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Key Points:

- Field measurements prove contribution of organic aerosols (OA) in anthropogenically influenced region to immersion mode ice nucleation (IN)
- OA oxygenated by photooxidation and lower relative humidity showed a correlation with increased at noon
- Nonvolatile OA at 350°C heating have a higher IN efficiency than that of black carbon

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

D. Liu,
dantongliu@zju.edu.cn

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Author Contributions:

Conceptualization: Ping Tian, Dantong Liu
Data curation: Kang Hu, Ruijie Li, Quan Liu
Funding acquisition: Huiwen Xue
Investigation: Ping Tian, Dantong Liu
Methodology: Ping Tian, Dantong Liu
Project Administration: Deping Ding
Resources: Yangzhou Wu, Kang Hu, Ruijie Li
Software: Kai Bi
Supervision: Hui He
Validation: Mengyu Huang
Visualization: Yaqiong Hu

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Evidence for Anthropogenic Organic Aerosols Contributing to Ice Nucleation

Ping Tian¹ , Dantong Liu² , Kai Bi^{1,3}, Mengyu Huang^{1,3} , Yangzhou Wu² , Kang Hu² , Ruijie Li^{1,3}, Hui He^{1,3}, Deping Ding^{1,3}, Yaqiong Hu⁴ , Quan Liu⁵ , Delong Zhao^{1,3}, Yan Qiu⁶, Shaofei Kong⁷ , and Huiwen Xue⁸

¹Beijing Key Laboratory of Cloud, Precipitation and Atmospheric Water Resources, Beijing Meteorological Service, Beijing, China, ²Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang University, Hangzhou, China, ³Field Experiment Base of Cloud and Precipitation Research in North China, China Meteorological Administration, Beijing, China, ⁴Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany, ⁵State Key Laboratory of Severe Weather & Key Laboratory of Atmospheric Chemistry of CMA, Chinese Academy of Meteorological Sciences, Beijing, China, ⁶Alliance Manchester Business School, University of Manchester, Manchester, UK, ⁷Department of Atmospheric Sciences, School of Environmental Studies, China University of Geosciences, Wuhan, China, ⁸Department of Atmospheric and Oceanic Sciences, Peking University, Beijing, China

Abstract The role of organic aerosols (OA) as ice nucleating particles (INPs) deserves attention because of their high atmospheric abundance. The low concentration of INPs poses challenges in identifying the ice nucleation (IN) of OA among a mix of aerosol types in ambient environment. This study coupled a catalytic stripper system (350°C heating) with a continuous flow diffusion chamber to online investigate the immersion INPs of ambient particles at −30°C at a suburban site. Significant reduction ($71 \pm 25\%$) of INP concentrations after evaporation suggested that INPs can be significantly contributed by volatile OA. In addition, nonvolatile OA were more efficient INPs than black carbon. Oxygenated OA by photooxidation and lower ambient promoted the IN activity at noon, when the OA may be more viscous. These results hereby present the first field evidence that OA in anthropogenically influenced regions can be efficient INPs well above the homogeneous IN temperature.

Plain Language Summary Ice nucleating particles have an important impact on weather and climate by modulating cloud microphysics. Globally, measurements have demonstrated the ubiquitous presence of ice nucleating particles (INPs); however, the contribution of abundant organic aerosols (OA) to INPs remains uncertain owing to their complex compositions and varying phase states. In this study, using concurrent measurements between ambient and heated INPs, we prove the important contribution of volatile OA at 350°C to immersion freezing INPs at −30°C, especially at noon, when OA are more solid-like because of their oxygenation by photooxidation and lower ambient relative humidity. In addition, nonvolatile OA were found to be a more efficient INPs than black carbon. Therefore, our results provide field evidence that OA in anthropogenically influenced regions could serve as an important atmospheric INPs at 8°C above the homogeneous freezing temperature.

1. Introduction

Ice nucleation (IN) determines the microphysical properties of mixed-phase and cirrus clouds, thus exerting an important impact on weather and climate (Boucher et al., 2013; DeMott et al., 2010). Heterogeneous IN can occur above −38°C and requires ice nucleating particles (INPs) (Pruppacher & Klett, 1997), among which process immersion freezing from existing supercooled liquid water drops is the dominant mechanism for midlatitude precipitation (Mülmenstädt et al., 2015; Westbrook & Illingworth, 2013). Despite the important role of INPs, their atmospheric sources and abundance remain to be clarified in detail (Kanji et al., 2017; Seinfeld et al., 2016).

The INPs refer to the immersion freezing mode unless otherwise stated in this study. The IN efficiency of particles is highly composition-dependent, and a few candidates are well established, including mineral dust (DeMott et al., 2003; Möhler et al., 2006), primary biological particles (Hartmann et al., 2013; Hoose, Kristjánsson, & Burrows, 2010), and sea-spray aerosols (DeMott et al., 2016; Wilson et al., 2015). However, the IN role of some particle species remains under debate because of inconsistent laboratory or field observations, such as black carbon (BC) (Adams et al., 2020; Kanji et al., 2020; Levin et al., 2016) and organic aerosols (OA)

Writing – original draft: Ping Tian, Dantong Liu

Writing – review & editing: Ping Tian, Dantong Liu, Kai Bi, Mengyu Huang, Yangzhou Wu, Kang Hu, Ruijie Li, Hui He, Deping Ding, Yaqiong Hu, Quan Liu, Delong Zhao, Yan Qiu, Shaofei Kong, Huiwen Xue

(Charnawskas et al., 2017; Frey et al., 2018; Ignatius et al., 2016; Prenni et al., 2009). Field observation studies have demonstrated ubiquitous INPs worldwide (Murray et al., 2021); however, the INP concentration may not be well explained by single parameterization (Hoose, Kristjánsson, Chen, & Hazra, 2010; Phillips et al., 2013). Some studies have found that anthropogenic pollutants may contribute to INPs (Wang, Laskin, et al., 2012) and glaciatic clouds in regions like East Asia (Rosenfeld et al., 2011) as well as influence the ice particle size (Zhao et al., 2019). However, other studies have not revealed a clear link between pollution and INP concentration (Levin et al., 2019; Bi et al., 2019), or demonstrated appreciable freezing at a relatively higher temperature (-6° to -20°C) (Chen et al., 2018).

