaining insights of the links between hygroscopicity of OA and its growth mechanisms, in this study, we retrieve and characterize the hygroscopic parameter of OA ( $\kappa_{\text{org}}$ ) by using field campaign observed data of hygroscopic growth factor and chemical composition in urban Beijing. We focus on contrasting the  $\kappa_{\text{org}}$  between NPF and non-NPF events respectively in order to understanding the effect of different formation processes on hygroscopicity of OA.

## 2. Field Measurements and Methods

Field measurements of aerosol physical and chemical properties were conducted at the Institute of Atmospheric Physics (IAP) of Beijing during summer 2017. The measurements at the sampling site represent of typical pollution conditions in urban Beijing (Sun et al., 2015). The sampling period covered May 19 to June 18, 2017. A Scanning Mobility Particle Sizer (SMPS) was used to measure particle number distribution in the size range of 10–600 nm. The SMPS consisted of a long differential mobility analyzer (DMA; model 3081A, TSI Inc.) and a condensation particle counter (CPC; model 3775, TSI Inc.). The Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) system was used to measure the hygroscopic growth factor (Gf) of particle. The HTDMA used in this study has been described previously (Fan et al., 2020; Levy et al., 2013; Wang et al., 2017; Zhang et al., 2017). In this study, the selected dry diameters were 40, 80, 110, 150, and 200 nm, respectively. A Nafion humidifier was used to humidify the quasi monodisperse particles to the specified relative humidity (90% RH). RH calibration was performed periodically with ammonium sulfate to maintaining RH within  $90\% \pm 0.5\%$ . A method developed by Gysel et al. (2009) was used to retrieve the Gf probability density function (PDF).

Non-refractory size-resolved submicron aerosol composition of Non-Refractory particulate matter (NR-PM<sub>1</sub> with diameter < 1  $\mu\text{m}$ ), including organics (Org), sulfate (SO<sub>4</sub>), nitrate (NO<sub>3</sub>), ammonium (NH<sub>4</sub>), and chloride (Cl), was measured with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Xu et al., 2015). Positive matrix factorization (PMF) analysis was performed to separate organic aerosol factors quantitatively by grouping the mass spectrometry and temporal variation for the purpose of source apportionment (Xu et al., 2017; Zhang et al., 2011). The ratio of oxygen to carbon (O:C) was determined by using an elemental analysis approach (Aiken et al., 2007). A five-factor solution was selected, including three SOA factors namely highly-oxidized oxygenated OA, less-oxidized oxygenated OA, and oxidized POA and two POA factors from hydrocarbon-like and cooking OA. The oxidized POA factor is related to higher signals of CO<sub>2</sub><sup>+</sup> and its spectrum is dominated by C<sub>x</sub>H<sub>y</sub><sup>+</sup>, indicating this kind of SOA is from the direct oxidation of POA (Xu et al., 2019), so it is named as oxidized POA. More details about operation of

the HR-AMS and PMF analysis can be found in supporting information (SI: Methods). We combined the bulk mass fraction of black carbon (BC) particles measured by a 7-wavelength aethalometer (AE33, Magee Scientific Corp; Zhao et al., 2017) with size-resolved BC distribution measured by a single particle soot photometer (SP2) in Beijing to obtain the size-resolved volume fraction of BC (Liu et al., 2019).

