Science of the Total Environment 607–608 (2017) 11–22

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Comparison of aerosol and cloud condensation nuclei between wet and dry seasons in Guangzhou, southern China

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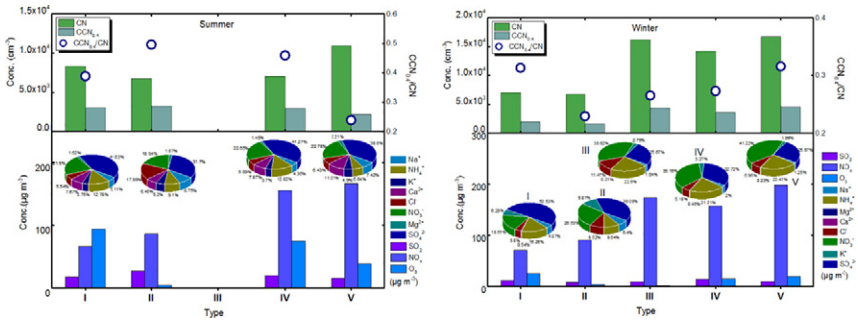
## HIGHLIGHTS

- CCN, CN and CCN/CN are of strong seasonality. $N_{CCN}$ and $N_{CCN}/N_{CN}$ are mostly higher in summer than in winter, but $N_{CN}$ is not.
- Air mass type and pollution sources had significant effect on CN loading as well as CCN concentration.
- Anthropogenic emissions and pollutant aging along transportation matter a lot in changing aerosol CCN activity.
- The pollution influences CN and aerosol CCN activation by different ways based on pollution conditions in two seasons.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 12 June 2017
Received in revised form 27 June 2017
Accepted 27 June 2017
Available online 4 July 2017

Editor: D. Barcelo

*Keywords:*
Aerosol
Cloud condensation nuclei
Pollution
Urban area

## ABSTRACT

Cloud condensation nuclei (CCN), condensation nuclei (CN) and aerosol chemical composition were measured simultaneously at an urban site of Guangzhou from July to August 2015 and in January 2016, and the seasonal variations of aerosol activated fractions ($N_{CCN}/N_{CN}$) as well as their relevant influence factors were further studied accordingly. $N_{CN}$ is generally higher in winter (dry season), whereas $N_{CCN}$ and $N_{CCN}/N_{CN}$ are mostly higher in summer (wet season) instead. In particular, $N_{CCN}$ and $N_{CCN}/N_{CN}$ are much lower at smaller supersaturation levels ($SS < 0.2$) in winter. In spite of similar diurnal variations for $N_{CCN}$ and $N_{CN}$, $N_{CCN}/N_{CN}$ indicates an opposite tendency, relatively lower at midday, dusk and before midnight. Other than the size of particles as well as their chemical composition, some other factors, such as mass, gas precursors, pollutant transportation, meteorological conditions, etc., also contribute to the variations of $N_{CCN}$ and $N_{CCN}/N_{CN}$. Particles from the local source or local-oceanic combination source cast influence on CN and CCN significantly, while the pollutants originating from and crossing over distant polluted areas contribute largely to CCN/CN. $N_{CN}$ and $N_{CCN}$ are relatively higher under pollution-free conditions in summertime and polluted conditions in wintertime, but $N_{CCN}/N_{CN}$ is just the opposite. On various polluted conditions, aerosol CCN activities are greatly discrepant between summer and

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http://dx.doi.org/10.1016/j.scitotenv.2017.06.246

winter, especially during mist or heavy haze periods. The results imply that anthropogenic pollutants exert critical impacts on aerosol CCN activation.



## 1. Introduction

Atmospheric aerosol is ubiquitous throughout the globe, and greatly affects climate and earth radiation balance through changing light scattering and absorption directly and affecting clouds and precipitation processes indirectly (Twomey, 1974; Lohmann and Feichter, 2005). For climate change prediction, one of the largest uncertainties arises from the impacts of primary and secondary aerosols on clouds and radiative forcing (IPCC, 2013). As a subset of aerosol, CCN not only matters in the formation of clouds and precipitation, but also affects atmospheric chemistry and physics (Pruppacher et al., 1997; Seinfeld and Pandis, 2006; Heintzenberg and Charlson, 2009; Pöschl et al., 2009), and even induces essential changes in meteorological models at all scales (Huang et al., 2007). Owing to the substantial increase of anthropogenic emissions of particles and gaseous precursors, aerosol-cloud interaction has changed cloud microphysical and radiative properties to more extent, which emphasizes the crucial function of CCN on predicting regional and global climate changes (Richter et al., 2005; Shao et al., 2006; Zhao et al., 2006; Rosenfeld et al., 2007; Li et al., 2007; Deng et al., 2008). On account of high spatiotemporal variability and complex transformation in the atmosphere, it is of great importance to acquire more information about CCN and aerosol at various regions.

Currently, the field measurements in different environments have pictured a map of global CCN distribution (Delene and Deshler, 2001; Baumgardner et al., 2003; Yum et al., 2005; Detwiler et al., 2010; Jurányi et al., 2010; Leng et al., 2016), and also explored the influence of the size, chemical composition, mixing state and even partial pressure of water vapor on aerosol CCN activation (Pruppacher et al., 1997; Baumgardner et al., 2003; Yum et al., 2005; Rose et al., 2008; Kuang et al., 2009; Gunthe et al., 2009; Sihto et al., 2011). Several investigations have shown that the particle size is more important than chemical composition to determine aerosol activation, despite a considerable change of CCN at low SS caused by chemical composition variation (Dusek et al., 2006; Hudson, 2007; Kuwata et al., 2008; Kuwata and Kondo, 2008; Kammermann et al., 2010; Rose et al., 2008). However, Cubison et al. (2008) and Mochida et al. (2006) argued that detailed chemical composition and mixing state should be paid more attention to in terms of aerosol CCN activity. The response of aerosol activation towards the mixing state of the particles indicates the potential contribution of major anthropogenic pollution sources to CCN group (Che et al., 2016; Wang et al., 2010). In fact, aerosols are mainly produced by primary emissions and secondary formation, influenced by local and regional pollutant sources and weather conditions (Zhang et al., 2010; Du et al., 2011; Cheng et al., 2008; Fu et al., 2008). To better understand CCN, more efforts are needed to focus on the relationship between precursors, CN and cloud droplet (CD) all over the world.

For pollutions, existent emissions and unfavorable atmospheric convection often cause huge particle loading and visibility (Vis.) impairment at the surface and thus threat human health seriously. In recent years, the complex air pollutions have emerged in China, like haze in winter and high concentration of ozone in summer, which have already received widespread attention from both scientists and policy-makers (Xu et al., 2011; Gao et al., 2007). The accumulating particles and unfavorable meteorological conditions (i.e. planetary boundary layer (PBL)) always deteriorate situation, and as a result, causing a serious and long-lasting polluted incident regionally (Leng et al., 2016). Numerous measurements have achieved meaningful CCN data at polluted places in China such as Beijing, Tianjin, Wuqing, Yufa, Shanghai, Hong Kong, Shouxian and suburban of Guangzhou (Yue et al., 2011; Zhang et al., 2012; Deng et al., 2011; Wiedensohler et al., 2009; Meng et al., 2014; Liu et al., 2011; Leng et al., 2014, 2016; Rose et al., 2010). Nonetheless, to date, there are still few studies of CCN measurement performed at one urban site of southern China.

Guangzhou, located in the Pearl River Delta (PRD) of southeastern China, is one of the mega cities undergoing rapid economic growth. Dominated by the Asian monsoon system, Guangzhou is mainly affluent with clean air masses from southwestern sea areas in wet season (summer) and polluted air masses from northern inland areas in dry season (winter) (Zhang et al., 2013). Extreme and continuing pollution accidents have been reduced due to improved air quality in recent years, however, haze event still happens yet (http://www.gdep.gov.cn/). Recognizing the important role of CCN on changing climate and precipitation, it is imperative to explore the relationship between CCN and pollution in this urban area, since few attentions had been paid on before.

This paper exhibits continuous online measurements of CCN and aerosol chemical composition during wet and dry seasons at an urban site of Guangzhou in 2015. It is aimed to characterize general aerosol CCN activity and relevant influence factors in the typical urban place located in southern China, and compare their seasonality to give insights into the discrepancy of aerosol CCN activation under different polluted conditions.