OA constitutes the most abundant aerosol species, which contribute significantly to cloud condensation nuclei at the global scale (Liu and Wang, 2010; Zhang et al., 2007); therefore, their IN activity may importantly determine the global budget of INPs. However, the very few number of INPs compared to the vast number of atmospheric OA (only $\sim 10\%$ of these OA are identified at molecular level (Hallquist et al., 2009)) challenges identification of the exact role of OA in acting as INPs. In addition, OA can span continuum phase states from liquid to glassy solid, with the latter preferably for heterogeneous freezing (Berkemeier et al., 2014; Koop et al., 2011). Laboratory studies showed contrasting results, with some finding OA could contribute to INPs under mixed-phase cloud conditions (Charnawskas et al., 2017; Ignatius et al., 2016), or inefficient INPs (Prenni et al., 2009). Other studies found the humic-like substances were INPs at -20°C (Chen et al., 2021); secondary OA (SOA) from the oxidation of naphthalene with hydroxyl radicals could serve as INPs at temperatures warmer than -37°C (Charnawskas et al., 2017; Wang, Lambe, et al., 2012); however, SOA from biogenic precursors like α -pinene could only serve as deposition INPs at cirrus temperature (Frey et al., 2018; Ignatius et al., 2016). Further, there is a lack of field evidence and explanation regarding the extent of which OA can contribute to atmospheric INPs, typically in anthropogenically influenced regions with high OA loadings. The difficulty in identifying the IN activity of OA arises from the extremely low concentration of INPs, which poses challenges in separating the information for specified component from bulk aerosols.

This study combined an online INP counter with an approach to measure INPs concurrently between ambient and heated aerosols, wherein the difference could be ascribed to OA (Hill et al., 2016; Suski et al., 2018; Tobo et al., 2014). This method was used to characterize the IN activities of OA influenced by anthropogenic pollution in a suburban environment in Beijing.

2. Experimental

The field experiment in this study was conducted from 4th to 26th September 2020 at the Beijing Cloud Laboratory and Observational Utilities Deployment Base (CLOUD Base), which is located at a typical suburban site approximately 65 km northwest of the center of Beijing, where local emissions are mainly from industrial factories, residences, and traffic (Bi et al., 2019). There were no dust events during the experimental period. The biological emission was weak during the late summer season (Hu et al., 2020). In the region of Beijing, the southerly transported air mass accumulated the pollution from the polluted southern region, but the cleaner northerly air mass diluted the concentration (Tian et al., 2019). The data was screened for the precipitation period to avoid the influence of wet removal.

We aimed to identify the role of INPs for particles with different levels of volatility. A catalytic stripper (CS) instrument (CS015, Catalytic Instruments Inc, Germany) is used to remove the volatile components among particles that can evaporate at 350°C . Previous studies using thermodenuder (that usually operates up to 250°C) have shown that $>90\%$ of aerosol substances could be removed (Huffman et al., 2009; Xu et al., 2019). The advantage of CS over the thermodenuder is that the evaporated gas can be rapidly catalyzed as a hydrocarbon, avoiding the potential recondensation of gases to the particle phase when a heated sample passes through a cooled environment (Amanatidis et al., 2013). Sampling after CS ascertains that only aerosols with vaporization temperatures higher than 350°C are measured, which will not include most ammonium inorganic salts, whereas BC and some OA will be retained, as confirmed by the downstream composition measurements. The particles surviving after CS at 350°C were designated as nonvolatile substances (NV_{350}), whereas the volatile matter (VOL_{350}) was evaporated by the CS. Particles composed of VOL_{350} can lose their number concentrations, or particles internally mixed with NV_{350} can partly lose their mass but not their number concentration. Both these losses can alter the aerosol composition and may influence their INP activities. Previous studies suggested the organic matter associated with