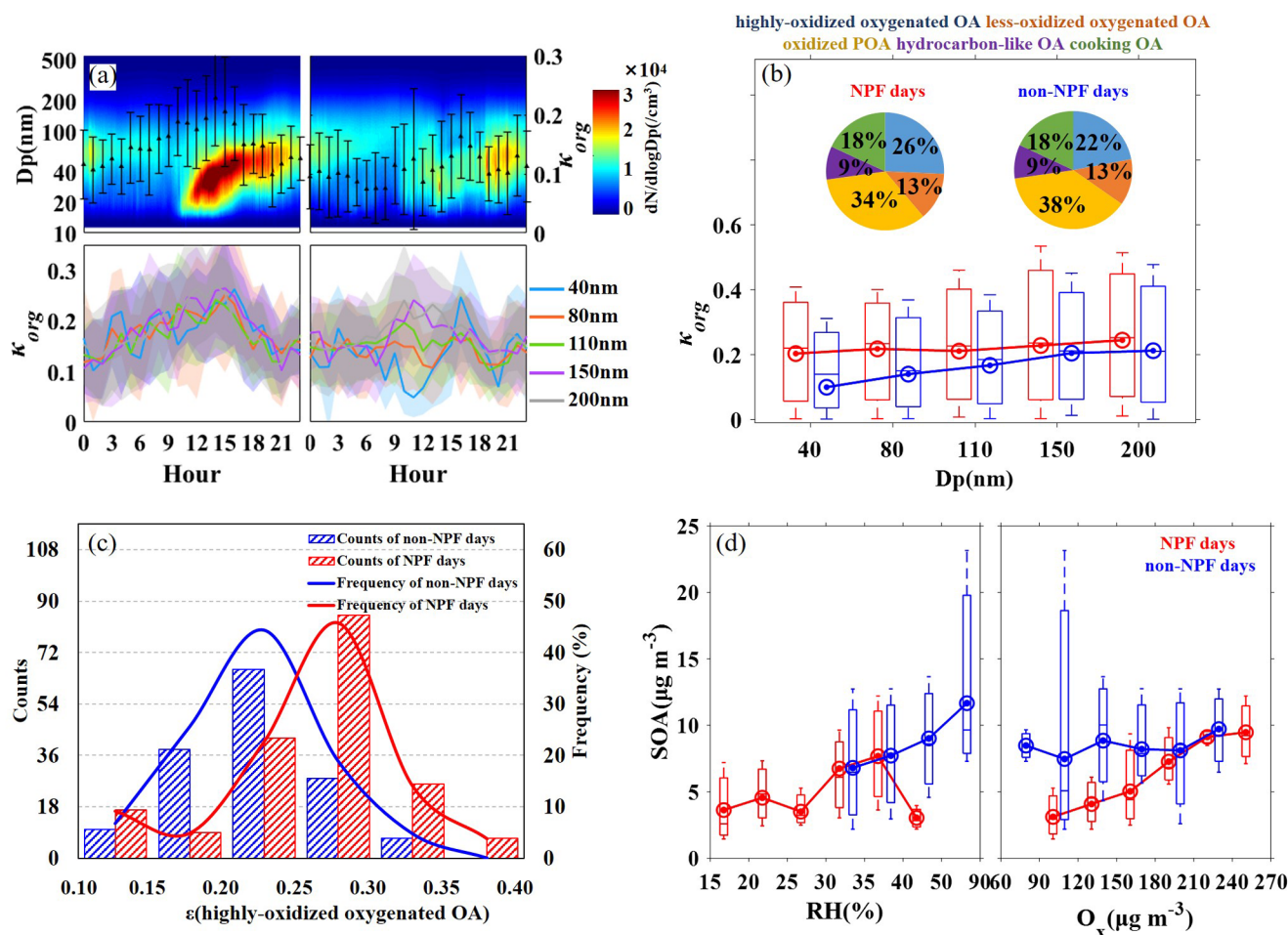
In this study, we use size-resolved  $\kappa$  derived from measured Gf to calculate the size-resolved  $\kappa_{\text{org}}$  based on the mixing rule with the size-resolved aerosol chemical compositions measured by AMS (Petters & Kreidenweis, 2007). The detailed calculation methods are presented in the supporting information (SI: Methods). Because the inversion involves measurements from HTDMA and AMS, we conducted a total mass closure to compare the mass concentration of  $\text{PM}_{10}$  measured by the two techniques, which are well consistent during the field campaign (Figure S1).

### 3. Results and Discussion

#### 3.1. $\kappa_{\text{org}}$ on NPF and non-NPF Days

NPF events, which are characterized by a distinct “banana” shape in the time series of particle number size distribution (PNSD), occur frequently during the campaign (Figure 1a and Figure S2). In this study, with criteria of that, a distinct new mode of particles appears in the PNSD and prevails for more than an hour showing continuous growth (Dal Maso et al., 2005), typical NPF events occurred on 10 days, accounting for approximately 42% days during the entire period. The  $\kappa_{\text{org}}$  between NPF and non-NPF days is contrasted to evaluate the effect of different particle formation processes on hygroscopicity of OA.