## 2. Instrumentation and observation

The instruments of CCN and aerosol measurements were fixed on the roof of a 50-meter-high building at the monitoring station of South China Institute of Environmental Science (SCIES), Ministry of Environmental Protection in Guangzhou, China (23.07°N, 113.21°E). The site is located in one densely-populated urban district without obvious industrial emission sources surrounded (Tao et al., 2014). The prevailing wind directions are southeasterly in summer and northeasterly in winter.

CCN number concentration was measured by using a continuous 500 $cm^3$/min-flow stream wise thermal gradient CCN counter (CCN-100, Droplet Measurement Technologies, USA) at five discrete SS levels. The principle and operation of this type of CCN counter is described in details elsewhere (Roberts and Nenes, 2005; Lance et al., 2006). The CCN counter was calibrated for airflow, pressure, temperature gradient and optical particle counter (OPC) after using standard ammonium sulfate to ensure stable SS (Leng et al., 2014) and reliable data before the measurement and periodically during the subsequent monitoring. A dryer (Nafion tube) was also applied to reduce the inhaled air relative humidity (RH) to below 20% before entering the counter.

A combination of Scanning Mobility Particle Sizer (SMPS, TSI 3080) and Aerodynamics Particle Sizer (APS) was employed to measure particle number concentrations within the range of 13 nm–20 μm. The AIM software of TSI company is employed to track the variation of size distributions together with applying multiple charge and diffusion correction. The SMPS, consisting of differential mobility analysis (DMA) and condensation particle counter (CPC), can count size-resolved particles of 13–800 nm with a high accuracy, while APS measures particles in 350 nm–20 μm. In order to extend the number size distribution to Stokes equivalent diameters by combining SMPS and APS measured range, the following equation was utilized by premising

spherical particle.

$$D_p = \frac{D_{pa} \times \sqrt{\rho_0}}{\sqrt{\rho_{p,dry}}} \quad (1)$$

where $\rho_0$ is the unit density (1.0 g $cm^{-3}$) and $\rho_{p,dry}$ is the average density of the dry density of the dry particles. Also, the inhaled air was dried by a Nafion tube before entering these instruments.

The dominate inorganic chemical species were measured hourly by a semi-continuous monitoring system, the In-situ Gas and Aerosol Composition (IGAC, Model S-611, Machine Shop, Fortelice International Co., Ltd., Taiwan) monitor, including major inorganic ions ($SO_4^{2-}$, $NO_3^-$ $Cl^-$, $Na^+$, $K^+$, $Ca^{2+}$ and $NH_4^+$) and precursor gases ($SO_2$, $HNO_3$ and $NH_3$). Young et al. (2016) have described the detailed analyzing methods with IGAC monitoring system. In addition, trace gases were collected and analyzed by gas analyzers every 5 min (Thermo Fisher Scientific Inc., Franklin, MA; Model 42i, Model 43i; Model 48i and 49i), such as nitrogen oxide ($NO_x$), sulfate dioxide ($SO_2$), carbon monoxide (CO) and ozone ($O_3$) (Tao et al., 2014, 2015). In addition, all the analyzers were carefully calculated every week. In consideration of the influences by sea salt and nitrate during summer, it was installed with a $PM_{10}$ inlet (URG-2000-30DBQ, URG) in summer and $PM_{2.5}$ cyclones (sharp-cut cyclone, R&P) in winter at the head of sampling. The mass concentration of $PM_{2.5}$ was obtained by Tapered element oscillating microbalance (Rupprecht & Patashnick Company, Inc.; Model 1400a) which was operated continuously.

Additionally, an automatic weather monitoring system (Vaisala Company, Helsinki, Finland, MAWS201) was employed to measure meteorological parameters, such as RH, temperature (T), pressure (P) and precipitation (PR). The Data of visibility (Vis.) was downloaded from the web of Weather Forecast & Reports (The weather company, an IBM business, LLC) (https://www.wunderground.com/). The HYSPLIT model is developed by the Air Resources Laboratory (ARL) of National Oceanic and Atmospheric Administration (NOAA), USA (http://www.arl.noaa.gov/ready/) (Draxler and Rolph, 2003), was also utilized to calculate 36-h air mass backward trajectories starting at 500 m height (AGL) every 6 h per day (Atwood et al., 2013).

## 3. Results and discussion

### 3.1. Characteristics of CN and CCN

Based on nearly 3-month-long measurements, we compare the characteristics of aerosol and CCN in wet (summer) and dry (winter) seasons. Fig. 1 exhibits time scales of hourly CN concentration ($N_{CN}$), CCN concentration ($N_{CCN}$) and $N_{CCN}/N_{CN}$ averages at 0.4% SS in both summer and winter. Because of similar inter- and intra-day variations of CCNs at different supersaturated levels, SS of 0.4% is selected as a proxy and used in the following discussion. Overall, $N_{CN}$ and $N_{CCN}$ almost change synchronously, but $N_{CCN}/N_{CN}$ does not keep the pace entirely. These three variables wave mildly in winter compared to obvious diurnal variations in summer. The fluctuation of $N_{CCN}/N_{CN}$ is generally moderate except for polluted periods, nevertheless, a sharp increase of $N_{CCN}/N_{CN}$ denotes more particles activated as a result of possible aerosol chemical changes.

Fig. 2 presents mean diurnal changes of hourly $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ averages in summer and winter. Notably, $N_{CN}$ and $N_{CCN}$ have similar diurnal variations, with a tri-modal pattern of pronounced peaks at midnight (0:00–1:00 LT), midday (12:00–13:00 LT) and around evening (17:00–20:00 LT) in summer, and a bi-modal pattern of peaks before and around midnight (19:00–22:00 LT and 0:00–1:00 LT) in winter. $N_{CCN}/N_{CN}$ ratios indicate the same variation features as $N_{CCN}$ and $N_{CN}$ in both summer and winter. Additionally, the first peak (2:00–6:00 LT), is higher than the other two (16:00–17:00 LT and 22:00–23:00 LT). Especially, the peak-valley differences of $N_{CCN}$, $N_{CN}$ and $N_{CCN}/N_{CN}$ are usually more significant in winter than in summer. The peaks of $N_{CCN}$ and $N_{CN}$ occurring at noon are possibly related to the increase of fine particles caused by secondary aerosol formation such as photochemical reaction, and the other peaks occurring around evening or at midnight may be caused by stagnant weather conditions and enhanced emissions from frequent human activities such as local traffic and cooking. Crosbie et al. (2015) reported that when the convective boundary layer grows and goes up in the afternoon, $N_{CN}$ decreases more slowly due to nucleation and growth of new particles. During wintertime, nitrite, generated under low temperature, also makes great contributions to a larger component of local aerosol particles. Compared with $N_{CCN}$ and $N_{CN}$, $N_{CCN}/N_{CN}$ varies discrepantly, which is mainly brought by relatively faster increase pace of $N_{CN}$ than $N_{CCN}$. Liu et al. (2011) observed that as $N_{CN}$ increases, $N_{CCN}/N_{CN}$ decreases dramatically and argued that CCNs are not dependent on dust particles without mixing with anthropogenic pollutants.

Additionally, the seasonal averages of $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ ratios at five SS levels are calculated for rainless periods in Table 1. $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ at 0.4% SS are on average of about 7638 $cm^{-3}$, 2990 $cm^{-3}$ and 0.42 in summer, and 10,314 $cm^{-3}$, 2775 $cm^{-3}$ and 0.297 in winter. To be more specific, $N_{CCN}$ has been measured in different environments, such as 1815 $cm^{-3}$ at Hong Kong (SS of 0.5%), 820 $cm^{-3}$ at Vienna (0.5%), 1761 $cm^{-3}$ at Himalaya (0.5%), 420 $cm^{-3}$ at Tucson (0.2%), 2929 $cm^{-3}$ at Shanghai (0.2%), 6000 $cm^{-3}$ at Beijing (0.17%), 5074 $cm^{-3}$ at Kanpur (0.5%) and 4075 $cm^{-3}$ at Seoul (0.6%) (Burkart et al., 2011; Deng et al., 2011; Leng et al., 2013; Meng et al., 2014; Bhattu and Tripathi, 2014; Crosbie et al., 2015; Kim et al., 2017; Roy et al., 2017). Compared with those previous studies, $N_{CCN}$ of Guangzhou is substantially lower than other urban sites at same or similar SS levels, especially when compared with Beijing in northern China, and even far below its own, which was measured in 2006 of 9760 $cm^{-3}$ (Rose et al., 2010). In addition, $N_{CCN}$ appears generally lower in clean areas than that in polluted places, and enlarges with gradually increasing SS levels.

