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Key Points:
- Nucleation-initiated haze events lead to more CCN-sized particles
- The effects of changes in particle size and composition on CCN activity during the evolution of haze events are quantified
- The source of CCN from new particle formation needs reevaluation in polluted regions where the subsequent growth of nucleated particles may last 2–3 days

Supporting Information:
- Supporting Information S1

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Significantly Enhanced Aerosol CCN Activity and Number Concentrations by Nucleation-Initiated Haze Events: A Case Study in Urban Beijing

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Abstract The evolution of haze, involving multiple processes such as nucleation, coagulation, and condensation, may exert complex effects on aerosols' cloud condensation nuclei (CCN) activity and number concentration (N_{CCN}). Based on field campaigns carried out in the winters of 2014 and 2016 in Beijing, we show that N_{CCN} was significantly enhanced by the evolution of haze, substantially driven by the nucleation process (or new particle formation). The enhancement factor of N_{CCN} by such nucleation-initiated haze episodes, E_N_{CCN}, defined as the ratio of N_{CCN} after haze events to N_{CCN} prior to haze events, ranged from 2.2 to 6.5 at a supersaturation (S) = 0.76% and from 4.2 to 17.3 at S = 0.23%, the magnitude of which partially depends on the severity of the haze event. The enhancements are much greater than those previously observed and those from model simulations of contribution from new particle formation. This suggests that CCN sources from new particle formation may be underestimated, needing reevaluation in polluted environments where the subsequent growth of newly formed particles can last 2–3 days, yielding more CCN-sized particles. We further quantified that the changes in particle size and composition during the nucleation-initiated evolution of haze are responsible for > 80% and 12–20%, respectively, of the enhancement in CCN activity. The changes in particle composition had a limited impact because most of the ambient particles were already hydrophilic, with hygroscopic parameters of 0.2–0.65.

1. Introduction

Aerosols in China and their role in deteriorating air quality and lowering visibility by forming severe haze have become a matter of great concern in recent years (Guo et al., 2014; Wang et al., 2016; Zhang et al., 2015). Aerosol particles can also serve as cloud condensation nuclei (CCN), further changing the global radiation balance (Intergovernmental Panel on Climate Change: Climate change, 2013), which is one of the largest uncertainties in the evaluation of aerosol effects on climate. During the evolution of haze, atmospheric aerosol chemical and physical processes, that is, nucleation, coagulation, and condensation, usually coexist and can influence aerosol CCN activity and number concentrations (N_{CCN}) by changing the particle number concentration, size, chemical composition, and mixing state (Wiedensohler et al., 2009; Zhang et al., 2014, 2017). Changes in these factors are intrinsically linked; that is, changes in chemical composition are often accompanied by simultaneous changes in particle size and mixing state, as has been observed from field measurements (Ren et al., 2018; Wang et al., 2017; Zhang et al., 2014, 2016, 2017) and lab experiments (e.g., Ma et al., 2013). During haze events, the coagulation process can lead to the formation of larger particles that are more CCN active. The number of particles would decrease, which may reduce N_{CCN} accordingly. Therefore, the effect of air pollution on N_{CCN} varies widely under different environmental conditions and remains highly uncertain (Farmer et al., 2015). The abovementioned impacts are expected to be more complex in heavily polluted urban areas where the atmosphere also encounters continuous influences from local sources (Li et al., 2011) and rapid secondary conversion of aerosol particles (Zhang et al., 2015).

The nucleation process has been demonstrated to increase N_{CCN} in various environments according to many studies (e.g., De España et al., 2017; Kalkavouras et al., 2019; Li et al., 2017; Rose et al., 2017; Shen et al., 2016; Sihto et al., 2011; Wu et al., 2017; Yue et al., 2011). However, most of these studies generally focus on growth periods of only several hours, typically from noontime to late afternoon. Previous field measurements have shown that the subsequent growth of newly formed particles can last 2–3 days, resulting in the frequent occurrence of haze events in Beijing (Guo et al., 2014). With particle size growth and changes in the composition of the newly formed particles, their CCN activity is expected to change during the evolution of haze. Currently, model simulations tend to underestimate observed N_{CCN} with the largest errors occurring in regions close to urban emissions (Fanourgakis et al., 2019; Sotiropoulou et al., 2007). In addition to underestimating emissions, different global models (e.g., Lee et al., 2013; Makkonen et al., 2009; Westervelt et al., 2013) may underestimate CCN from new particle formation (NPF) sources (mostly with a CCN enhancement factor of less than 2.0) because they only account for the effect of NPF within a short period of several hours. An evaluation of such nucleation-initiated haze effects on CCN activity and its N_{CCN} is essential to improve CCN estimates in polluted regions and to better understand the intrinsic connections between air quality, weather, and climate.

Two field campaigns were conducted in the winters of 2014 and 2016 in urban Beijing when haze events, mostly driven by the nucleation process, frequently occurred. Investigated here are the effects of such nucleation-initiated haze events on CCN activity and its N_{CCN}. The paper is structured as follows. Section 2 describes the experiments and methodology. Section 3.1 shows the observed periodic variations in N_{CCN} regulated by the haze events. Section 3.2 discusses the enhancements in N_{CCN} and its relationship with the severity of pollution. Section 3.3 examines the sensitivity of CCN activity and its N_{CCN} to variations in particle size and composition (characterized by the hygroscopic parameter, κ). Section 3.4 analyzes the correlation between aerosol number concentrations (N_{CN}) and N_{CCN} to evaluate the effect of the nucleation process and haze evolution on estimating N_{CCN}. Conclusions are given in Section 4.

2. Experiment and Methodology

2.1. Site and Instrumentation

The sampling site in urban Beijing (39.97°N, 116.37°E, 49 m above sea level) is located at the meteorological tower branch of the Institute of Atmospheric Physics, Chinese Academy of Sciences. Local traffic and nearby cooking emissions (Sun et al., 2015) influence the site, which experiences frequent haze events and pollution plumes.