The averaged diurnal variations of the PNSD,  $\kappa_{\text{org}}$  of different particle size on NPF days and non-NPF days are shown in Figure 1a. The obvious banana-shaped profile occurred around noontime and early afternoon (9:00–17:00 Local Time; LT) and is indicative of NPF (Figure 1a). The mean  $\kappa_{\text{org}}$  increases significantly when NPF occurs, while there is no increase in  $\kappa_{\text{org}}$  around noontime on non-NPF days (Figure 1a), particularly for the 40 nm particles. Compared with non-NPF days, the  $\kappa_{\text{org}}$  for 40–200 nm are noticeably higher on NPF days, with the largest disparity for 40 nm particles (Figure 1b) that is closely related to NPF. This suggests that the nucleation generates more hygroscopic OA. As a result, the  $\kappa_{\text{org}}$  is relative independent on particle size on NPF days when the nucleation enhanced the  $\kappa_{\text{org}}$ . On non-NPF days, the  $\kappa_{\text{org}}$  shows increase with increase of particle size because the larger particles are generally internally mixed and more aged and hygroscopic (Chen et al., 2020; Zhang et al., 2014). The mean bulk  $\kappa_{\text{org}}$  is  $0.19 \pm 0.07$  and  $0.11 \pm 0.07$  on NPF and non-NPF days, respectively, corresponding to a remarkable increase of 73% in  $\kappa_{\text{org}}$  and 20% in the overall hygroscopicity,  $\kappa_{\text{bulk}}$  (Table S1). Figure 1b shows that the volume fractions of less-oxidized oxygenated OA, hydrocarbon-like OA, and cooking OA are similar between NPF days and non-NPF days, while the frequency distribution of volume fraction of highly-oxidized oxygenated OA exhibits a significant shift from left to right, showing an increase from 15%–25% on non-NPF days to 20%–35% on NPF days (Figure 1c), accompanying with a decrease of volume fraction of oxidized POA from non-NPF to NPF days. This indicates that the NPF yield more highly-oxidized oxygenated OA. The “banana” type of NPF typically occurs under clear conditions with strong ultraviolet radiation (UV) and low RH (Figure S3) conditions. The mass loadings of SOA on NPF days highly depends on  $\text{O}_x$  ( $\text{O}_x = \text{NO}_2 + \text{O}_3$ ) (Figure 1d), a conserved tracer of photochemical processing (Herndon et al., 2008; Xu et al., 2017). While, on non-NPF days, it closely depends on RH (Figure 1d). Therefore, nucleation due to the photooxidation of VOCs and subsequent growth of the nucleated particles generates large amounts of more water-soluble organic components, such as organic acids (Guo et al., 2020; Qiu et al., 2012), likely explaining the enhanced water uptake capacity of OA. On the other hand, non-NPF events typically correspond to polluted conditions with low UV and high RH (Figure S3; Guo et al., 2020), and oligomerization via aqueous reactions likely represents a key pathway for OA growth (Gomez et al., 2015; Zhao et al., 2006). This provides an explanation for the less hygroscopicity of OA during non-NPF events since primary OA (i.e., POA, hydrocarbon-like OA, and cooking OA) likely experiences significant growth by aqueous reactions to form less water-soluble oligomers (Xu et al., 2014). Our results indicate that NPF in polluted urban atmosphere, which is primarily driven by photochemical oxidation of anthropogenic VOCs (Guo et al., 2020), generates more hygroscopic OA. Another earlier study showed a weakened hygroscopicity of OA during NPF in a forest region area, where the newly formed particles are mainly formed from biogenic SOA (Deng et al., 2018), implying plausible effects of different NPF sources on hygroscopicity of OA.