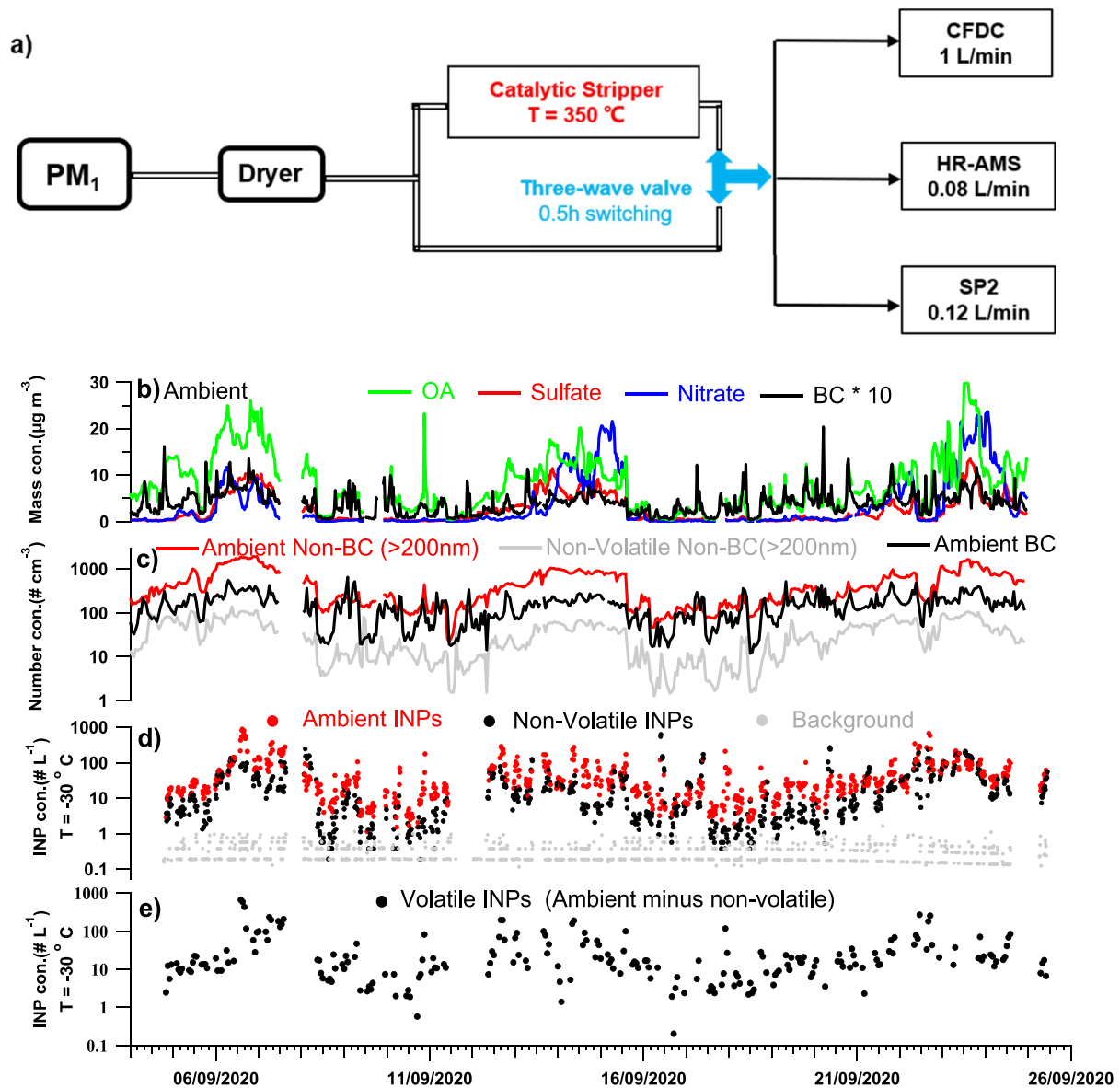


Figure 1. Overview of the experiment. (a) Schematic showing the experimental setup, indicating switching measurements between the ambient and heated sampling line (to measure NV_{350} compositions without evaporation at 350°C). (b) Mass concentrations of ambient key species (organic aerosol, sulfates, nitrates, and black carbon (BC)). (c) Number concentrations of ambient BC and non-BC ($d > 200\text{nm}$) for the ambient and NV_{350} composition. (d) Ambient, NV_{350} , and background ice nucleating particle (INP) number concentrations at -30°C . (e) VOL_{350} INP number concentration (ambient minus NV_{350}).

agricultural soil sources may importantly contributing to INPs (O'Sullivan et al., 2014), where the authors also found the reduction of INPs by heating the soil samples (Hill et al., 2016; Tobo et al., 2014). This means the OA mixed with soil or arable dust may also in part contribute to the INPs observed here, though the urban nature of the experimental site and the absence of dust events during the experiment indicated that mineral materials may have less influence. However, without further detailed source apportioning work, the arable dust or soil sources cannot be excluded from the current experiment.

In addition to the CS line, ambient measurements without heating were also performed concurrently using a three-wave switching valve between the CS and ambient sampling line every 30 min (Figure 1a). Therefore, we could characterize both the NV_{350} and the total ambient aerosol. The VOL_{350} can be determined by subtracting the NV_{350} component from the total ambient measurement. A series of online instruments were connected after the switching valve to measure the particles between the ambient and CS lines (Figure 1a). The thermophoresis

and diffusion loss of CS could be corrected by comparing the BC number concentration between ambient and CS lines, which was approximately 5% during the experiment and was corrected for the CS line (Figure S1 in Supporting Information S1).

The ambient INP concentration was measured online using a continuous flow diffusion chamber ice activation spectrometer (CFDC-IAS, Handix Scientific Inc., USA). The principles of the CFDC-IAS are identical to those of the Colorado State University CFDC (DeMott et al., 2017; Rogers, DeMott, Kreidenweis, & Chen, 2001), and can additionally achieve continuous online measurements of ambient INPs; it had been previously deployed in the field in Beijing (Bi et al., 2019). Inside the CFDC, the ambient aerosols are directly activated to cloud droplets before being frozen (immersion freezing) after injection into the center lamina, where the temperature and supersaturation are controlled by the temperature gradient of the two concentric cylinders covered with ice (the vertical temperature difference of both walls was within 0.5°C). Supersaturation with respect to water was set at $106 \pm 1\%$ in this study to ascertain the immersion freezing mode, though it may also potentially include the deposition mode INPs that can activate as relative humidity (RH) increases for the sample entering the instrument (DeMott et al., 2017). Measurements of INPs by scanning RH up to 6% water supersaturation indicated that the deposition INPs only contributed to <7% for the ambient INPs here (Figure S2 in Supporting Information S1). An optical particle counter at the bottom of the CFDC chamber after an isothermal region (allowing for continue ice growth, while evaporating cloud droplets) was used to discriminate the ice crystals for particle diameters larger than 5 μm . A $\text{PM}_{2.5}$ cyclone cutoff inlet was installed before CFDC sampling to eliminate larger aerosols. During the measurement, the background INP count was automatically checked every 5 mins, and was maintained at $<1 \text{ L}^{-1}$ throughout the experiment (Figure 1d). The ice in the chamber was renewed every 4 hours. To obtain high time resolution (in 10 min), a single temperature was set at -30°C rather than with step change. Note that given the short residence time of samples in the CFDC (5–10s) according to the sampling and total flow rates of 1 and 10 L min^{-1} , respectively, will not allow sufficient time for the full phase transformation of the sampled aerosols (Berkemeier et al., 2014; Price et al., 2015), for example, deliquesce in water supersaturation if OA were initially solid. This means that the aerosols sampled by CFDC represent their original phase state in the ambient environment but are not modified by the instrument. This also means that the particles could freeze instead at lower RH before they transited to the CFDC steady state. For certain time, ice particles downstream of the CFDC were sampled onto a copper TEM grid coated with carbon film (carbon type-B, 300-mesh copper, Tianld Inc., China) using a 2.9 μm single-jet inertial impactor (Kreidenweis et al., 1998; Rogers, DeMott, & Kreidenweis, 2001), and the ice residues were analyzed by a scanning electron microscope (SEM, Model: S-4800, Hitachi Inc., Japan) combined with an energy dispersion X-ray (EDX, Model: EX-350, Hitachi Inc., Japan).

The aerosol chemical compositions, which can vaporize at 600°C , including ammonium sulfate, nitrate, and OA were measured using a high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Inc., USA) (Canagaratna et al., 2007). Ionization efficiency (IE) calibration was conducted using the size-selected (300 nm) ammonium nitrite before and after the observation. The IE of sulfate, nitrate, chloride, and ammonium was estimated to be 1.0, 1.1, 1.3, and 3.63, respectively, and a default value of 1.4 was assumed for the OA. A constant collection efficiency factor (0.5) for all components was used to compensate for particle loss through the lens and for bounce at the vaporizer (Huang et al., 2017). The atomic oxygen to carbon ratio (O:C) was calculated from the high-resolution mass spectra obtained using the improved ambient method (Canagaratna et al., 2015).