Two field campaigns were conducted at the site in the winters of 2014 and 2016: from 8 November to 15 December 2014 and from 16 November to 10 December 2016, during which severe haze events occurred frequently and periodically. During both field campaigns, instruments were placed in a container ($2 \times 6 \times 2$ m), and atmospheric aerosol particles were collected through a sampling inlet deployed on top of the container (~3 m above the ground). In 2014, a custom-made, high-flow scanning mobility particle sizer (SMPS; Collins et al., 2002; Gasparini et al., 2004; Wang & Flagan, 1990) combined with a Droplet Measurement Technologies CCN counter (DMT-CCNc) (Lance et al., 2006) was used to measure size-resolved N_{CCN} and particle number size distributions (PNSDs). The flow to the CCN counter was 0.5 liter per minute (lpm) and that to the condensation particle counter (CPC; TSI model 3760A) was 1.5 lpm. The sheath flow rate for the custom-made differential mobility analyzer (DMA) was 6 lpm. In 2016, a TSI SMPS was combined with the DMT-CCNc to measure size-resolved N_{CCN} (D. Rose et al., 2008). Split into two parts was the sample flow exiting the DMA: 0.5 lpm for the CPC and 0.5 lpm for the CCN counter, in which the sheath-to-aerosol flow ratio was 10. The sheath flow rate of the TSI DMA was 3 lpm. Aerosol PNSDs measured over a 5-min period spanned the size ranges of 10–400 and 15–600 nm in 2014 and 2016, respectively. The aerosol inlet was equipped with a TSI Environmental Sampling System (model 3031200), consisting of a sharp-cut particulate matter with a diameter of 1 PM_1 cyclone and a bundled Nafion dryer. Sampled particles were dried to relative humidity (RH) less than 30% prior to introduction into the charge neutralizer and DMA. The DMA, controlled by TSI-AIM software, scanned one size distribution every 5 min. The supersaturation (S) levels set for each CCN measurement cycle were 0.07%, 0.1%, 0.2%, 0.4%, and 0.8%. A full measurement cycle took 70 min (14 min for each S level) and 60 min (20 min for $S = 0.07\%$ and 10 min for the other S levels) to complete in 2014 and 2016, respectively. The S levels of the CCNc were calibrated with ammonium sulfate before and

after the field campaigns, following the procedure outlined by D. Rose et al. (2008). Therefore, the S in this study is effective supersaturation after the calibration. Since the size-resolved N_{CCN}, not the bulk N_{CCN} that can be extremely high in the urban atmosphere, was measured during the campaign, it is thus not sensitive to the counting efficiency of the CPC. The relative error caused by the depletion of water vapor would be insignificant in the CCNc. According to our measurements, at a typical S of ~0.3–0.4% in clouds, we derived a critical diameter, D_{crit}, of ~60–70 nm, corresponding to 50% of condensation nuclei (CN) particles that can be activated to CCN. Therefore, the CCN-sized particles in this study refer to particles with diameters larger than 60 nm.

Size-resolved, non-refractory submicron aerosol species, including organics, sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), and chloride (Chl), were measured using an Aerodyne high-resolution, time-of-flight aerosol mass spectrometer (HR-ToF-AMS; DeCarlo et al., 2006). Positive matrix factorization (PMF) with the PMF2.exe (v4.2) algorithm was used to analyze the HR-ToF-AMS organic spectral matrices following the procedures outlined by Paatero and Tapper (1994). DeCarlo et al. (2006) and Xu et al. (2015) provide more detailed descriptions of the operation and calibration of the HR-ToF-AMS. An aethalometer (model AE33, Magee Scientific Corporation) measured the black carbon concentration in particulate matter (PM) with diameters of less than 2.5 μm. Instruments located on the meteorological tower at the site measured meteorological variables, that is, horizontal wind speed (WS), wind direction, RH, and temperature (T).

2.2. Derivation of the Hygroscopic Parameter (κ)

In this study, the hygroscopic parameter κ is calculated using a simple mixing rule based on chemical volume fractions for an assumed internal mixture (Petters & Kreidenweis, 2007):

$$\kappa = \sum_i \varepsilon_i \kappa_i, \tag{1}$$

where κ_i and ε_i are the hygroscopicity parameter and volume fraction, respectively, for the individual (dry) components in the mixture and i is the number of components in the mixture. Here the particles' bulk chemical composition consisting mainly of organics, $(NH_4)_2SO_4$, and NH_4NO_3 is used to calculate κ. The values of κ are 0.61 and 0.67 for pure $(NH_4)_2SO_4$ and NH_4NO_3, respectively, derived from laboratory experiments (Petters & Kreidenweis, 2007). The following linear function was used to estimate κ_{org} in our study (Mei et al., 2013): $\kappa_{org} = 2.10 \times f_{44} - 0.11$, where f_{44} is the fraction of the total organic signal at m/z 44. The particle hygroscopicity is thus the volume average of the three participating species. Species volume fractions were derived from mass concentrations and densities of the participating species. The κ calculated from the time series of the bulk chemical composition of PM with diameters of less than 1 μm (PM_1) shows the variation in particle hygroscopicity during the evolution of haze.

Size-resolved κ is also derived using κ-Köhler theory based on CCN activity data to quantify the effect of changes in particle size and composition during the evolution of haze on CCN activity. For $\kappa > 0.1$, the following expressions can be used (Petters & Kreidenweis, 2007):

$$\kappa_{CCN} = \frac{4A^3}{27 D_p^3 S_c^2}, \tag{2}$$

$$A = \frac{4\sigma_w M_w}{RT\rho_w}, \tag{3}$$

where S_c is the particle critical supersaturation derived using the approach described by D. Rose et al. (2008) and Mei et al. (2013), D_p is the particle dry diameter, M_w is the molecular weight of water, σ_w is the surface tension of pure water, ρ_w is the density of water, R is the gas constant, and T is the absolute temperature.