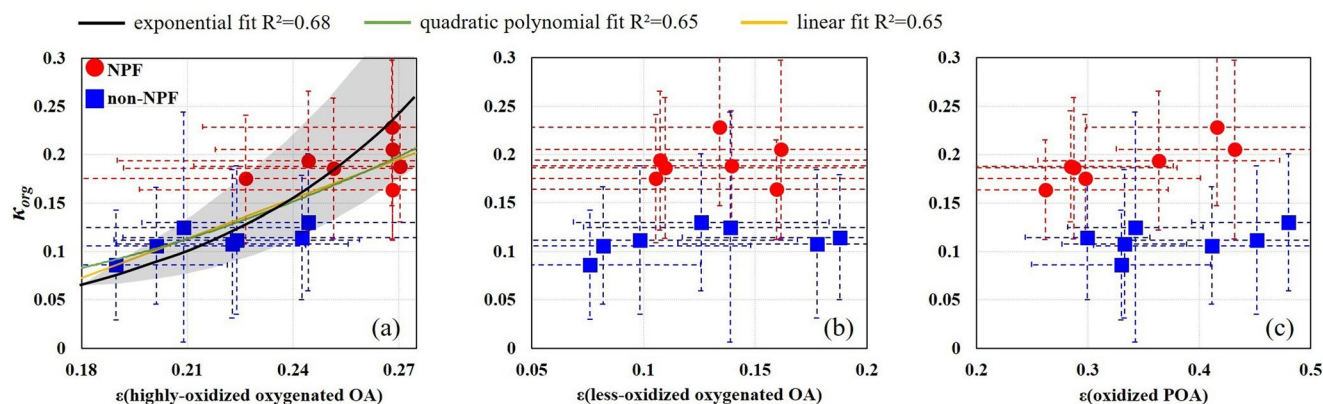


**Figure 1.** (a) Diurnal variations of PNSD and  $\kappa_{org}$  on NPF (left panels) and non-NPF days (right panels); The shade regions denote the error bars ( $\pm 1\sigma$ ). (b) The dependence of  $\kappa_{org}$  on  $D_p$  on NPF and non-NPF days during 9:00–15:00 LT. The pie charts embedded in the figure represent the mean volume fraction of five OA constituents during 9:00–15:00 LT. (c) The counts (left y-axis) and frequency (right y-axis) distribution of the volume fraction of highly oxidized oxygenated OA during 9:00–15:00 LT on NPF and non-NPF days. (d) Dependence of SOA mass concentration on RH and  $O_x$  on NPF and non-NPF days during 9:00–15:00 LT. The mean (circle), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 5th and 95th percentiles (lower and upper whiskers) are presented in the figure. NPF, new particle formation; OA, organic aerosol; PNSD, particle number size distribution; RH, relative humidity; SOA, secondary organic aerosol.

### 3.2. Dependence of the $\kappa_{org}$ on Volume Fraction of OA

The dependence of  $\kappa_{org}$  on the changes of the volume fraction of different kinds OA on NPF and non-NPF days is shown (Figure 2). The bulk  $\kappa_{org}$  increases monotonically (with a correlation coefficient,  $R^2$ , of  $>0.65$  from different fits methods) from  $\sim 0.1$  to  $\sim 0.22$ , when the volume fraction of highly oxidized oxygenated OA increases from  $\sim 18\%$  to  $27\%$  (Figure 2a). On the other hand, an increase of  $\kappa_{org}$  with the volume fraction of less-oxidized oxygenated OA and oxidized POA are not apparent (Figure 2b and 2c). The remarkably larger  $\kappa_{org}$  always occurs during NPF events. In other words, OA from NPF exhibits the largest water uptake capacity, independent on changes in the fraction of the less-oxidized oxygenated OA and oxidized POA. Those results again indicate the critical role of nucleation process in enhancing the  $\kappa_{org}$ , while the aqueous oligomerization during non-NPF events yields less water-soluble products (e.g., oligomers; Xu et al., 2014). As a result, it shows that the hygroscopicity of highly-oxidized oxygenated OA is generally 2.5 and 5-folds of those of oxidized POA and less-oxidized oxygenated OA, respectively, illustrated by the slopes from a linear correlation analysis during the whole campaign (Figure 3). In addition, the increases of volume fraction of hydrocarbon-like OA and cooking OA result in decreasing  $\kappa_{org}$ . Note that, although both the cooking OA and hydrocarbon-like OA are thought to be nonhygroscopic (Petters & Kreidenweis, 2007), it shows that the