The composition of BC mass and its number concentration was measured using a single particle soot photometer (SP2, DMT Inc, USA) (Liu et al., 2010). SP2 uses a laser-induced incandescence technique to incandesce light-absorbing aerosols (such as BC) for irradiating detectable visible light. The incandescence signal is linearly proportional to the refractory BC mass, which is calibrated by the Aquadag standard (Acheson Inc., USA) and corrected with a value of 0.75 for ambient BC (Laborde et al., 2012). In addition, SP2 can also measure particles which is only light-scattering but not light-absorbing via the scattering signal. Thus, BC-containing and non-BC particles can be distinguished based on the presence of the incandescence signal. The lower cutoff diameter for non-BC particles is 200 nm (Liu et al., 2014), which is suitable for estimating INPs, as particles smaller than 200 nm tend to have very low efficiency for IN (Kanji et al., 2017; Pruppacher & Klett, 1997). We used the SP2-measured non-BC to designate particles without containing a BC component to explicitly characterize the other types of aerosols apart from BC (e.g., OA and mineral dust) for their ice nucleating activity.

Size distribution was measured using an aerodynamic particle sizer (APS, Model 3321, TSI Inc., USA) at 0.5–2.5 μm . The lower limit of the aerodynamic diameter of 500 nm (N_{500}) was equivalent to the optical diameter

of ~ 400 nm detected by SP2 (Text S1 in Supporting Information S1), and both instruments showed high consistency in measuring the number concentration of these larger particles (Figure S3 in Supporting Information S1). PM_{10} and $PM_{2.5}$ mass concentrations were measured using the Grims optical particle counters (Model: EDM 180, GRIMM Inc., Germany). Some ambient aerosols were also collected on quartz filters and analyzed offline using a Fourier transform infrared spectrometer (FTIR, Thermo Scientific Inc., USA) in order to determine functional groups. Meteorological parameters including temperature, RH, wind direction, wind speed, and precipitation were continuously measured at the observation site. Daily average pollen concentrations and pollen categories were measured manually using an optical microscope (Galán et al., 2014).

3. Results

3.1. INP Characteristics of Volatile and Nonvolatile Particles

Figure 1b shows the ambient mass concentrations of key components, including OA, inorganic salts, and BC (their mass concentrations after CS are shown in Figure S4 in Supporting Information S1). It shows that after vaporization at 350°C , $>97\%$ of inorganic salt had been removed, and 11% of the OA mass remained in the NV_{350} bulk along with the nonvolatile BC (100% remaining) (Figure S4 in Supporting Information S1). This is consistent with the particle number concentration measured using SP2; further, non-BC remained after CS, although at a much lower fraction than that of BC (Figure 1c). This means there was a fraction of OA that is externally mixed with BC and could not be vaporized at 350°C . VOL_{350} -OA tended to be partially mixed with inorganics internally, as implied by a consistent modal size accumulation mode from the AMS measurement (Figure S5 in Supporting Information S1). The NV_{350} particles may also contain minerals, which cannot be measured by AMS.

The ambient and NV_{350} INP concentrations spanned approximately three orders of magnitude from one to nearly a thousand number per liter at -30°C . There was a considerable decrease ($71 \pm 25\%$) in INP concentrations after CS compared with the concurrent ambient measurement. The difference between the ambient and NV_{350} concentration was attributed to the INPs for VOL_{350} particles (Figure 1e). If VOL_{350} and NV_{350} substances were externally mixed among particles, the number concentration of VOL_{350} particles could be determined by subtracting the NV_{350} components from the total ambient numbers. Comparison of non-BC number concentrations between ambient and NV_{350} (Figure 2c) showed that ambient non-BC was one order of magnitude higher than NV_{350} , implying that around 90% VOL_{350} was externally mixed with NV_{350} and could be removed by heating. The other 10% VOL_{350} substances could already be internally mixed with the NV_{350} components in particles, and evaporation of these may also reduce the INPs of NV_{350} aerosols. Both ways indicated the presence of INP activity for the VOL_{350} aerosols.

Figure S6 in Supporting Information S1 shows the IN efficiency for NV_{350} , VOL_{350} , and ambient particles, which are termed INPs occupying the particle number concentration with $d > 200$ nm (N_{200}). NV_{350} aerosols showed IN efficiency approximately one order of magnitude higher than that of VOL_{350} . However, the VOL_{350} INP concentration was mostly higher than that of NV_{350} because VOL_{350} had a number concentration one order of magnitude than that of NV_{350} . The INP number concentration measured here was generally consistent with observations from anthropogenically polluted regions in China ($10\text{--}700\text{ L}^{-1}$) (Bi et al., 2019; Yin et al., 2012), but higher than previous results reported from North America ($10\text{--}100\text{ L}^{-1}$) (DeMott et al., 2017; Knopf et al., 2021; Tobo et al., 2013), Amazon ($1\text{--}40\text{ L}^{-1}$) (Schrod et al., 2020), Europe ($10\text{--}200\text{ L}^{-1}$) (Boose et al., 2016; Lacher et al., 2018; Schneider et al., 2021), Japan ($1\text{--}50\text{ L}^{-1}$) (Tobo et al., 2020), and North and South polar region ($<1\text{ L}^{-1}$) (Hartmann et al., 2021; Welti et al., 2020). A previous study using droplet arrays found no apparent link between INPs and anthropogenic pollution down to -25°C (Chen et al., 2018). This contrast may result from the higher operating temperature; further, offline measurements involving investigation of freezing behavior in water suspensions may not completely represent the status of airborne aerosols. An experiment was conducted in winter on a mountain site (which represents the top of the boundary layer (Liu et al., 2021)), which also showed a positive correlation with OA concentration (Figure S7 in Supporting Information S1). The higher INP efficiency per unit mass of OA in winter may be due to the lower RH and lower temperature in winter, when the particles tend to be more viscous (Figure S7 in Supporting Information S1). Continuous online measurements of INPs in anthropogenically influenced regions remain rare; the results presented here may thus provide insights into the INP activities of airborne aerosols.