3. Results and Discussion

3.1. Periodic Cycles of N_{CCN} Regulated by Nucleation-Initiated Haze Events

In general, a typical feature of an NPF event is the distinct "banana" shape of the observed PNSD measured by the SMPS. Newly formed particles experience subsequent growth through coagulation, condensation, and other processes along with changes in both particle size and composition. As the particles grew, the mass

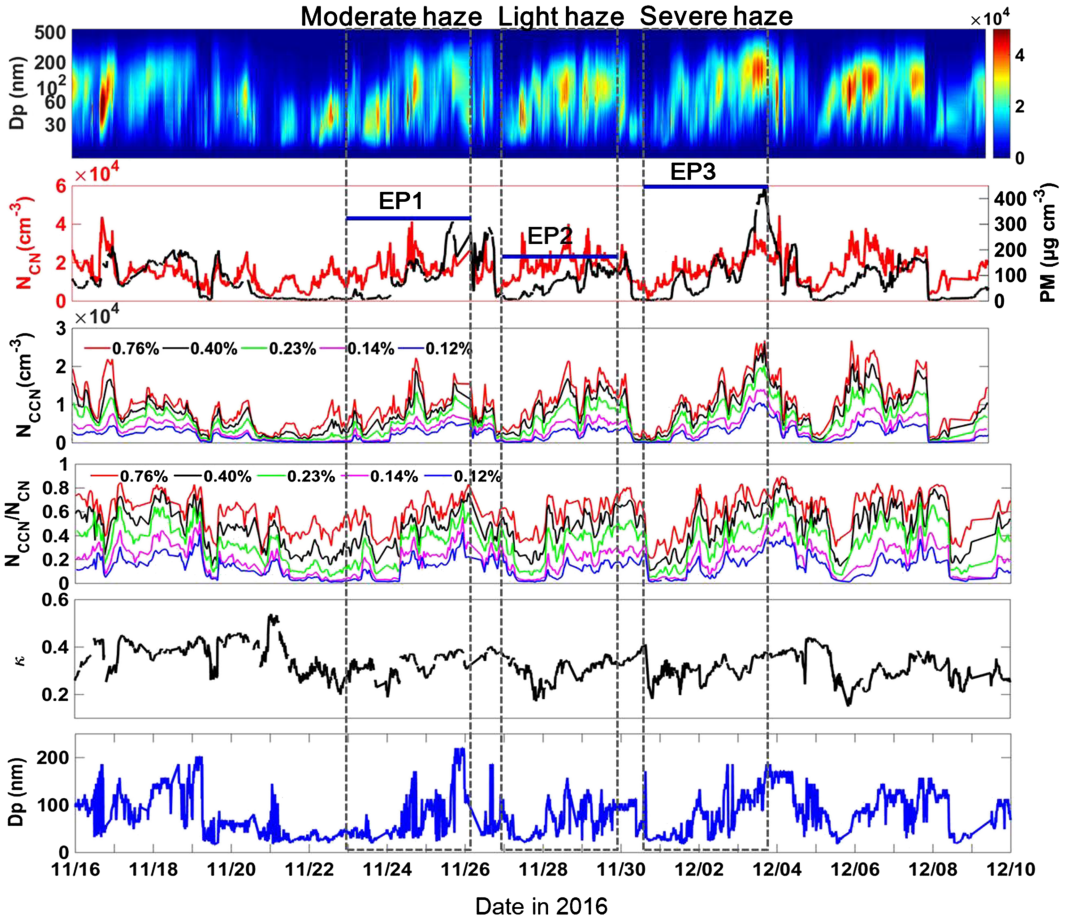

Figure 1. Time series of the (from top to bottom) particle number size distribution, particle number concentration (N_{CN}) and particle mass concentration (PM_1), CCN number concentration (N_{CCN}), ratio N_{CCN}/N_{CN}, and particle hygroscopic parameter (κ) calculated from chemical composition. Data are from 16 November to 10 December 2016. The different colors of N_{CCN} and N_{CCN}/N_{CN} denote results measured at different supersaturation levels: 0.12% (in blue), 0.14% (in magenta), 0.23% (in green), 0.40% (in black), and 0.76% (in red). Three haze episodes (EP1, EP2, and EP3) are selected for further investigation. The fourth episode (outlined but not labeled) is not considered in the study because the PM_1 mass concentration is similar to that of EP2.

concentrations of PM_1 increased significantly, that is, typically greater than 150–200 μg m^{-3}, resulting in haze events (Figure 1). The background mass concentration of PM_1 was less than 50 μg m^{-3}. The haze events demarked in Figure 1 appear to have been initiated by a persistent and continuous growth of newly formed particles under static atmospheric conditions, with a rapid rise in mass concentration of PM_1 from 20–30 to 150–400 μg m^{-3}. Here this is called the nucleation-initiated haze evolution. The N_{CCN} was enhanced periodically by the nucleation-initiated haze events, typically characterized by the rapid continuous growth of N_{CCN} for 2–3 days as the haze event evolved. N_{CCN} can be as high as 10,000–30,000 cm^{-3} when S ranges from 0.23% to 0.76%.

High N_{CN} are observed during nucleation periods, but N_{CCN} was much lower because of the smaller particle size and lesser hygroscopicity of the newly formed particles due to a large mass fraction of 50–60% organics (Figure 2). Under low horizontal ground WS conditions (typically, WS < 2 m s^{-1}) (Figure S1 in the supporting information), particles grow continuously to larger sizes with a stronger hygroscopicity. This is closely associated with the rapid formation of inorganic components likely through the aqueous phase process under high ambient RH conditions (>70%), as proposed in recent studies (e.g., G. Wang et al., 2016). Size-resolved chemical composition data show that there were large shifts in peak diameters for the major components (organics, sulfate, nitrate, and ammonia) going from clean to hazy periods (Figure 3).