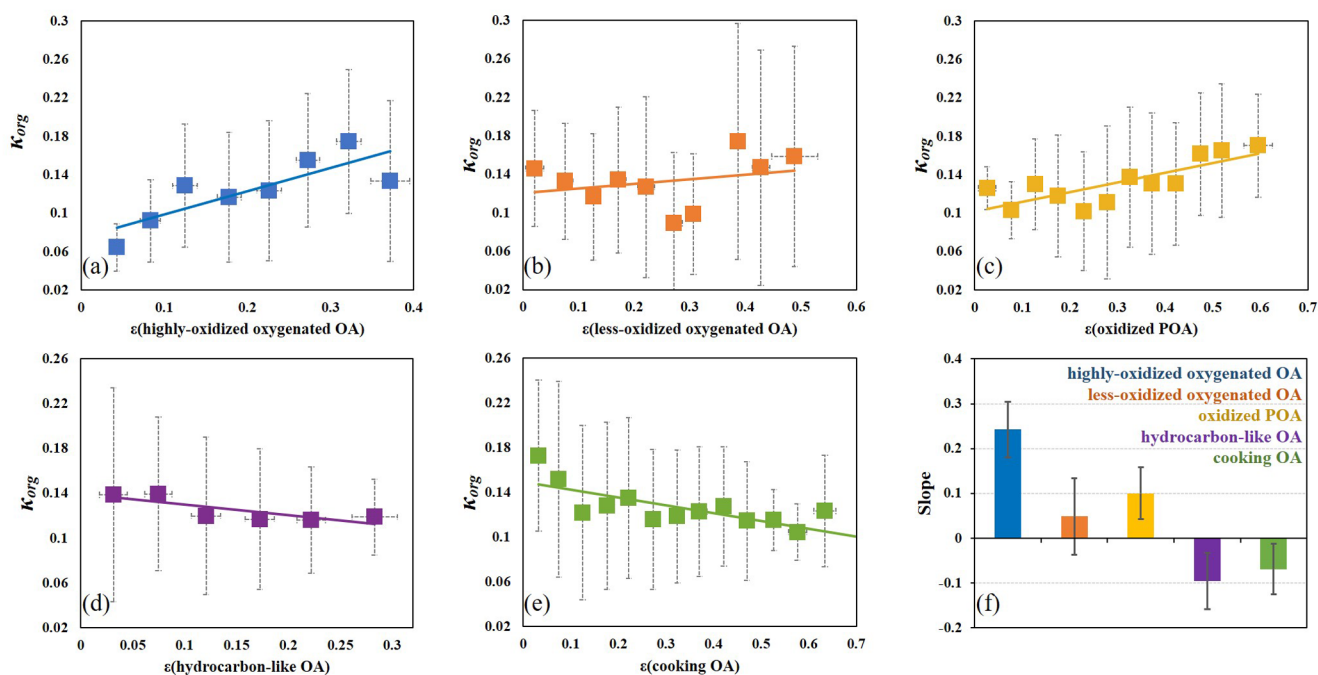


**Figure 2.** The dependence of  $\kappa_{org}$  on volume fraction of three OA types on NPF days (red dots) and non-NPF days (blue square) during 9:00–15:00 LT. (a) Highly oxidized oxygenated OA; (b) less-oxidized oxygenated OA; and (c) oxidized POA. Different fittings of  $\kappa_{org}$  and  $\epsilon$  highly oxidized oxygenated OA are represented by lines of different colors: the exponential fit (black); quadratic polynomial fit (green); linear fit (orange). The gray shadow is an auxiliary display of exponential fitting. The error bars represent  $\pm 1\sigma$ . NPF, new particle formation; OA, organic aerosol; POA, primary organic aerosol.