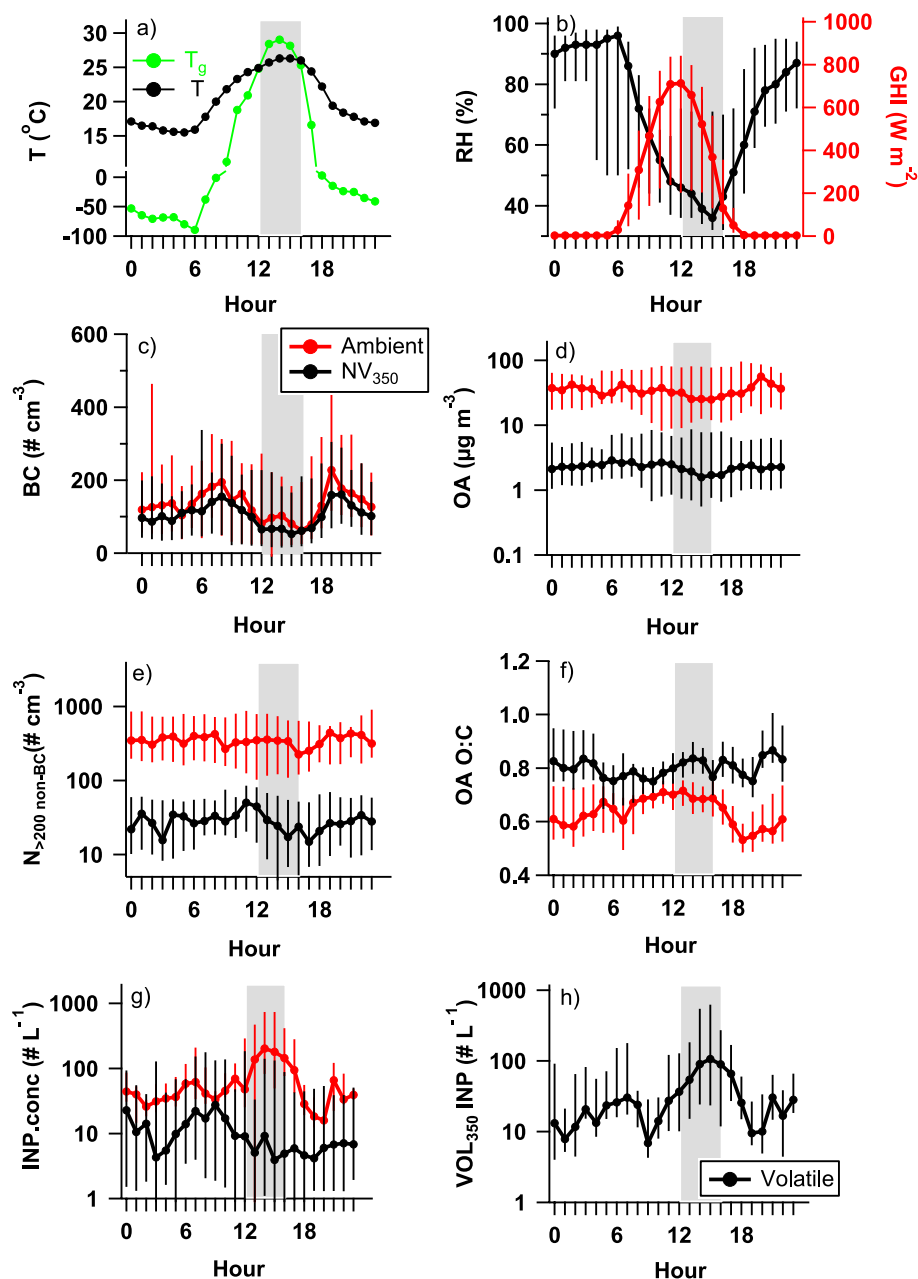


Figure 2. Diurnal variations of ice nucleating particles (INPs) and aerosol physiochemical properties. (a) Ambient temperature and calculated glass transition temperature (T_g) of organic aerosols (OA), (b) relative humidity and direct solar radiation, (c) number concentration of black carbon (BC), (d) mass concentration of OA, (e) number concentration of non-BC particles ($d = >200$ nm), (f) oxygen over carbon ratio of OA, (g) INP number concentration at -30°C . (h) VOL_{350} INP number concentration. From (c) to (g), the red line and black line represent the total ambient and NV_{350} particles, respectively.

Figure 2 shows the diurnal variation of key parameters for the entire data set. During the post-monsoon season, the temperature at the site reached up to 30°C (Figure 2a) in the early afternoon, with the RH reaching a minimum of 30%; at night, the RH could nearly reach saturation (Figure 2b). Here, a gray vertical bar is used to indicate the time window in the day when solar radiation is the most intensive and the temperature is the highest (Figure 2a). Pollutants such as BC showed a typical diurnal pattern in anthropogenically influenced environments, wherein the concentration peaked in the morning rush hour, and was diluted in the midday by the developed boundary layer (Figure 2c). Total OA showed no apparent diurnal variation because of its mixed primary and secondary sources, and 11% mass loading remained after CS (Figure 2d). The oxidation state of OA, reflected by O:C,

showed marked enhancement throughout midday to early afternoon because of photooxidation (Figure 2f). Note that the O:C ratio of OA after CS showed systematic enhancement compared with ambient OA and the absence of a diurnal pattern because the NV_{350} OA had low volatility and was more oxygenated (Huffman et al., 2009). The INP concentration showed contrasting diurnal patterns (Figure 2g), with the ambient total INPs peaking at midday (matching the time window marked by the Gy bar), but this peak was absent for NV_{350} . This means that the ambient INPs prevailed despite the dilution effect of the developed boundary layer at noon. This corresponded with the remarkable increase of INP concentration at midday for VOL_{350} (Figure 2i). The highest INP concentration was dominated by pollution events (also for diurnal variation) on September 6th, 7th, 12th, 13th, 14th, and 22nd (Figure 1), though some episodes had coincident enhancements of both organic and inorganic aerosols. The overall positive correlation between INPs and OA mass concentration ($r = 0.57$ and $p < 0.01$) indicates the potential contribution of OA to INPs (Figure S7 in Supporting Information S1). The scatter of this correlation indicates that factors such as RH and the oxidation state of OA may influence its INP activities; the detailed analyses for these are described below.