During polluted periods, more anthropogenic aerosols easily activate to be CCN and directly influence $N_{CCN}/N_{CN}$ ratio. Che et al. (2016) discovered that the mean $N_{CCN}/N_{CN}$ ratio at SS of 0.45% ranges from 0.46 to 0.71 in Lin'an when air quality degrades from the clean to the polluted. A similar situation was also observed in Shanghai, $N_{CCN}/N_{CN}$ of 0.28 in clean periods and 0.41 in hazy days at SS of 0.2% (Leng et al., 2014).

Overall, $N_{CN}$ is far higher in winter than in summer, but for $N_{CCN}$, it is higher in summer than in winter at relatively smaller SS (<0.6%) and turns opposite at larger SS (0.8%). $N_{CCN}/N_{CN}$ is obviously higher in summer than in winter at each same SS level. Especially, in winter, $N_{CCN}$ and $N_{CCN}/N_{CN}$ are much lower at smaller SS (<0.2%), which is consistent with the result of Beijing in summer under high temperature, high relative humidity and strong ultraviolet radiation (Matsui et al., 2011). Except for emission and rain scavenging, it can be possibly explained by secondary aerosol formation (e.g. NPF) producing more fine particles when competing with the increase of preexisting particle in both size and hygroscopicity (Kuang et al., 2009; Kerminen et al., 2005; Kulmala et al., 2004). Additionally, the main sources of carbonaceous aerosols in winter are coal combustion and automobile exhaust, which are characterized with submicron particles of poor hygroscopicity (Tao et al., 2014). To our knowledge, CCN and aerosol CCN activation depend on the number, size, chemical composition and mixing state of particles, and so on (Rose et al., 2008; Sihto et al., 2011). In the following sections, particle properties and other influence factors will be focused on in order to gain more insights into the seasonal differences of aerosol CCN activity.

### 3.2. Influence factors on CN and CCN

#### 3.2.1. Particle size and amount

Atmospheric particles should be large enough (i.e. 50–100 nm) to activate into CCN in boundary-layer clouds (Kerminen et al., 2012). In order to lucubrate aerosol evolution, the measured CN is classified into

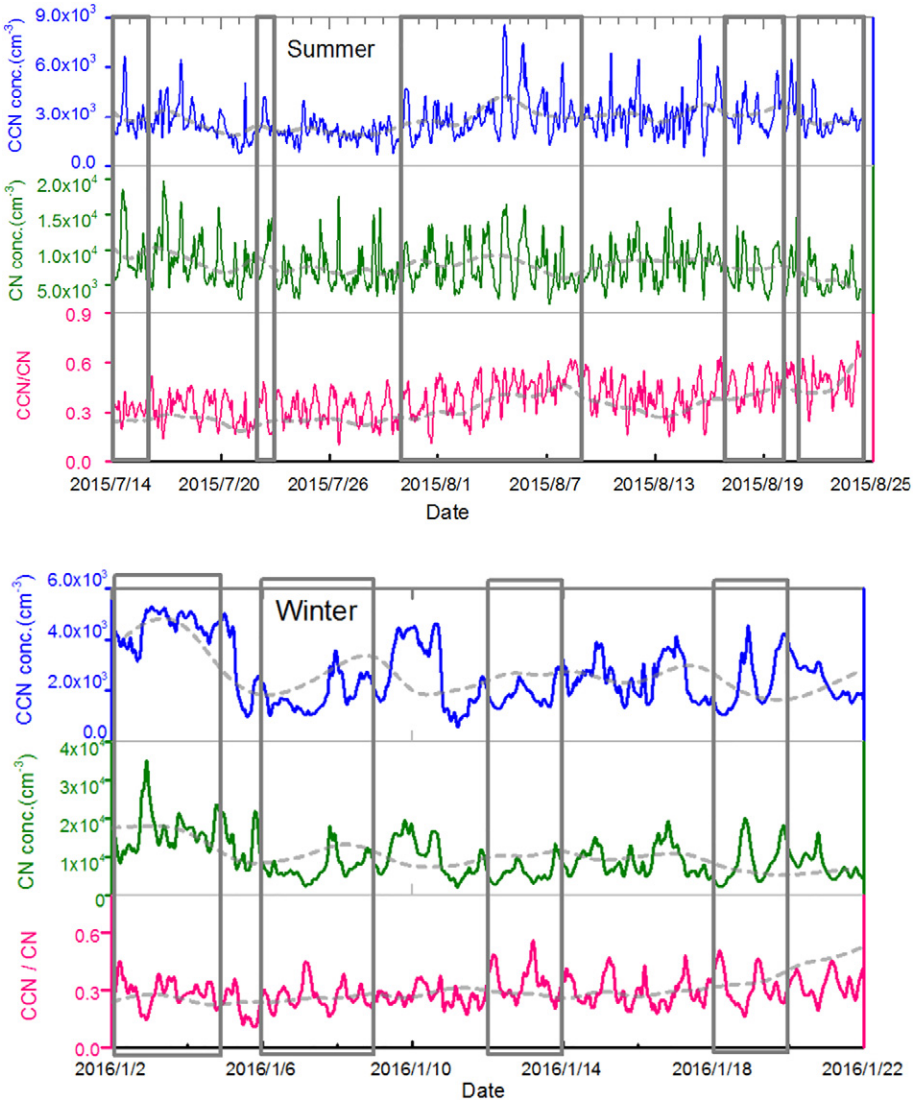


**Fig. 1.** Time series of hourly condensation nuclei ($N_{CN}$), cloud condensation nuclei ($N_{CCN}$) and $N_{CCN}/N_{CN}$ at 0.4% SS in summer and winter. The grey lines are daily averages, and the grey boxes represent rainless days.

three categories according to size as nucleation (10–20 nm), Aitken (20–100 nm) and accumulation (100–750 nm) modes. Generally speaking, the particles of 20–200 nm preponderate in CN group, occupying 87–92%, and the width of CN spectrum is larger in winter than in summer (Fig. 3). As expected, ultrafine particles preponderate in the population of urban aerosol (Gao et al., 2007), and ambient

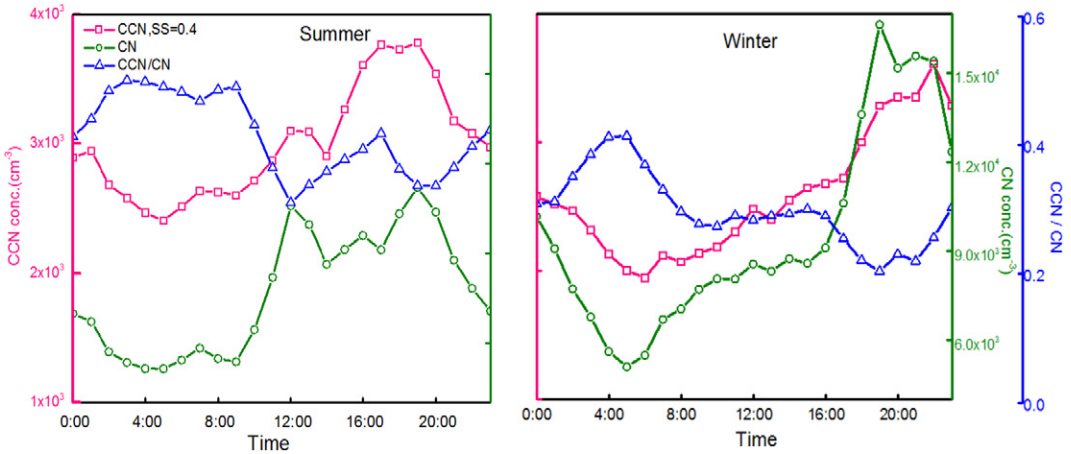


**Fig. 2.** Diurnal variations of hourly $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ at 0.4% SS in summer and winter.