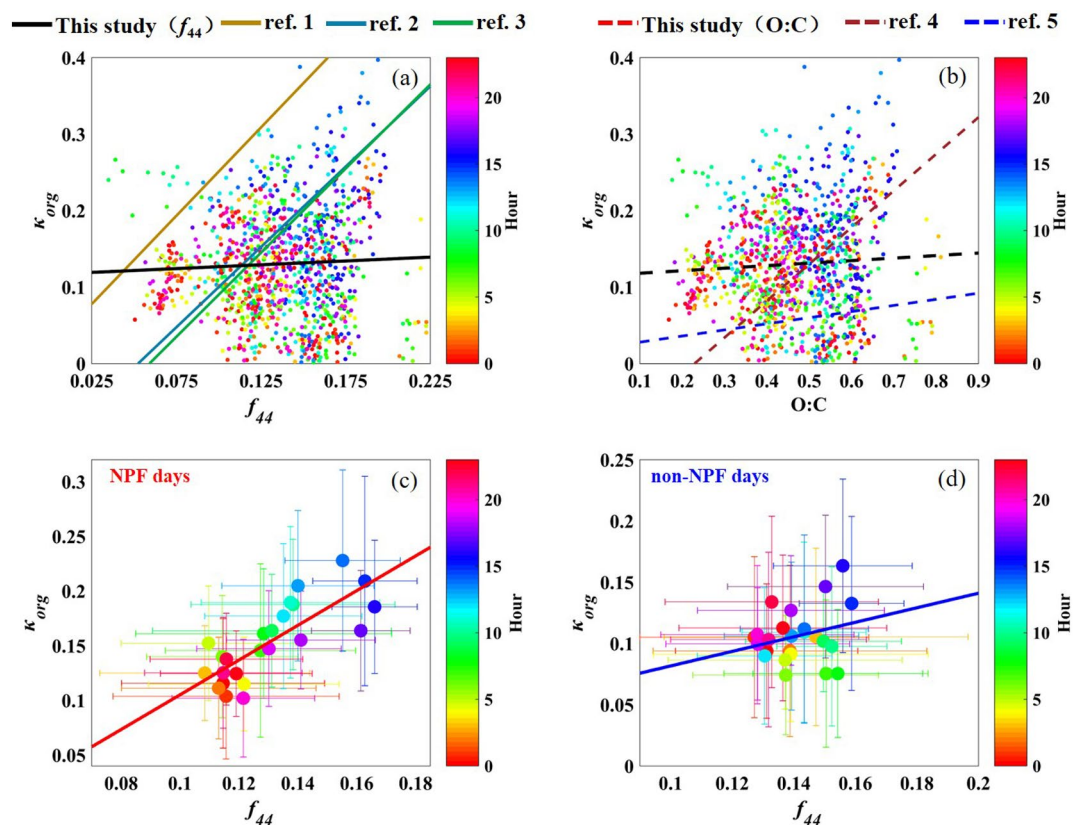
former is less hydrophobic with less negative slope than that of the latter one, likely due to the lower ratio of O/C of hydrocarbon-like OA in Beijing than that of cooking OA (Sun et al., 2016).

### 3.3. Dependence of $\kappa_{org}$ on $f_{44}$ and O:C

To evaluate the oxidation degree on hygroscopicity, we assessed the dependence of changes of  $\kappa_{org}$  on the variations of  $f_{44}$  and O:C, along with comparison with previous studies (Figure 4). Figure 4a and 4b show that there exists little correlation of  $\kappa_{org}$  with  $f_{44}$  and O:C, indicating that both parameters alone cannot represent or parameterize the hygroscopicity of OA. The weak dependence of hygroscopicity of OA on the oxidation degree is attributable to the complex formation and composition of OA in this polluted urban area, considering the two growth mechanisms by photooxidation and oligomerization as well as their effects

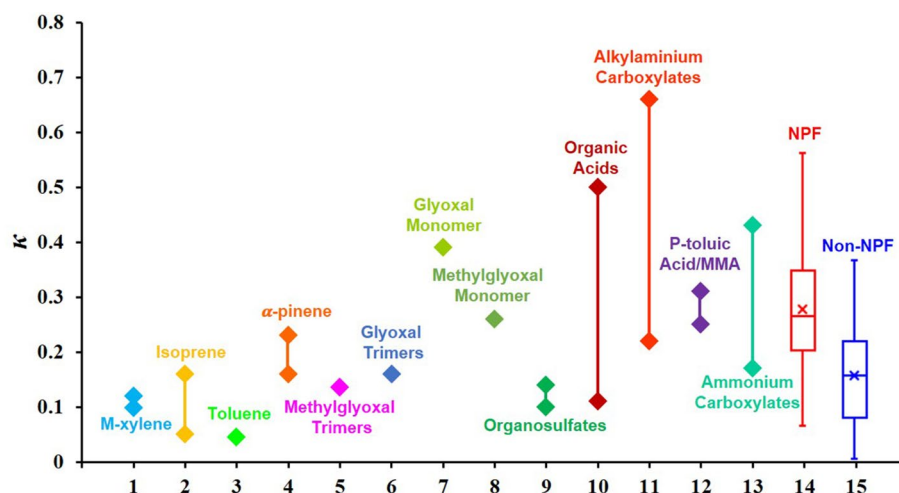


**Figure 3.** The dependence of  $\kappa_{org}$  on volume fraction of the five organic components ((a)–(e)) and the contribution (denoted by the slopes of the linear fit of  $\kappa_{org}$  vs. volume fraction of the five organics) of each component to  $\kappa_{org}$  (f). The error bars represent  $\pm 1\sigma$ .