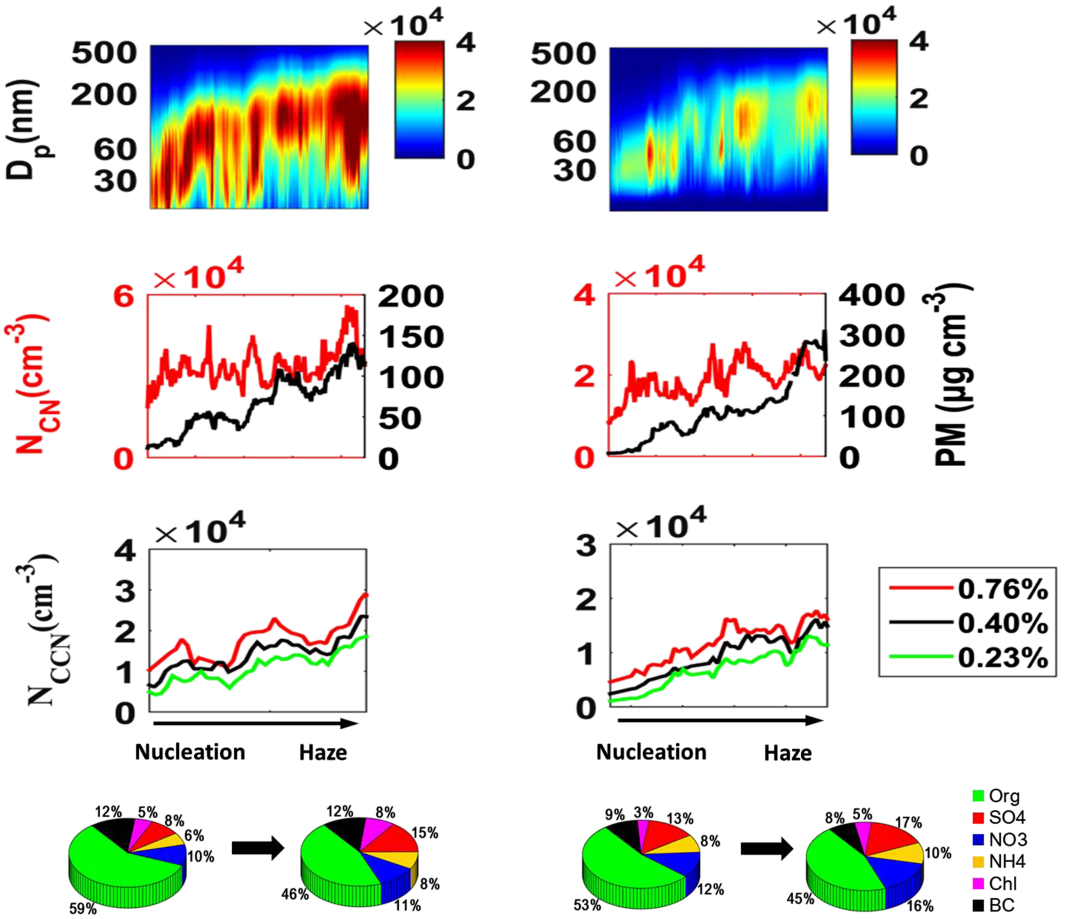

Figure 2. Mean variations in the (from top to bottom) particle number size distribution, condensation nuclei (CN) number concentrations (N_{CN}) and mass concentration of PM_1, and cloud condensation nuclei (CCN) number concentration (N_{CCN}). Results at different supersaturations are denoted by lines with different colors, going from clean (nucleation) to hazy conditions. Pie charts at the bottom show the mean chemical composition of PM_1 going from clean (nucleation) to hazy conditions. Left and right sets of panels are for 2014 and 2016, respectively.

The variation in N_{CN} was small during the transition from nucleation to hazy periods, with a slight upward trend at times. This suggests that the effect of coagulation on the removal of particles in this urban atmosphere was probably secondary or minor. Besides sources from nucleation processes, continuous strong emissions of primary particles from vehicles and other sources in urban Beijing contributed greatly to total N_{CN}. Therefore, it may be that at urban sites such as Beijing, rapid interactions between multiple atmospheric processes involving newly formed particles, primarily emitted particles (e.g., black carbon), and high level of precursor gases would accelerate the growth rate of nucleation-mode particles, leading to more particles acting as CCN. Small fluctuations of N_{CCN} during the haze events are observed, showing similar patterns to that of CN number concentrations. That is mainly due to the disturbances of meteorological conditions, such as abrupt changes in the prevailing wind direction from south to north (Figure S1).

3.2. Enhancements in N_{CCN}

In general, comparing N_{CCN} prior to and after an NPF event quantifies the effect of NPF only on CCN (e.g., Laaksonen et al., 2005). The N_{CCN} enhancement factor is defined as the ratio of the maximum N_{CCN} to the minimum N_{CCN} during the NPF event. To quantify the effect of nucleation-initiated haze events on CCN, a similar definition of CCN enhancement, E_N_{CCN}, was applied here. The E_N_{CCN} was calculated as the ratio of N_{CCN} after the nucleation-initiated haze event to N_{CCN} prior to the nucleation-initiated haze event. Using this method, E_N_{CCN} ranged from 2.2 to 6.5 at $S = 0.76\%$ and from 4.2 to 17.3 at $S = 0.23\%$ during the study