**Table 1**
Seasonal averages of cloud condensation nuclei ($N_{CCN, SS}$), condensation nuclei ($N_{CN}$) and $N_{CN}$ to $N_{CCN}$ ratio.

| Season | Episode | SS [%] | $N_{CCN,SS}$ [$cm^{-3}$] | | | | $N_{CN}$ [$cm^{-3}$] | | | | $N_{CCN}/N_{CN}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Min | Max | Mean | Std | Min | Max | Mean | Std | Mean | Std |
| Summer | Entire period | 0.2 | 419 | 4017 | 1538 | 556 | | | | | 0.22 | 0.09 |
| | | 0.4 | 1074 | 8621 | 2990 | 1235 | | | | | 0.42 | 0.12 |
| | | 0.6 | 1012 | 11,757 | 3847 | 1653 | | | | | 0.53 | 0.13 |
| | | 0.8 | 1187 | 13,181 | 4517 | 1930 | | | | | 0.62 | 0.14 |
| | | 1.0 | 1426 | 14,307 | 5044 | 2126 | | | | | 0.69 | 0.15 |
| | | All | | | | | 2143 | 18,875 | 7638 | 3330 | | |
| | Clean period | 0.2 | 419 | 4017 | 1484 | 588 | | | | | 0.20 | 0.08 |
| | | 0.4 | 1075 | 8621 | 3017 | 1450 | | | | | 0.39 | 0.12 |
| | | 0.6 | 1012 | 11,757 | 3994 | 1971 | | | | | 0.50 | 0.13 |
| | | 0.8 | 1187 | 13,181 | 4788 | 2316 | | | | | 0.60 | 0.14 |
| | | 1.0 | 1426 | 14,307 | 5415 | 2542 | | | | | 0.67 | 0.15 |
| | | All | | | | | 2652 | 18,875 | 8246 | 3595 | | |
| | Polluted period | 0.2 | 614 | 3562 | 1599 | 603 | | | | | 0.26 | 0.12 |
| | | 0.4 | 1172 | 7218 | 2883 | 1158 | | | | | 0.45 | 0.13 |
| | | 0.6 | 1420 | 9249 | 3605 | 1508 | | | | | 0.55 | 0.14 |
| | | 0.8 | 1656 | 10,633 | 4145 | 1683 | | | | | 0.63 | 0.15 |
| | | 1.0 | 1798 | 11,028 | 4560 | 1840 | | | | | 0.70 | 0.16 |
| | | All | | | | | 2143 | 17,003 | 7193 | 3775 | | |
| Winter | Entire period | 0.07 | 46 | 120 | 115 | 88 | | | | | 0.011 | 0.005 |
| | | 0.1 | 77 | 177 | 165 | 114 | | | | | 0.017 | 0.007 |
| | | 0.2 | 373 | 620 | 542 | 243 | | | | | 0.063 | 0.027 |
| | | 0.4 | 1494 | 4875 | 2775 | 1367 | | | | | 0.297 | 0.082 |
| | | 0.8 | 1900 | 9721 | 4550 | 2740 | | | | | 0.446 | 0.086 |
| | | All | | | | | 3448 | 20,706 | 10,314 | 6204 | | |
| | Clean period | 0.07 | 21 | 108 | 58 | 21 | | | | | 0.010 | 0.004 |
| | | 0.1 | 40 | 208 | 92 | 32 | | | | | 0.015 | 0.007 |
| | | 0.2 | 241 | 604 | 395 | 74 | | | | | 0.068 | 0.026 |
| | | 0.4 | 1032 | 4875 | 1979 | 740 | | | | | 0.313 | 0.090 |
| | | 0.8 | 1217 | 9721 | 3066 | 1697 | | | | | 0.451 | 0.094 |
| | | All | | | | | 2748 | 20,706 | 7043 | 4027 | | |
| | Polluted period | 0.07 | 19 | 378 | 184 | 93 | | | | | 0.012 | 0.006 |
| | | 0.1 | 28 | 533 | 254 | 120 | | | | | 0.018 | 0.008 |
| | | 0.2 | 169 | 1216 | 735 | 244 | | | | | 0.054 | 0.018 |
| | | 0.4 | 1443 | 5304 | 3901 | 1151 | | | | | 0.279 | 0.062 |
| | | 0.8 | 2133 | 12,587 | 6634 | 2553 | | | | | 0.447 | 0.073 |
| | | All | | | | | 5390 | 37,406 | 14,967 | 6093 | | |

aerosol enjoys a wider distribution during polluted periods (Leng et al., 2016).

The statistical analysis explicates that $N_{CCN}$ is closely related to accumulation mode $N_{CN}$ (correlation coefficient, $R^2 = 0.63$) in summer while it is associated with both Aitken $N_{CN}$ ($R^2 = 0.84$) and accumulation mode $N_{CN}$ ($R^2 = 0.99$) in winter. This result reveals that the size is expected to be very critical to particle activation, in particular of accumulation mode size. As seen in Fig. 4, $PM_{2.5}$ is perceived to correlate strongly with $N_{CCN}$ and $N_{CN}$ in summer ($R^2 = 0.7$) and winter ($R^2 = 0.75$ and 0.95).

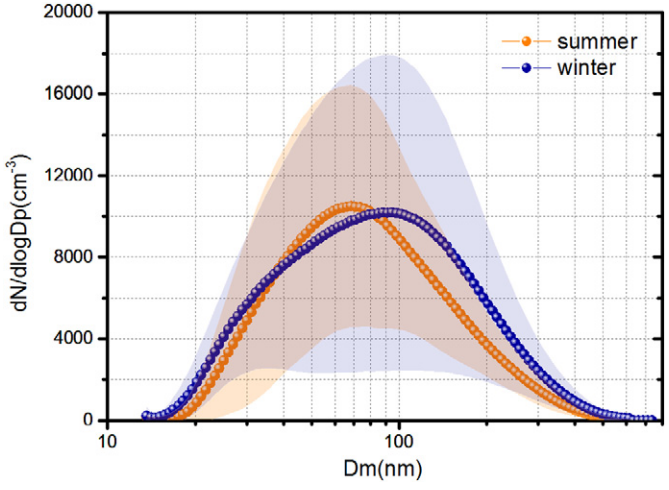


**Fig. 3.** Mean aerosol number concentration spectrum of 10–750 nm in summer and winter.

Unfortunately, a poor linear relationship is found between $N_{CCN}/N_{CN}$ and $PM_{2.5}$, indicating that although it is important to activation to some extent, particle amount incompletely reflects aerosol CCN activity.

### 3.2.2. Particle chemical composition

Aerosol is able to absorb water vapor to enhance light extinction and then reduce visibility, and it is mainly caused by the fact that soluble inorganic ions take up about 30% of the particles in the urban atmosphere (Hillamo et al., 1998; Andrews et al., 2000; Chow et al., 2006; Seinfeld and Pandis, 2006; Lin et al., 2013). Besides ambient particle size, hygroscopicity linking closely with particle chemical compositions and especially mixture with water soluble materials, plays an important role in aerosol CCN activation (Kulmala et al., 2007). The more space of the particles occupied by water soluble components, the higher $N_{CCN}$ concentration emerges in the atmosphere (Leng et al., 2014).

Major water soluble inorganic ion (WSII) concentrations of particles are displayed in Fig. 5, including four anions of $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $F^-$ and five cations of $Na^+$, $NH_4^+$, $Ca^{2+}$, $K^+$, $Mg^{2+}$. Overall, with growing $PM_{2.5}$, WSII amounts usually increase accordingly, in particular of sulfate, nitrate and ammonium. The mean integrated WSII concentration is 18.5 μg $m^{-3}$ in summer, much lower than the measurement in 2014 by Tao et al. (2017). In summer, the maximum contents are $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ with averages of 7.8, 4.1 and 2.4 μg $m^{-3}$, accounting for 42%, 22% and 13% of total WSIIs, respectively. As for winter, the dominated fractions of WSIIs are still $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$, with averages of 10.2, 8.7 and 5.7 μg $m^{-3}$, which account for 36%, 31% and 20% of total WSIIs (28.3 μg $m^{-3}$), respectively. As a whole, WSIIs totally account for 57.3% and 54.2% of $PM_{2.5}$ in summer and winter, respectively.