3.2. Contribution of VOL_{350} Organic Aerosols to INPs

The VOL_{350} particle composition includes a fraction of OA and inorganic salts. Inorganic salts are not immersion mode INPs because of their high hygroscopicity and can be completely dissolved in water; hence, they cannot provide a solid site for IN. Figure 3a shows a positive correlation ($r = 0.67$) between VOL_{350} -INPs and VOL_{350} -OA mass concentrations, implying the role of VOL_{350} -OA in contributes to INPs. Figure 3b shows that the INP numbers per unit OA mass (INPs/OA) decreased dramatically under high RH. Higher INP efficiency was found when the O:C ratio was high and under low RH, but a lower INP efficiency was found at higher RH, even with a high O:C ratio.

Among VOL_{350} particles, primary biological particles are efficient INPs (Möhler et al., 2007) and lose ice nucleating activities upon heating (Hill et al., 2014); thus, they may be measured among the VOL_{350} particles. The contribution of biological particles to the measured INPs could be mostly excluded in this case because their size is usually in the super-micron range (Möhler et al., 2007), which is too large to be sampled by the total PM_{10} inlet (Figure 1a) and CFDC inlet, even though fractured pollen may be sampled. The measured daily pollen concentration did not correlate with VOL_{350} -INPs (Figure S8 in Supporting Information S1). The microscopy images of ice residues collected after the CFDC column also showed no signs of the biological components such as pollen and bacteria (Figure S9 in Supporting Information S1). All together, these facts confirmed the negligible contribution of biological particles to the measured VOL_{350} -INPs. The presence of OA as INPs was also confirmed by single particle microscopy analysis after direct sampling downstream of the CFDC (Figure S9 in Supporting Information S1), indicating that OA is a component of ice residues.

3.2.1. Theoretical Support for the INP Activity of Organic Aerosols

The glassy state of certain groups of OA may enable IN (Ignatius et al., 2016); some small ice-nucleating macromolecules such as polysaccharides from pollen could also act as IN catalyst (Pummer et al., 2012; Pummer et al., 2015); further, nonadecanol can initiate freezing without being solid (Zobrist et al., 2007). The amorphous nature of OA indicated that it undergoes a transition from solid and semisolid to a fully deliquesced liquid (Reid et al., 2018; Zobrist et al., 2008). Under high moisture and temperature, OA are less likely to occur in a solid state. First, VOL_{350} INPs were elevated at noon when RH was the lowest at 30%–50% (Figure 2b), well below the deliquescing RH (60%) for most hydrophilic OA (Koop et al., 2011). Thus, moisture was not a limiting factor, but temperature should be investigated further. The glass transition temperature (T_g) is established as the single parameter determining the phase state of OA and is composition dependent; OA is solid if the ambient temperature is below T_g (Koop et al., 2011). The T_g is mainly determined by molecular weight (MW); at a similar MW, T_g could also be influenced by functional groups, as reflected by the elemental O:C ratio (Li et al., 2020). The increased O:C ratio corresponded with the enhancement of VOL_{350} INPs, suggesting that the increase in the oxidation state of OA may be involved in enhancing the IN activities. An increase in O:C ratios indicates an enhanced oxidation state of OA and potentially reduced volatility, which is highly associated with enhanced viscosity (Koop et al., 2011; Shiraiwa et al., 2017). To explicitly determine the transition temperature threshold