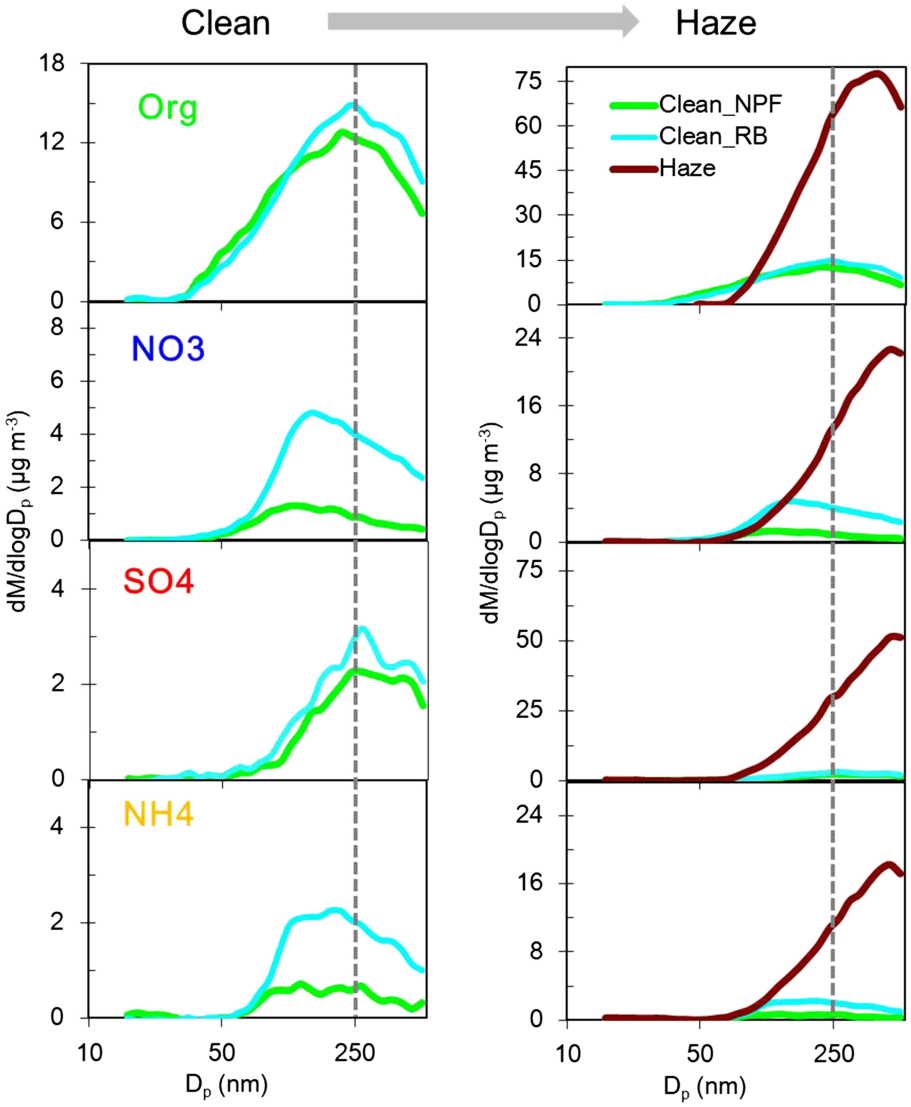

Figure 3. An example showing the size-resolved changes in particle chemical composition under clean (nucleation, in green) and hazy (in dark red) conditions for the EP3 haze event observed in 2014. Also shown is the size-resolved chemical composition during clean periods representing regional background conditions (without nucleation events, in light blue).

periods considered (Figures 4a and S2 and Table S1). The higher enhancement of N_{CCN} at low S mainly occurs because a larger D_{crit} is required at lower S. N_{CCN} at lower S is thus more sensitive to particle size growth during the evolution of haze. Also, the solute effect is more important at lower S (Koehler, 1936).

The nucleation process has been shown to increase N_{CCN} in various environments around the world, typically with enhancement factors ranging from 1.0 to ~5 (e.g., Kalkavouras et al., 2017; Leng et al., 2014; Shen et al., 2016; Sihto et al., 2011; Wu et al., 2017; Yue et al., 2011). Compared to that enhanced by the nucleation process, enhancements in N_{CCN} by the nucleation-initiated haze events derived in this study were much greater (Figure 4b). The enhancements due to NPF reported in previous studies were generally obtained based on a much shorter growth period of only several hours (typically from noontime to late afternoon). This study shows that sustainable and persistent growth of nucleated particles lasted 2–3 days, during which N_{CCN} substantially increased. Currently, model simulations tend to underestimate observed N_{CCN}, showing the largest errors in regions close to urban emissions (Fanourgakis et al., 2019; Sotiropoulou