According to the Köhler theory (Köhler, 1936), the effective hygroscopicity parameter κ proposed by Petters and Kreidenweis (2007) is

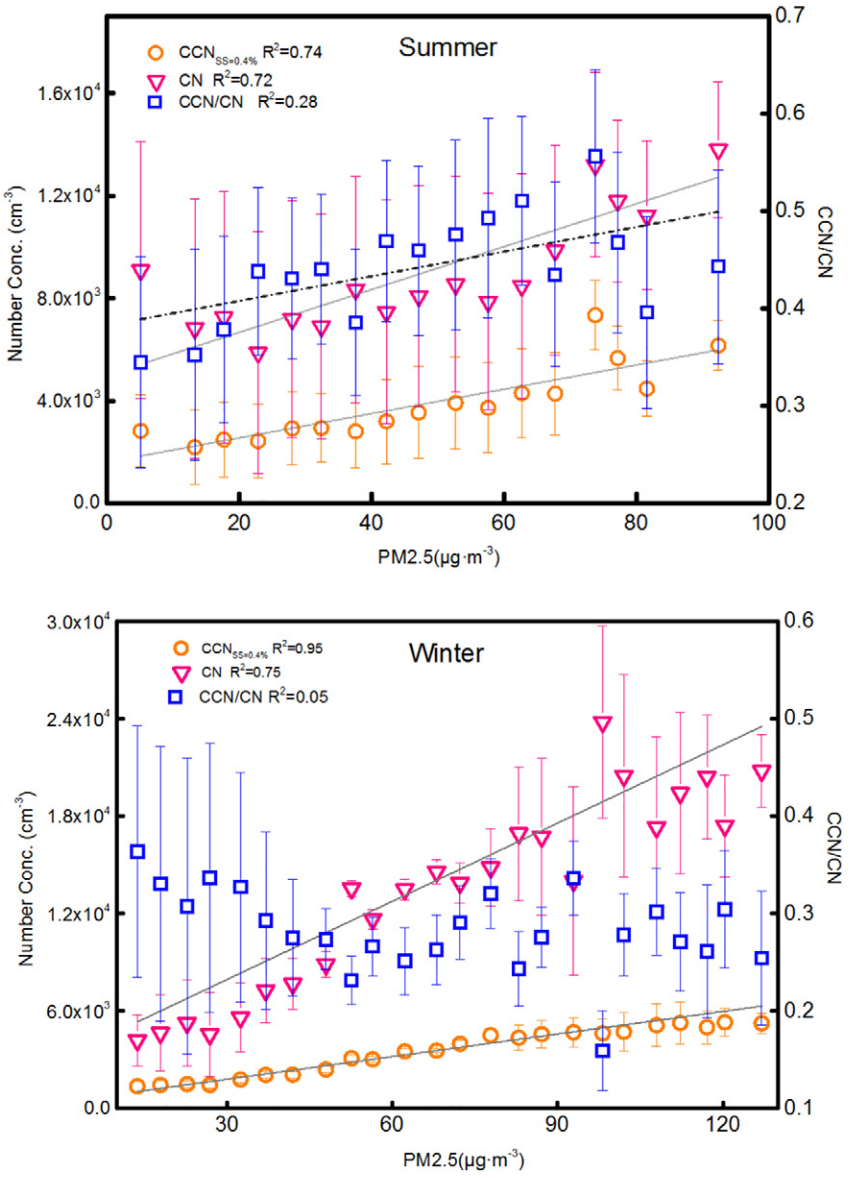


**Fig. 4.** Scatter plots of mean $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ at 0.4% SS vs. $PM_{2.5}$ concentrations that are segmented at 5 μg $m^{-3}$ and averaged over every bin.

capable to describe the relationship between particle size and critical SS. (Rose et al., 2010). Given the assumption that aerosols are internally mixed, the parameter κ is calculated/reckoned through weighting the volume fractions of chemical components to describe the particle ability of uptaking water vapor to activate into CCN and to explaining the differences of hydrophilic characters between wet and dry seasons.

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (2)$$

Here, $\varepsilon_i$ is the volume fraction of the chemical composition, and $\kappa_i$ is the κ-value of the chemical components. κ is about 0.6 for ammonium sulfate and nitrite, 1.0 for sodium chloride and marine aerosols, and zero for black carbon (BC) and insoluble compounds (Niedermeier et al., 2008; Rose et al., 2010; Leng et al., 2014). In Guangzhou, nitrate and sulfate have been proved to be the great contributors to particle inorganic components (Tao et al., 2012), and the calculated κ is on average of approximately 0.3 in summer and 0.22 in winter, consistent to $N_{CCN}/N_{CN}$ seasonality (Table 1). In brief, the particle hygroscopicity can not only largely determine aerosol CCN activation, but also effectively reflect particle chemical composition and its variation, particularly water soluble substance.

Water soluble $NO_3^-$ and $SO_4^{2-}$ are always transformed from gaseous precursors by homogeneous or heterogeneous chemical reactions in the atmosphere. To evaluate the transformation degree of $SO_2$ and $NO_2$, nitrogen oxidation ratio (NOR) and sulfur oxidation ratio (SOR) are calculated by the equations of Tao et al. (2012). Averaged SOR is 0.21 in summer and 0.39 in winter, basically higher than 0.1, while NOR is 0.09 in both summer and winter, implying that $SO_2$ oxidation plays a significant role in particle formation and growth. Even so, there exists no obvious evidence to illustrate the strong relation between aerosol CCN activity and SOR at different time scales.

$NO_3^-/SO_4^{2-}$ has been widely used as one indicator to qualitatively judge whether the key contributor to sulfate and nitrogen is mobile or stationary sources (Arimoto et al., 1996). When the ratio is <1, stationary sources are believed as the first origination, otherwise, mobile sources generally contribute more. At present, $NO_3^-/SO_4^{2-}$ is on average of 0.56 in summer and of 0.66 in winter, implying that stationary sources emit relatively more emissions than mobile in Guangzhou nowadays. In addition, $NO_3^-/SO_4^{2-}$ is usually higher in polluted periods than in clean periods, such as 0.57 vs. 0.54 in summer and 1.11 vs. 0.38 in winter. It's worth noting that the pollutants are significantly influenced by primary emissions from mobile sources (e.g. vehicle), which

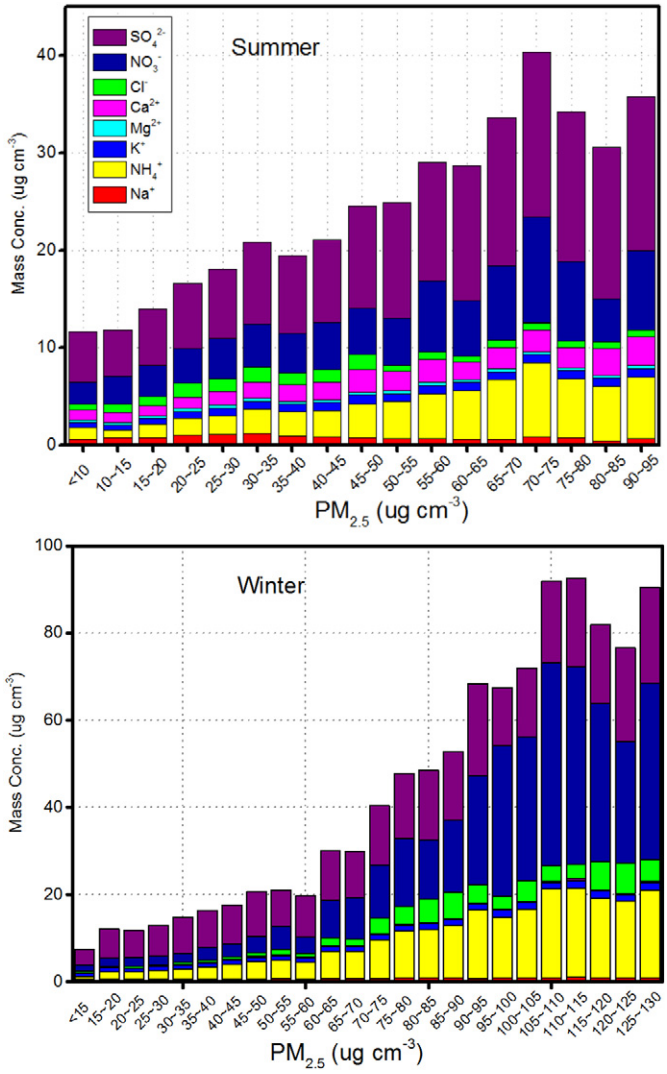


**Fig. 5.** Mean water soluble ion composition distributions of $PM_{2.5}$ in summer and winter.

indirectly throw lights on the origin and evolution process of CN and even CCN during wintertime. Tian et al. (2016) have also observed that $NO_3^-/SO_4^{2-}$ is 0.54 during 20% of best visibility time and 0.58 during 20% of worst visibility time in Suzhou in January 2013, which is similar with our results but contrary to Wang et al.'s (2006) results of 0.64 in haze days and 0.83 in normal days in Beijing.