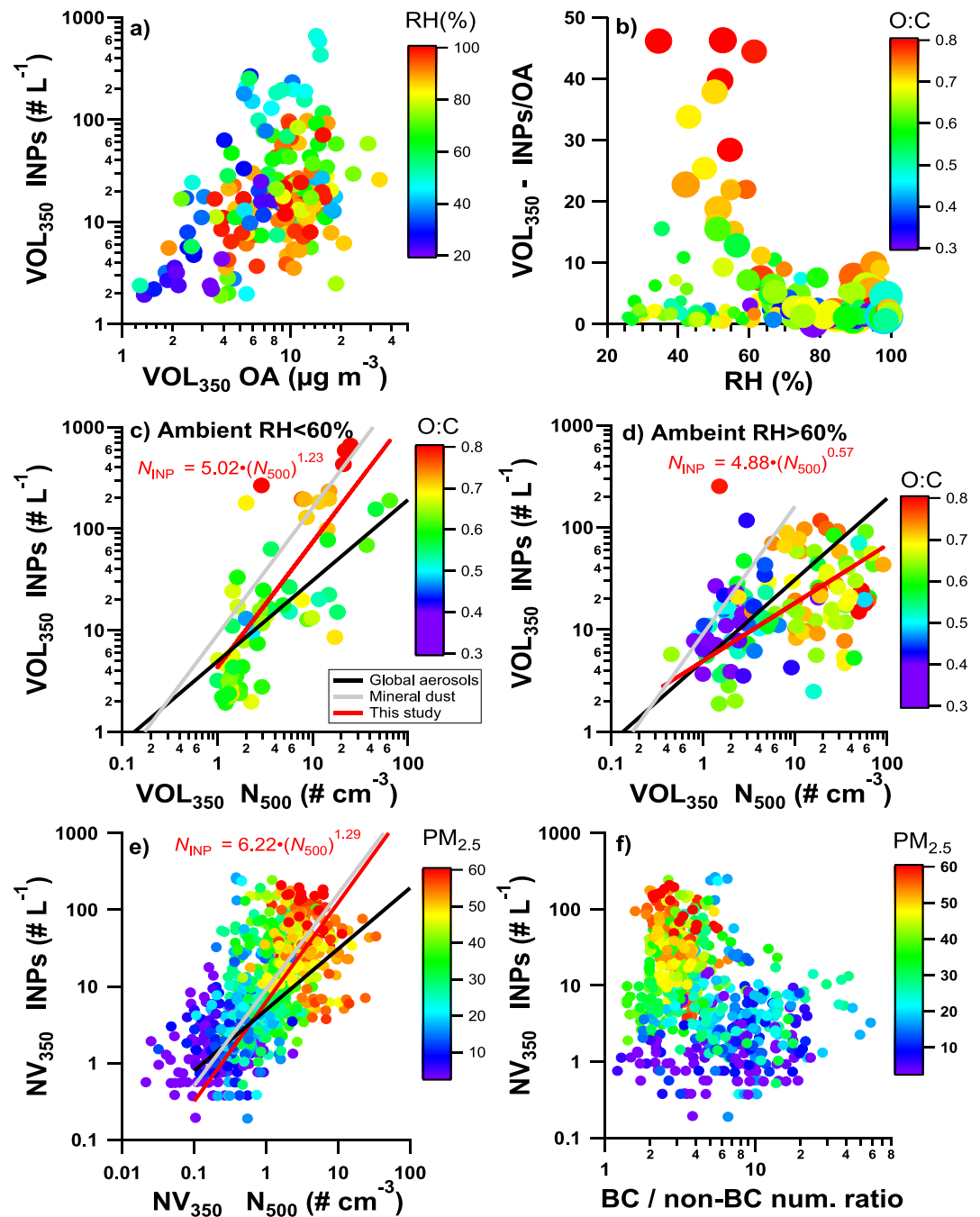


Figure 3. Correlations between VOL₃₅₀ ice nucleating particle (INP) concentrations at -30°C (a–d) and other key parameters. (a) VOL₃₅₀-INPs versus the VOL₃₅₀-organic aerosols (OA) mass concentration colored by ambient relative humidity (RH), (b) VOL₃₅₀ INPs/OA versus RH, colored by the O:C and sized by the PM_{2.5} mass concentration, (c) VOL₃₅₀-INPs versus VOL₃₅₀-N₅₀₀ under ambient RH < 60% and (d) for ambient RH > 60% colored by the O:C. The power parameterizations of VOL₃₅₀-INPs as a function of N₅₀₀ are shown for this study, along with those of referenced global aerosols (DeMott et al., 2010) and mineral dust (DeMott et al., 2015). Correlation between the NV₃₅₀ INP concentration and the NV₃₅₀ N₅₀₀ (e), and black carbon (BC) over non-BC number concentration ratio (f) colored by the PM_{2.5} mass concentration.

for ambient OA, we calculated the T_g based on the measured O:C ratio of bulk OA, using Equation 1 (Shiraiwa et al., 2017):

$$T_g = A + B \times M + C \times M^2 + D \times (O : C) + E \times M \times (O : C) \quad (1)$$

where M is 200 g mol^{-1} , which tends to be the minimum estimate for aerosols in urban environments (Jimenez et al., 2009; Li et al., 2016; Samburova et al., 2005), and is also applicable to the Beijing region (Cai et al., 2021). The coefficient values are $A = -21.57 \text{ K}$, $B = 1.51 \text{ K mol g}^{-1}$, $C = -1.7 \times 10^{-3} \text{ K mol}^2 \text{ g}^{-2}$, $D = 131.4 \text{ K}$, and $E = -0.25 \text{ K mol g}^{-1}$.

Note that the above calculation is for T_g at RH = 0%, when no water is associated with OA. Water has an extremely low T_g and can act as a plasticizer to reduce the T_g of aerosols. Therefore, a higher RH will decrease the T_g of OA owing to the water growth on aerosols. The T_g for the mixture of aerosols and liquid water can be calculated using the Gordon-Taylor equation (Koop et al., 2011):

$$T_g(\text{mixing}) = \frac{(1 - w_{OA}) \times T_{g,w} + \frac{1}{k_{GT}} \times w_{OA} \times T_{g,OA}}{(1 - w_{OA}) + \frac{1}{k_{GT}} \times w_{OA}} \quad (2)$$

where w_{OA} is the mass fraction of OA in a deliquesced aerosol, $T_{g,w}$ is the glass transition temperature of pure water with a value of 136 K, and k_{GT} is the Gordon-Taylor constant, which is assumed to be 2.5 (Zobrist et al., 2008). The w_{OA} is calculated using the hygroscopicity parameter of OA at 0.1 (Petters & Kreidenweis, 2007).

Figure 2a shows the diurnal variation of the calculated T_g (green line) considering the O:C ratio of OA and ambient RH. The ambient temperature is also shown for reference purposes. It clearly shows the time window when the ambient temperature was lower than T_g from noon to early afternoon (12:00–16:00), coinciding with the time for elevated INP concentration. This means that OA tended to be glassy at this time of the day, and that these solid OA could have contributed to the increased INP concentrations, while OA at other times, particularly at night when RH was high, tended to be liquid and contributed less to the INPs. Compared with the limited previous rebounding observations in this area, this also suggested that the phase state changes to liquid when the RH is higher than 60% (Liu et al., 2019).

The chemical composition as measured by the infrared FTIR spectrometer confirmed the abundance of alcohol groups in the daytime (by the addition of OH radical) but a lack of carbonyl groups in the sample (Figure S10 in Supporting Information S1). This is consistent with a previous study in the Beijing urban environment, in which carboxylic acid species were scarce (Ji et al., 2015). It is well known that hydroxylated organic monolayers can facilitate IN with an alcohol head; however, the IN efficiency can be reduced in the presence of a carboxylic head (Qiu et al., 2017). Alcohol compounds can be produced by hydroxyl radical photooxidation (Schwantes et al., 2019). This may explain the substantially enhanced INPs observed at noon from the viewpoint of chemical composition.