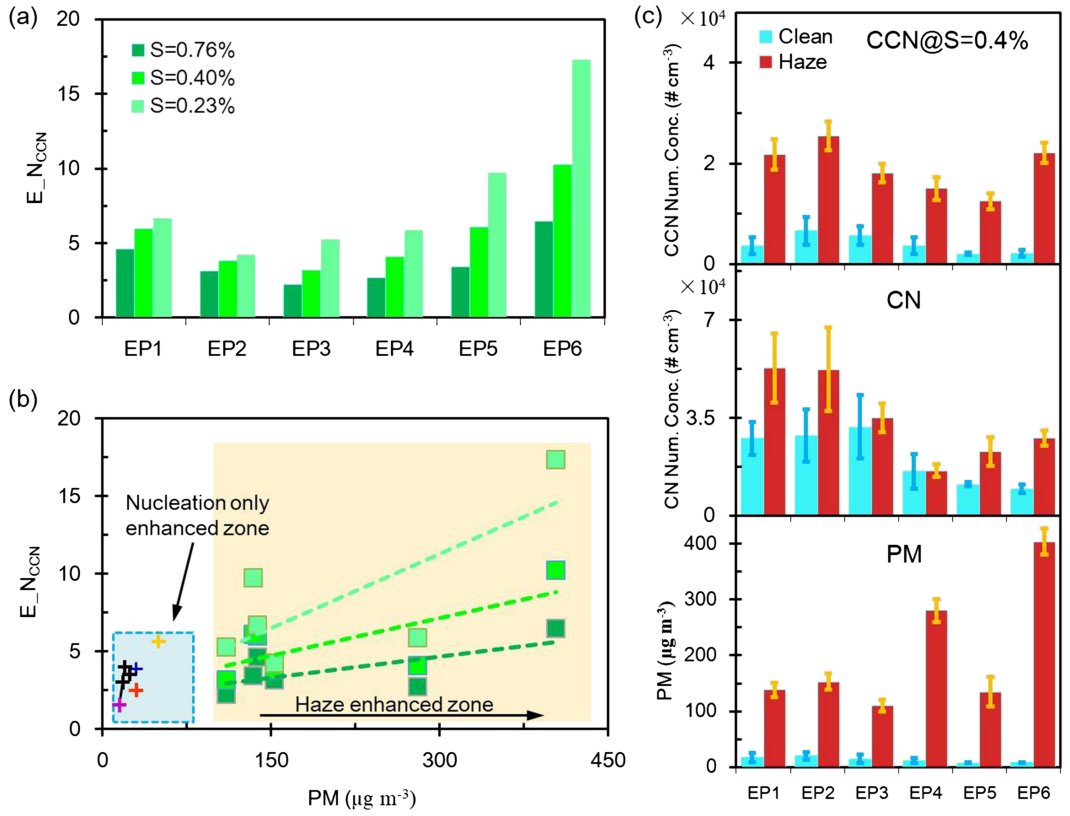

Figure 4. Enhancements in CCN number concentration (E_N_{CCN}), defined as the ratio of N_{CCN} after haze events to N_{CCN} prior to haze events. (a) E_N_{CCN} at supersaturations (S) of 0.23%, 0.40%, and 0.76% for the selected haze episodes. (b) Variations in E_N_{CCN} as a function of mass concentration of PM_1. The observed enhancements in N_{CCN} by nucleation (or new particle formation) events reported in the literature (i.e., Leng et al., 2014; Shen et al., 2016; Wu et al., 2017; Yue et al., 2011) are also plotted with cross symbols for comparison. (c) N_{CCN} (at $S = 0.4\%$), N_{CN}, and mass concentrations of PM_1 under clean (in blue) and hazy (in red) conditions. Six episodes are selected for analysis: EP1, EP2, and EP3 corresponding to the cases observed in 2016 (shown in Figure 1) and EP4, EP5, and EP6 corresponding to the cases observed in 2014 (shown in Figure S1).

et al., 2007). Besides underestimations in emissions and aerosols concentrations in these regions, the underestimation may also be likely due to a significant underestimation of CCN from NPF sources (a CCN enhancement factor of less than 2.0) by different global models (e.g., Lee et al., 2013; Makkonen et al., 2009; Westervelt et al., 2014). Results presented here suggest that it is likely that the high level of precursor gases and the strong oxidation at urban sites not only favors nucleation but also drives the subsequent persistent growth of newly formed particles, resulting in more CCN-sized particles. Therefore, the NPF effect on CCN activity and N_{CCN} need to be reevaluated in regions with heavy anthropogenic emissions.

Figure 4b shows that the magnitude of E_N_{CCN} partially depends on the severity of the haze, characterized by the PM_1 mass concentration. For each haze event selected, N_{CCN} corresponded to a significant increase in the mass concentration of PM_1. However, a large increase in N_{CCN} does not necessarily mean a simultaneous increase in N_{CN}, for example, EP1 in Figure 4c. Some haze episodes with high PM_1 mass concentrations (such as EP1) have smaller E_N_{CCN} than haze episodes with lower PM_1 mass concentrations, reflecting the abrupt change in wind direction from south to north (as shown in Figure 1) that is unconducive to haze formation and maintenance.

3.3. Sensitivity of CCN Activity and N_{CCN} to Variations in Particle Size and Composition

For further investigation is the dependence of critical supersaturation (S_c) on particle diameter (D_p) under different atmospheric conditions and the dependence of S_c on κ at a given D_p (Figure 5). Air masses were classified as clean with nucleation events (denoted as Clean_NPF), clean without nucleation events

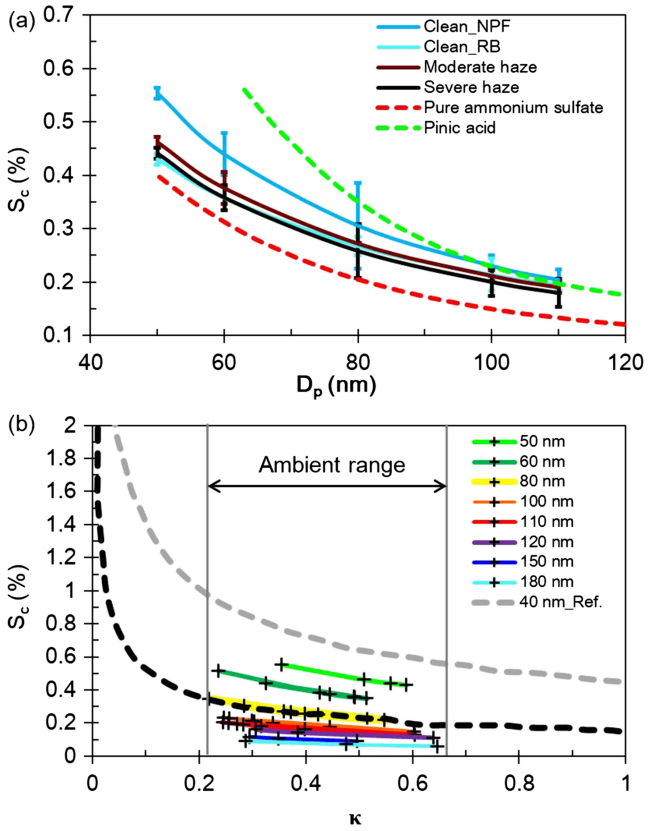

Figure 5. (a) CCN activity (denoted as critical supersaturation, S_c) as a function of particle diameter (D_p) under different atmospheric conditions. The activity curves of pure ammonia sulfate and pinic acid are plotted for reference. (b) S_c as a function of particle hygroscopic parameter (κ) at a given particle diameter during the field campaigns and from theoretical calculations (for 40 and 80 nm) based on Koehler theory. The uncertainty (1σ) of each measured point is within ±(0.02–0.05%).