### 3.2.3. Pollutant transportation and sources

Air mass trajectory analysis has been used in recent studies to explore the influence of pollutant transportation on aerosol and CCN at larger scales (Rojas et al., 2006). Clustered backward trajectories can examine the main movement pathways of air masses arriving at target locations in the atmosphere and track the potential originations of their carriers. 36-h air mass back trajectories starting at 500 m above the ground level (AGL) in all the rainless days were calculated and clustered into some major pathways (Fig. 6).

In summer, air masses arriving at Guangzhou mainly come from the oceanic zones of South China Sea, such as cluster-1 (35%), cluster-2 (21%) and cluster-3 (15%), and northern inland areas, such as cluster-4 (25%) and cluster-5 (4%). Compared with cluster-2 crossing over a long distance, cluster-1 and cluster-3 move slowly and pass coastal areas, carrying more local pollutants and mixing with marine materials. Cluster-4 and cluster-5 carry continental and anthropogenic pollutants from distant inland areas. In winter, air masses come from remote continent or surrounding areas, such as local cluster-1 (31%) and cluster-2 (36%), slow-moving cluster-3 (31%) and fast-moving cluster-4 (2%). As a consequence, all the clusters can be summarized as both continental and marine types in summer, and the only continental type in winter.

Clearly, in summer, $N_{CN}$ and $N_{CCN}$ are always larger in marine type air and lower in continental type air, but $N_{CCN}/N_{CN}$ is just the opposite to them (Fig. 6), consistent with the conclusion made by Liu et al. (2011). $SO_4^{2-}$, $NH_4^+$, $Ca^{2+}$ exist abundantly in continental type air, while marine type air is rich in $NO_3^-$, $Cl^-$, $Na^+$. Although originating from the same oceanic area, $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ of the marine type air differ a lot, especially in the fact that the minimum $N_{CN}$ and $N_{CCN}$ appear in cluster-2 while the minimum $N_{CCN}/N_{CN}$ appears in cluster-3. Additionally, it is found more $SO_4^{2-}$, $NH_4^+$, $NO_3^-$, $Ca^{2+}$ in slow moving cluster-1 and cluster-3, and more $Cl^-$, $Na^+$ in fast moving cluster-2. Regarding the continental air, $N_{CN}$ is larger in cluster-4, but $N_{CCN}$ and $N_{CCN}/N_{CN}$ are relatively larger in cluster-5 featuring a long travelling distance. There are more $SO_4^{2-}$, $NH_4^+$, $Ca^2$ in fast moving cluster-5, and more $NO_3^-$, $Cl^-$ in slow moving cluster-4. In winter, $N_{CN}$ and $N_{CCN}$ are the largest in local cluster-1 and the lowest in slow cluster-2, which is in accordance with the result of Yum et al. (2007). However, $N_{CCN}/N_{CN}$ reaches maximum in cluster-2 and minimum in cluster-3. Correspondingly, $SO_4^{2-}$, $NH_4^+$, $NO_3^-$, $Cl^-$ have a similar situation with $N_{CN}$ and $N_{CCN}$, and $Ca^{2+}$, $Na^+$, and $K^+$ have no great differences among these clusters.

In summary, $N_{CN}$ and $N_{CCN}$ were closely associated with aerosol chemical composition, in particular of water soluble substance such as $SO_4^{2-}$, $NH_4^+$ and $NO_3^-$, but $N_{CCN}/N_{CN}$ is not the same. The local source contributes significantly to CN and CCN, indicating the role of water soluble ions in high concentration, especially $SO_4^{2-}$ and $NO_3^-$, most obviously in cluster-1 of winter. A combination of pollutants from local and oceanic sources also contributes largely to CN and CCN, indicative of high concentration of water soluble ions, especially $NO_3^-$, most obviously in oceanic type air of summer. The pollutants originating from and crossing over distant polluted areas contribute largely to $N_{CCN}/N_{CN}$, illustrating more $SO_4^{2-}$, $NH_4^+$, $Ca^{2+}$ and less $NO_3^-$, $Cl^-$, $Na^+$ in continental type air of summer, when compared to cluster-4 of winter. For oceanic type air in summer, compared with cluster-2, it is clear that cluster-1 and cluster-3 move relatively more slowly, and as the particles' aging time gets prolonged, $SO_4^{2-}$, $NH_4^+$, $NO_3$ increase and $Na^+$, $Cl^-$ decrease accordingly, thus resulting in higher $N_{CN}$ and $N_{CCN}$. Note that anthropogenic pollutants possess relatively complex compositions and consequently cause discrepancy of aerosol hygroscopicity. In a word, atmospheric transport changes a lot of aerosol chemical properties in case of downwind due to source diversity, air mass moving speed, particle mixing and aging state, particle decomposition (e.g. nitrate), and so on, which significantly restricts aerosol CCN activity.

### 3.2.4. Meteorological conditions

To our knowledge, meteorological conditions can affect CN and CCN to some extent through indirectly altering aerosol physic-chemical properties (Leng et al., 2016; Liu and Li, 2014). Fig. 7 displays the mean $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ at 0.4%, and 0.8% SS as a function of temperature, which are averaged every 1 °C bin. In summer, $N_{CN}$ and $N_{CCN}$ firstly decrease down to the trough, and then increase up to the peak, and then decrease significantly with growing temperature from 25 °C to 36 °C, while $N_{CCN}/N_{CN}$ slightly increases with small fluctuation. In comparison, during winter, $N_{CN}$ and $N_{CCN}$ almost increase steadily up to peak and then decrease with rising temperature from 10 °C to 25 °C, while $N_{CCN}/N_{CN}$ fluctuates with a decreasing trend.

In fact, atmospheric temperature is a momentous factor, on which secondary aerosol formation and growth, and pre-existing particle aging may rely. Owing to soluble substances dominant in marine aerosols for most air masses in summer, activated CCN enjoys higher proportion with little differences. As described by Liu et al. (2011), the different phases of aerosol can be shifted as temperature changes. Just like nitrate, volatile aerosols can vaporize and deplete easily at high