We observed the evidence of OA acting as immersion freezing INPs at a temperature warmer than that reported in other studies, for instance, isoprene initialized secondary organic aerosol (SOA) was found to nucleate at temperatures $< -30^\circ\text{C}$ in the laboratory (Ignatius et al., 2016; Ladino et al., 2014), and naphthalene-induced SOA, a surrogate of anthropogenic SOA types, showed higher ice nucleating efficiency than biogenic SOA (Charnawska et al., 2017). Further, recent studies have suggested that the phase state is a key factor in determining the contribution of OA to INPs (Kilchhofer et al., 2021; Wagner et al., 2015, 2017). Biogenic SOA was previously reported to not show a glass transition, which is shown by anthropogenic SOA (Liu et al., 2016), indicating that the latter may be more likely to be solid under low RH and serve as INPs. Notably, the ambient environment represents a complex mix of organic compounds; for example, biogenic sources of isoprene-induced SOA also include other anthropogenic sources (Xu et al., 2015). We were not able to conclude the exact molecular formula contributing to the INPs, but the results of this study revealed that in a typical polluted region, a substantial increase of INPs mostly corresponded with the pollution period, and that the number concentration could reach 870 L^{-1} , being elevated by a factor of 5–20 compared to that in the night, because of photooxidation processes (from the diurnal variation in Figure 2g). Considering the high INP efficiency of OA at noon, these INPs can be transported to the troposphere along with the development of the planetary boundary layer. During this upward transport, these OA may undergo phase transition (Liu et al., 2021) and their INP efficiency may be enhanced due to the lower

temperature and lower RH at higher altitudes. This may exclude the case when OA are activated close to a warmer cloud base, where they could spend minutes in cloud droplets before freezing occurs. Unless OA are completely liquefied or dissolved in water, they may contribute to immersion freezing (Berkemeier et al., 2014). Satellite observations have also indicated that potential heterogeneous IN could be induced by anthropogenic sources over this region (Zhao et al., 2019). The OA that are not activated or released after droplet evaporation may be transported to altitudes lower than -30°C and contribute to INPs in the deposition or immersion mode if being incorporated into clouds at such levels.

3.2.2. Parameterization of VOL_{350} INPs

Following established INP parameterization in a power function against aerosols ($d > 500$ nm, denoted as N_{500}) number concentration, a similar parameterization was also determined for VOL_{350} -OA, as shown in Figure 3. A threshold RH of 60% was used to separate the influence of phase state on the potentially deliquesced OA. This clearly shows an enhanced INP ability at $\text{RH} < 60\%$ (Figure 3c) by a factor of 10 compared with that at high RH (Figure 3d). The INP number concentration (at -30°C) as a function of N_{500} can be expressed as:

$$N_{\text{INP}} = 5.02 \times N_{500}^{1.234} \quad \text{when } \text{RH} < 60\% \quad (3)$$

$$N_{\text{INP}} = 4.87 \times N_{500}^{0.5674} \quad \text{when } \text{RH} > 60\% \quad (4)$$

At $\text{RH} < 60\%$, the INP efficiency of VOL_{350} -OA was between the global mean INP concentration predicted by DeMott et al. (2010) (named as D10) and mineral dust particles (DeMott et al., 2015) (Figure 3c), while under $\text{RH} > 60\%$, the INP efficiency of OA was lower than that of D10 (Figure 3d). Notably, our ambient INPs, as a function of N_{500} , could be well fitted to D10 (DeMott et al., 2010) (Figure S9a in Supporting Information S1), which may have been neutralized by the INPs of OA under high and low RH conditions. This indicates that our observation of overall bulk aerosols in a semiurban environment is within the global generic characteristics, but the composition of the aerosol bulk population can induce heterogeneity in INP efficiency. Here, using field evidence, we prove the important contribution of anthropogenic OA to INPs; this may also explain the ubiquitous INPs at the global scale from the composition aspect. The INP efficiency of OA at warmer temperatures was not evaluated in this study; thus, the full temperature dependence of the power fitting parameters was not obtained. We postulate that OA only exhibit apparent INPs when turning to the solid phase. This may be also implied by many previous studies that only observed INPs for OA at sufficiently low temperatures (Ignatius et al., 2016; Wang, Laskin, et al., 2012).

3.3. The INP Efficiency of NV_{350} Aerosols

NV_{350} aerosols had a higher INP efficiency (one in 10^2 – 10^4 particles) than that of VOL_{350} aerosols (one in 10^3 – 10^5 particles) (Figure S6 in Supporting Information S1), and close to that of dust (Figure 3e). As discussed above (Figure 1c), the NV_{350} particles contained $77 \pm 15\%$ of BC number, where the remaining were OA. The super-micron dust was largely removed by the impactor, and the diurnal variation of NV_{350} INPs corresponded to the morning rush hour (Figure 2g). Both BC and OA were positively correlated with the NV_{350} INPs (Figure S11 in Supporting Information S1), suggesting that both may have contributed to the NV_{350} INPs, as evidenced by electron microscopy, wherein both OA and BC were found in the ice residues of NV_{350} particles (Figure S9 in Supporting Information S1). To compare INP efficiency between BC and OA, NV_{350} INPs were investigated as a function of the BC/non-BC number ratio (Figure 3f). The increased ratio of BC/non-BC corresponded with a decreased INP number concentration, which suggested that NV_{350} OA tended to be more efficient INPs than BC. This is likely consistent with a few recent studies (Adams et al., 2020; Kanji et al., 2020; Schill et al., 2020), which indicated that BC from a range of combustion sources was poor immersion freezing INPs at the mixed phase cloud temperature. This in turn implies that both NV_{350} and VOL_{350} OA contributed the most important INP sources in this anthropogenically influenced environment. However, the exact source of these organic substances, such as from arable dust, may not be excluded without further source apportioning or investigation in the particle mixing state.

4. Conclusion

In this study, by concurrent online measurements of IN particle (INP) number concentration and compositions between unheated and heated (at 350°C with vapor being rapidly catalyzed) ambient samples, we showed clear field evidence that anthropogenic OA can be efficient INPs at −30°C, which is 8°C above the homogenous freezing temperature. The observation showed that OA was largely contributed by secondary substances or oxidized primary emission in a high oxidation state, which importantly contributed to the immersion INPs over the anthropogenically polluted region. This particularly occurred at the time when intense solar radiation and lower RH, during which strong convective mixing of the boundary layer may efficiently transport these oxygenated aerosols to the upper colder levels, further influencing the formation of low-level clouds. The results also imply that OA, not necessarily with extremely low volatility, could be in a solid state and contribute to the INPs. The results here explain the possible causalities that OA may have contributed to the ice nuclei in the regions short of highly efficient INPs (such as dust). Considering the abundant OA loading on a global scale, their role in modulating ice number concentration and potential consequent impacts on weather and climate should be further investigated. Additional measurements with wider spatiotemporal coverage, including those from environments influenced by levels of anthropogenic activity, as well as the investigation on the INP activities of OA at multiple temperatures, should further improve our understanding regarding the INP activities of OA.

Data Availability Statement

Processed data are available from the link: <https://doi.org/10.17632/h9tf7m77pj.1>.

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