(representing the regional background and denoted as Clean_RB), with moderate haze, and with severe haze. Overall, increases in D_p and κ played an important role in decreasing S_c, i.e., enhancing CCN activity. Variations in S_c for particles with the same diameter reflect the impacts of changes in chemical

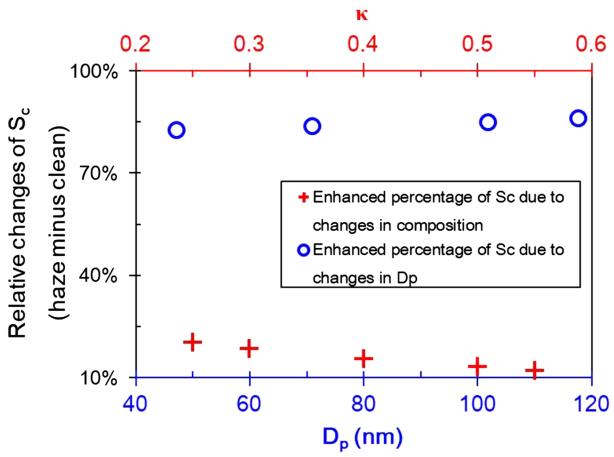

Figure 6. Relative changes in the critical supersaturation (S_c) from clean to hazy days due to changes in particle chemical composition (represented by the particle hygroscopic parameter, κ; red crosses) and D_p (blue circles).

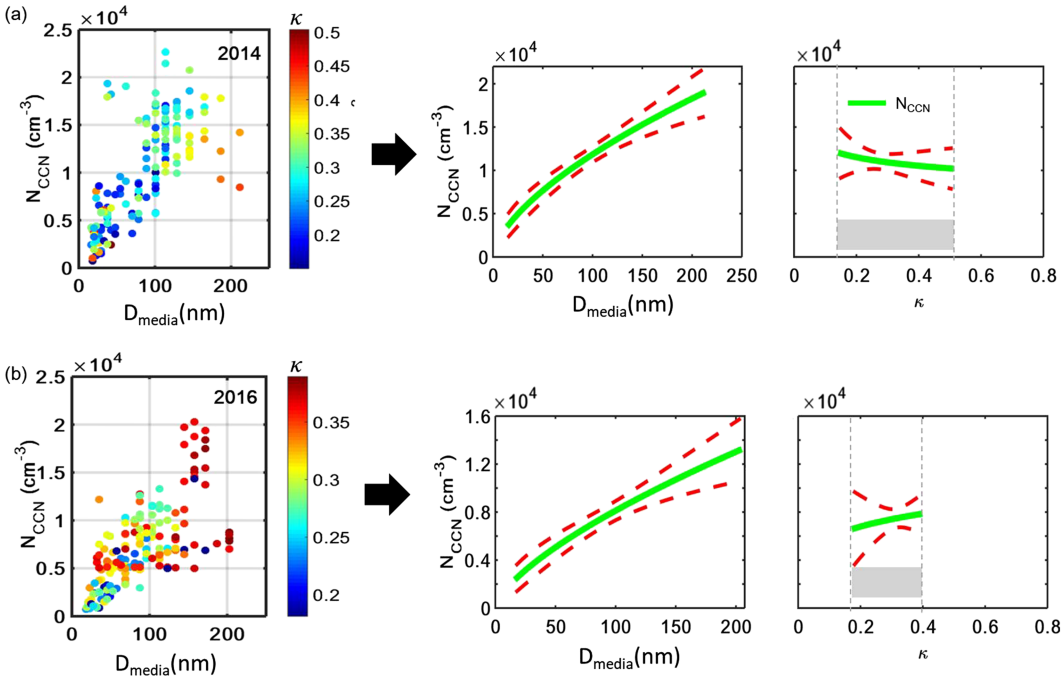

Figure 7. Particle median diameter (D_{media}) and hygroscopic parameter (κ) observed at the initial nucleation period (leftmost panels) and during hazy periods (two rightmost panels) in (a) 2014 and (b) 2016. The CCN number concentration (N_{CCN}) presented here is observed at $S = 0.23\%$. The fitted sensitivities of N_{CCN} to D_{media} and κ based on observations are also shown (green lines). The dotted red lines indicate the range of estimated N_{CCN} at the 95% confidence level.

composition. This allows for the quantification of the effects of changes in chemical composition during the evolution of haze on CCN activity. The evolution of haze reduced the S_c of newly formed particles. The required S_c to activate 50-nm particles decreased from 0.55% ± 0.01% during nucleation periods to 0.45% ± 0.01% during haze events, indicating that the CCN activity was enhanced by ~20% due to changes in aerosol composition. As the particle size increased, the effect due to changes in aerosol composition on S_c became less significant; for example, CCN activity was enhanced by ~12% for particles with diameters of 110 nm. This is because the curvature effect becomes less important as particle diameters increase (Koehler, 1936). Since ambient particles are generally a mixture of inorganics and organics, their CCN activity (or S_c) falls somewhere between that of pure ammonia sulfate and pinic acid. Under clean conditions without nucleation events, which represents the regional background case, particles were also very CCN active with similar S_c to that observed during haze periods.

S_c is sensitive to small changes of less hygroscopic particles ($\kappa < 0.1$; Figure 5b) (Farmer et al., 2015; Petters & Kreidenweis, 2007), while for particles that are already very hygroscopic, that is, $\kappa > 0.2$, the further enhancement of their water solubility (or increase in κ) will not significantly change S_c. During the two field campaigns, ambient particles were already hydrophilic with κ values in the range of 0.2 to 0.65, within which S_c was almost invariant at a given particle diameter. However, at any given κ within the observed range, the CCN activity of particles from clean to hazy conditions was enhanced by more than 80% due to the growth in particle size (Figure 6). This suggests that the growth in particle size is responsible for more than 80% of the enhancement in CCN activity, while changes in particle chemical composition only contribute 12–20% to the enhancement during the evolution of haze.