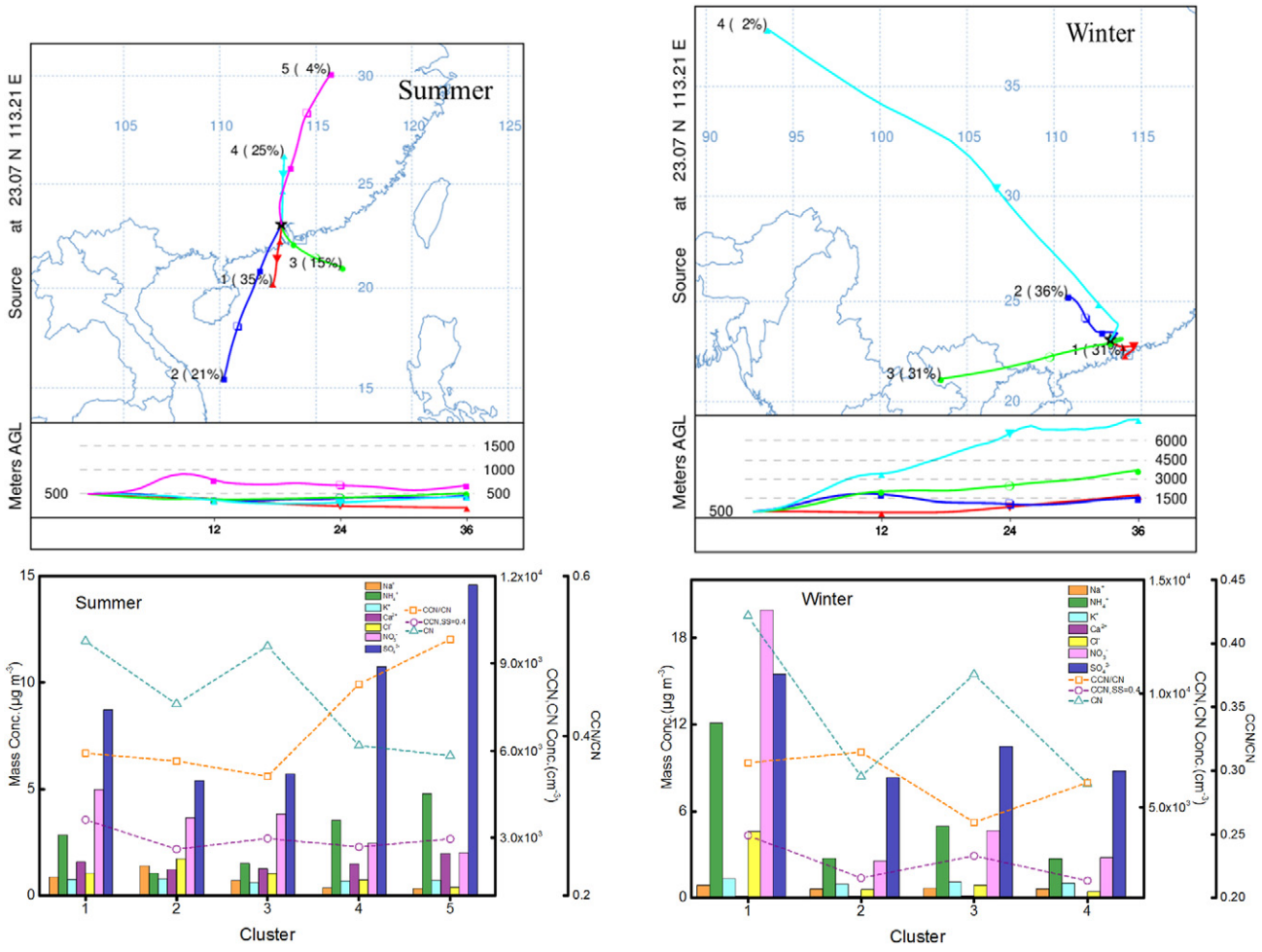


**Fig. 6.** Clustered 36-h air mass backward trajectories and corresponding major water-soluble inorganic chemical compositions in $PM_{2.5}$, $CCN_{0.4}$, CN and $CCN_{0.4}$/CN in summer and winter.

temperature during distant transportation. Another reason for this dependency may be associated with aerosol chemical reaction such as photochemical, liquid and multiphase reactions, especially in strong atmospheric oxidizing conditions. Obviously, sunny conditions (i.e. $O_3$) with higher temperature and RH may promote new particle formation and surface heterogeneous reactions.

However, in winter, relative low temperature, together with stagnant conditions, always result in pollutions (e.g. haze) and as $N_{CN}$ increases, $N_{CCN}$ and $N_{CN}/N_{CCN}$ decrease at smaller SS (<0.8%) and grow at bigger SS (≥0.8%) (Table 1). A large number of particles and gaseous pollutants accumulate in PBL to improve particle aging by surface heterogeneous reactions, especially in strong atmospheric oxidizing conditions. Moreover, increasing carbonaceous material from primary emission and secondary transformation, in particular of secondary organic aerosol (SOA), exerts a nonnegligible force on water soluble components and aerosol CCN activation. By the way, besides temperature, the intrinsic meteorological conditions to affect CCN and CN formation have rarely been studied because they are believed as unimportant.

### 3.3. Aerosol CCN activation under pollution conditions

The pollution provides one perfect opportunity to explore atmospheric processes and factors that change aerosol physical and chemical properties, such as size, water soluble content, mixing state and aging degree, and subsequently disturb aerosol CCN activation.

According to the widely known definition of haze, mist and fog by World Meteorological Organization (WMO), visibility (Vis.) and relative humidity (RH) have been used as key criterions to classify weather situations related to pollutions, especially with particulate pollutants (Che et al., 2016; Leng et al., 2016), and weather-pollution has been categorized into six types of clean, haze, heavy haze, mist, transition from mist to fog, and fog during the whole investigation (Table 2). Notably, if RH keeps between 80% and 90%, it is viewed as a complex of mist-fog coexistence or their transition. Additionally, $PM_{2.5}$, up to 75 μg $m^{-3}$ or more, (one of the government standards of air quality (AQ) in China), is equally taken as the standard to identify pollutions.

Table 1 also features $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ in clean and polluted periods. Overall, $N_{CCN}$ and $N_{CCN}/N_{CN}$ generally increase with rising SS in both clean and polluted periods, especially in winter time, and the maximum is almost over 10 times of the minimum. Furthermore, $N_{CN}$ and $N_{CCN}$ are relatively higher in clean periods of summer and in polluted periods of winter, and $N_{CCN}/N_{CN}$ is almost the opposite. As for clean periods, $N_{CCN}$ and $N_{CCN}/N_{CN}$ are higher in summer than in winter, with largest discrepancy over 3 times of $N_{CCN}$ at low SS (≤0.2%). However, in polluted periods, $N_{CCN}$ are higher in summer than in winter at low SS (≤0.2%) with largest discrepancy over 2 times, but lower instead at high SS (≥0.4%). However, $N_{CCN}/N_{CN}$ is always larger in summer than in winter at any same SS.

In order to comprehend pollution influence on aerosol CCN activation, several related criterions are utilized to analyze the extents of pollution conditions (Table 2). Considering the differences between the two seasons, ozone level exceeding 200 μg $m^{-3}$, according to China's government standard of $O_3$ in urban residential areas (Grade II), is set as an additional criterion for further investigation, especially in summer. As expected, more high-$O_3$ periods are found in summer, and relatively higher $O_3$ levels mostly occur in clean and haze days (Fig. 8).

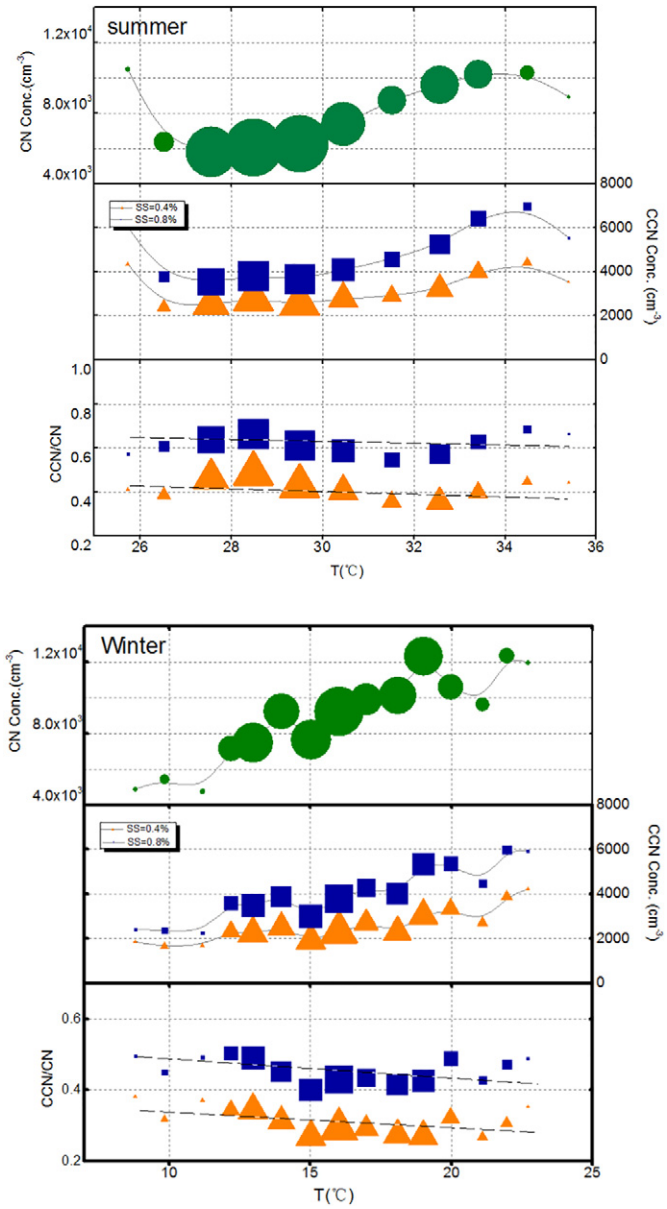


**Fig. 7.** Scatter plots of mean $N_{CN}$, $N_{CCN}$ and $N_{CCN}/N_{CN}$ at 0.4% and 0.8% SS vs. temperatures that are segmented at 1 °C and averaged over every interval.