**Figure 4.** (a) The  $\kappa_{org}$  versus  $f_{44}$ . The dots with different color are  $f_{44}$  correspond to observed time of the day during the campaign as shown by the color bar. (b) The  $\kappa_{org}$  versus atomic O:C ratios. The dots with different color are atomic O:C ratios correspond to observed time of the day during the campaign as shown by the color bar. Also shown for comparison are literature results: ref. 1: Riau and Central Kalimantan, Indonesia (J. Chen et al., 2017); ref. 2: Sacramento, USA (Mei et al., 2013); ref. 3: Jungfraujoch and Mexico (Duplissy et al., 2011); ref. 4: Kyoto, Japan (Deng et al., 2018); ref. 5: Beijing (Wu et al., 2016). ref. 1–ref. 3:  $\kappa_{org}$  versus  $f_{44}$ . ref. 4 and ref. 5:  $\kappa_{org}$  versus O:C ratio. (c) The linear fitting of hourly averaged  $\kappa_{org}$  and  $f_{44}$  on NPF days; (d) The linear fitting of hourly averaged  $\kappa_{org}$  and  $f_{44}$  on non-NPF days. The error bars represent  $\pm 1\sigma$ .

on the oxidation state and hygroscopicity. A higher  $f_{44}$  occurs more frequently during daytime (around 10:00–15:00) on NPF days, when an improved correlation ( $\kappa_{org} = 1.59 \times f_{44} - 0.05$ ,  $R^2 = 0.61$ ) is obtained from the hourly mean  $\kappa_{org}$  as a function of the  $f_{44}$  values (Figure 4c). No apparent improved correlation is obtained when we link the  $\kappa_{org}$  to the  $fCO_2^+$  ( $\kappa_{org} = 1.50 \times fCO_2^+ - 0.03$ ,  $R^2 = 0.57$ ; Figure S4) instead of  $f_{44}$  on NPF days due to that the  $CO_2^+$  ion contributes about  $\sim 90$ – $95\%$  to  $f_{44}$ . Also, the correlation between  $\kappa_{org}$  and other AMS tracer ions fraction ( $C_2H_3O^+$ ,  $CHO^+$ ,  $C_3H_5O^+$ ) is absent (Figure S4). This further demonstrated that these tracer ions are not sufficient to parameterize the  $\kappa_{org}$  since the OA molecular information is missing from the AMS measurements. The evidence of a larger  $f_{44}$  corresponding to higher  $\kappa_{org}$  during daytime on NPF days also implies that more hygroscopic OA is mainly produced from strong photochemical oxidation during nucleation process. On the other hand, the non-NPF processes result in higher  $f_{44}$  but less hygroscopic OA, and thus a poor correlation (Figure 4d), consistent with oligomerization with an increasing oxidation but lower  $\kappa_{org}$ . Our result contrasts with those previously observed at remote forest sites by Deng et al. (2018) and Chen et al. (2017); both studies showed apparent dependence of  $\kappa_{org}$  on  $f_{44}$ , when OA is formed from biogenic precursors. At a relative clean site, Zhang et al. (2014; 2016) also found that the higher  $f_{44}$  corresponds to high hygroscopicity and CCN activity. The distinct chemical composition, formation mechanisms, and the types of VOCs jointly regulate the variation in water uptake capacity of OA with the oxidation degree or  $f_{44}$  values (Timonen et al., 2013; Xu et al., 2014, 2017). Therefore, this study provides further evidence that the oxidation state alone is insufficient to characterize hygroscopicity, the molecular information of OA and unique formation mechanisms should be considered.



**Figure 5.** The  $\kappa$  values for different kinds of organics reported in literatures (1. Guo et al., 2016; 2. Khalizov et al., 2013; 3. Qiu et al., 2012; 4. Ma et al., 2013; 5–8. Xu et al., 2014; 9. Estillore et al., 2016; 10. Petters and Kreidenweis, 2007; Kumar et al., 2009; 11, 12. Gomez-Hernandez et al., 2016; 13. Dinar et al., 2008) and that measured on NPF and non-NPF days. NPF, new particle formation.