Further examined was the overall sensitivity of N_{CCN} to changes in diameter (denoted as median diameter, D_{media}) and chemical composition (or κ). The increase in particle size played a leading role in increasing N_{CCN}, while an increase in κ did not increase N_{CCN} (Figure 7). The N_{CCN} observed in 2014 shows a slight reduction with increasing κ. This is because an increase in κ or D_p likely occurs along with a reduction in total N_{CN} caused by aerosol particle coagulation processes or dilution by meteorology, thereby decreasing total N_{CCN}. That most of the observed ambient particles were already hydrophilic partially explains the insensitivity of N_{CCN} to κ. Our results suggest that a direct link between N_{CCN} and aerosol particle size or composition cannot reasonably explain the integrated effects from all of the abovementioned factors.

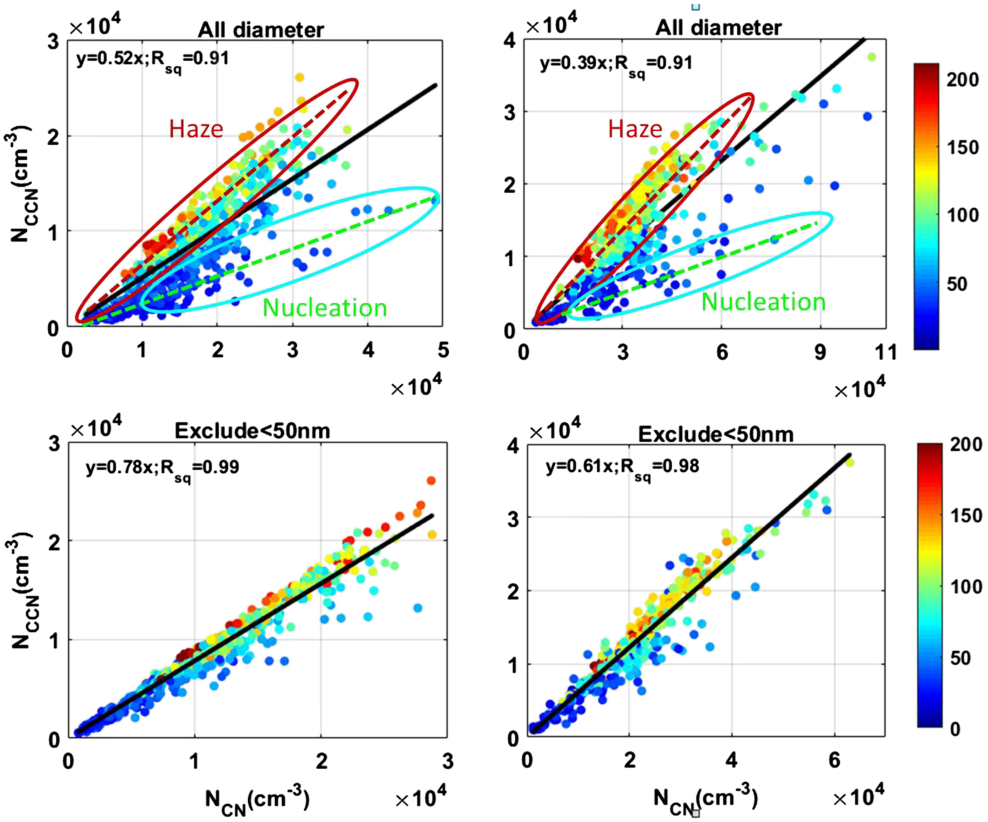

Figure 8. CCN number concentration (N_{CCN}) at supersaturation $S = 0.4\%$ as a function of total particle number concentration (N_{CN}; top panels) and $N_{CN} \geq 50$ nm (bottom panels) in 2014 (left panels) and 2016 (right panels). The different colors are observations with different particle median diameters (unit: nm). The black solid lines are the linear best fit lines through the data. The top panels show linear best fit lines through data from nucleation periods (green dashed lines) and hazy periods (red dashed lines). Linear-fit equations and coefficients of determination (R_{sq}) are also given.

3.4. Correlation Analysis

The correlation between N_{CN} and N_{CCN} was analyzed to evaluate the impact of nucleation and the evolution of haze on predicting N_{CCN}. Nucleated particles have $D_p < 50$ nm, so $D_p = 50$ nm is used to classify particles as nucleation particles or haze in this study. N_{CN} and N_{CCN} (at $S = 0.4\%$) correlate well (with a coefficient of determination greater than 0.97) if nucleated particles are excluded (Figure 8). The slopes (ratio of N_{CCN} to N_{CN}, defined as the activated fraction) changed from 0.52 to 0.78 in 2014 and from 0.39 to 0.61 in 2016 before and after removing the nucleated particles, suggesting that ~60–80% of the CN particles from haze sources can serve as CCN. However, only about 20–30% of nucleated particles are within the CCN size range. The aerosol CCN activity from nucleation and haze-related sources are distinct, suggesting the importance of incorporating the impacts of different atmospheric processes when parameterizing CCN.

4. Conclusions and Implications

The impact of different atmospheric processes on CCN concentrations is expected to be more complex in heavily polluted regions, leading to more challenges in accurately predicting N_{CCN}. Field measurements made in the winters of 2014 and 2016 in Beijing showed that N_{CCN} greatly increased during nucleation-initiated haze events. Enhancement factors of N_{CCN} ranged from 2.2 to 6.5 ($S = 0.76\%$) and from 4.2 to 17.3 ($S = 0.23\%$), the magnitude of which partially depended on the severity of the haze episode. The effect of growth in particle size and chemical composition on CCN activity was quantified. The increase in particle size was responsible for more than 80% of the enhancement in CCN activity, while changes in particle chemical composition contributed 12–20% to the enhancement during the evolution of haze. This is mainly

because ambient particles were already hydrophilic with a hygroscopic parameter of 0.2–0.65, within which S_c showed small changes at a given particle diameter. Enhancements in CCN by nucleation-initiated haze events were much greater than that by NPF. This implies that it may be necessary to reevaluate CCN sources from NPF events, particularly in polluted environments. It is important to consider and include the impact of a longer time scale because the subsequent growth of newly formed particles may last 2–3 days, which this study shows led to more CCN-sized particles.

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