Apparently, ozone and solar radiation accelerate photochemistry reactions in the ambient air, and then promote the formation and growth of new particles (Tian et al., 2016; Baumgardner et al., 2003). The enhancement of secondary formed aerosols (i.e. sulfate, nitrate) mainly enlarges the quantity of fine particles that are easily to activate into CCN although in extremely small size (Deng et al., 2011; Gunthe et al., 2011; Wang et al., 2010; Shen et al., 2008). In summer, high ozone levels occurred in clean and haze periods, and the bigger corresponding $N_{CCN}/N_{CN}$ ratio was found in haze rather than in clean periods (Fig. 8), illustrating that the pollution enlarges the proportion of activated CCN through particle aging, indicative of water soluble substance of $SO_4^{2-}$, $NO_3^-$, $NH_4^+$ as well. Compared with haze periods, heavy haze appeared together with lower visibility and ozone concentration, and also the significant rising of $N_{CN}$ and the declining of $N_{CCN}$ and $N_{CCN}/N_{CN}$. The possible reason is that the increased hydrophobic or hydrophilic carbonaceous components (i.e. BC), strengthen particle coagulation and weaken particle aging in the case of high particle concentration. As for the mist, in contrast to haze, the larger aerosol CCN activity was mainly dependent on particle heterogeneous or/and liquid-phase reactions in environment of higher relative humidity and gaseous pollutant amount (i.e. $SO_2$). It's worth noticing that $Na^+$ and $Cl^-$ enjoy the highest proportion among the soluble chemical substances, indicating sea salts' contribution to promoting aerosol CCN activity to some extent.

**Table 2**
Key criterion for different pollution conditions.

| Type | Visibility (km) | Relative humidity (%) | Episode |
|---|---|---|---|
| I | VIS ≥ 10 | RH ≤ 80 | Clean |
| II | 5 ≤ VIS < 10 | 80 < RH ≤ 90 | Mist |
| III | VIS < 5 | 80 < RH ≤ 90 | Transition from mist to fog |
| IV | 5 ≤ VIS < 10 | RH ≤ 80 | Haze |
| V | VIS < 5 | RH ≤ 80 | Heavy haze |
| VI | VIS < 10 | RH > 90 | Fog |

On the whole, in winter, $N_{CCN}$ and $N_{CN}$ increases with descending visibility and ascending $PM_{2.5}$, and $N_{CCN}/N_{CN}$ changes smoothly around 0.3 except for mist period (Fig. 8). Since the pollutions majorly come from local primary emissions in winter (Tao et al., 2012, 2014), particle aging probably plays a more important role in enhancing aerosol CCN activity. In summary, aerosol CCN activation is mainly influenced by the secondary formation and growth of particles in summer, while particle aging is the top influence factor in winter. Surprisingly, CN and aerosol CCN activity perform very differently between summer and winter in both heavy haze and mist periods.

Leng et al. (2014) observed that aerosol CCN activity is relatively lower in fog-haze cases (the transition period of haze and fog) than that in hazy cases in winter of Shanghai. Che et al. (2016) found that aerosol CCN is more active during heavy haze (0.6–0.7) than during clean periods (0.5) at Lin'an of the Yangtze River Delta. There may exist different physic-chemical mechanisms and processes of aerosol CCN activation under various pollution conditions. Recently, the homogeneity and mixing state of particles is an open question in understanding aerosol CCN activation and predicting CCN spectra, in particular of heavy pollution and haze-fog transition periods.

## 4. Conclusions

Guangzhou is one of the mega cities in the coastal areas of South China. This study presents recent ground-based measurements of aerosol and cloud condensation nuclei (CCN) to lucubrate the CCN seasonal variation and its relation with condensation nuclei (CN), and to compare the influences of pollutions on aerosol CCN activation in summer and winter.

CCN, CN and aerosol activated fraction (CCN/CN) exhibit a strong seasonality. The mean $N_{CCN}$ of Guangzhou is far lower than that of northern cities such as Beijing and Shanghai at same or near supersaturation (SS) levels. On the whole, $N_{CCN}$ and $N_{CCN}/N_{CN}$ are mostly higher in summer than in winter, but $N_{CN}$ is on the contrary. Particle size, amounts, chemical composition and hygroscopicity, even atmospheric transportation and meteorological conditions determine the apparent ability of ambient aerosol to activate into CCN together. Anthropogenic emissions and pollutant aging along transportation matter a lot in changing aerosol CCN activity. The pollution hugely influences CN and aerosol CCN activation by different ways based on pollution conditions in summer and winter time. In future, more information of pollution formation and forcing to CCN of two seasons will be presented.

The urban pollution provides important chances to explore how anthropogenic pollutants affect the physical, chemical and hygroscopic properties of aerosol and CCN. The secondary particle formation as a result of photochemical reactions and its growth process, and the particle aging can possibly promote particle hygroscopicity and then activate aerosols. In the future, more efforts are needed to focus on the mist-fog-haze transition for aerosol is very complicated.

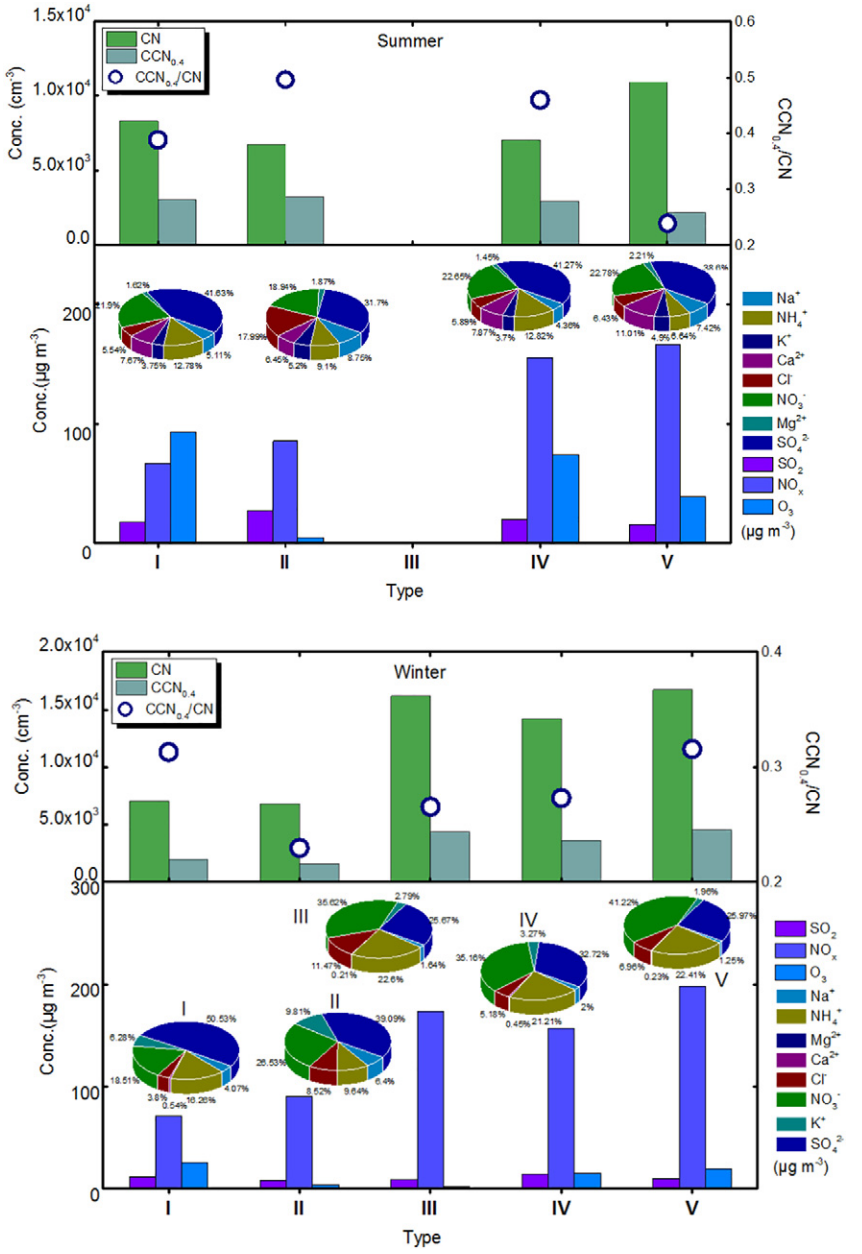


**Fig. 8.** CCN, CN, CCN/CN ratio and corresponding major chemical compositions under different pollution conditions.

## Acknowledgments

This research is supported by the National Natural Science Foundation of China (41475109, 41475119, 21577021, 21377028, 91637101), the National Key Research and Development Program of Ministry of Science and Technology (2016YFC0202003, 2014BAC16B01), and partly by the Science and Technology Commission of Shanghai Municipality (16ZR1431700) and suggestions from the Jiangsu Collaborative Innovation Center for Climate Change.

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