### 3.4. Comparison of the Field Observed Hygroscopicity of OA with that of Different Kinds of Organics

To further obtain insights on the formation of organic aerosols and the link to hygroscopicity of OA, we compare the field observed hygroscopicity of secondary formed OA (e.g., highly or less-oxidized oxygenated OA) with that of different kinds of organics (Figure 5). The hygroscopic parameter of these SOA ( $\kappa_{\text{SOA}}$ ) is calculated by assuming the POA (e.g., cooking or hydrocarbon-like OA) is hydrophobic with  $\kappa$  value of 0. On NPF days, these secondary formed OA is very hygroscopic, with mean  $\kappa_{\text{SOA}}$  of  $0.28 \pm 0.12$ , and the value can be as high as 0.56. The results show that the water uptake capacity of the OA on NPF days is similar to that of organic acids, alkylammonium carboxylates or organic ammonia (Figure 5), which are reported more water soluble with  $\kappa$  of about 0.1–0.5 (Kumar et al., 2009; Petters & Kreidenweis, 2007), 0.2–0.66 (Gomez-Hernandez et al., 2016), and 0.17–0.43 (Dinar et al., 2008), respectively. This may indicate that the very hygroscopic OA, such as organic acids, carboxylic organic amine and ammonia organic salts may be largely formed during the nucleation and growth process on NPF days in polluted urban Beijing. On non-NPF days, the mean  $\kappa_{\text{SOA}}$  is  $0.15 \pm 0.09$ , with maximum value of 0.37, showing much weaker water uptake capacity than that of obtained during NPF days. The values on non-NPF days are closer to those of organic polymer (e.g., methylglyoxal trimer, glyoxal trimer dihydrate [GTD]; Xu et al., 2014) or organosulfates (e.g., benzyl sulfate; Estillore et al., 2016). Since the observed ratio of O:C is within the range of about 0.2–0.7 (Figure 4b), the organosulfates, which are generally with ratio of O:C of  $>1.0$  (Altieri et al., 2009), should not be the primary products during our observed periods. In addition, these photochemical oxidation products of biogenic VOCs (e.g., isoprene, m-xylene; Guo et al., 2016; Khalizov et al., 2013; Ma et al., 2013), although which are with similar  $\kappa$  to that of our observation, are not expected to be dominant on non-NPF days due to low ambient concentrations in Beijing. While it is usually with high levels of anthropogenic VOCs (e.g., toluene, benzene) in urban atmosphere (Guo et al., 2020). In summary, the different formation mechanism of OA may explain the discrepancy of hygroscopicity of OA on NPF and non-NPF days. It is further demonstrated that the OA on NPF days may primarily formed by photooxidation, being more hygroscopic, while the non-NPF days the mechanism of oligomerization is dominant, yields less hygroscopic products. However, this needs to be fully clarified by the specific molecular information of OA in future field measurements.

## 4. Conclusions

While OA accounts for large proportion of ambient fine particles, the factors regulating the variations of its hygroscopicity remain unclear. Our simultaneous measurements of ambient fine particles chemical composition and hygroscopic growth factor during summer 2017 in Beijing reveal a remarkably-enhanced  $\kappa_{\text{org}}$  on

NPF days compared to non-NPF days. The mean  $\kappa_{\text{org}}$  of OA during NPF events is  $0.19 \pm 0.07$ , which is about 73% higher than that during non-NPF events. While non-nucleation processes (e.g., oxidized POA or oligomerization) also produce OA, their hygroscopicity exhibits little enhancement. A correlation between the hygroscopicity and oxidation state is absent for OA, indicating that the oxidation degree alone is insufficient to characterize hygroscopicity of OA in polluted urban atmosphere. Our results reveal that the measured distinct water uptake capacity of OA between NPF and non-NPF events is attributed to the different OA growth processes, that is, nucleation-initiated photochemical oxidation of VOCs to produce water-soluble products (e.g., organic acids) and aqueous oligomerization to yield less water-soluble products, respectively. The specific molecular information of OA warrants to be investigated combining other techniques (e.g., off-line ion chromatography) in future to provide direct evidence of our results inferred from the field measurements. Also, it is critical to account for the distinct OA growth mechanisms in atmospheric models for evaluation of their impacts on air quality and climate.

## Data Availability Statement

All data used in the study are available on <https://data.mendeley.com/datasets/3n72dcjdfv/1> or from the corresponding author upon request (fang.zhang@bnu.edu.cn).

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