

## Answers to the report by anonymous Referee #1

We thank Referee 1 for reviewing our manuscript and also for useful hints and suggestions. Below, comments from the referee are given in blue while our new answers are given in purple, with passages including new text given in italic. Additionally, the new text is marked yellow in the revised version of the manuscript.

### General Comment:

The original manuscript has been significantly improved. Most of my previous concerns were nicely addressed in the revised version. The reviewer has three additional comments that would like to clarify before the manuscript is accepted for its publications in ACP.

### Major Comments:

1. The reviewer is surprised the authors completely ignored meteorology in this study. A detailed analysis of the meteorological variables and air masses is required to explain ambient observations, even in urban areas.

Authors: We added two plots showing trajectories and also wind direction and wind speed, to show the meteorological condition during the sampling period, together with the following text (line 234-245):

Additionally, Fig.2 shows 2-day back-trajectories obtained by the NOAA HYSPLIT model, with one trajectory related to each sampled filter, starting at the median sampling time of each filter. Fig. 3 shows minutely recorded data for wind-direction and wind-speed collected by (Met One 591) and (Met One 590) located on the same roof top as the aerosol sampling equipment. Both pictures are colored-coded with respect to PM<sub>2.5</sub> mass concentrations. The air masses that came from north or north-western directions were generally coincident with higher wind-speeds. They brought clean air with lower PM<sub>2.5</sub> mass concentrations. They did cross desert regions, however, Beijing was reported to be affected by desert dust in mainly only spring (Wu et al., 2009). Typically, the air masses coming from south and south-west of Beijing moved slowly and spent much more time over industrialized regions, resulting in high particulate matter mass concentrations. This here observed pattern is typical for Beijing, and these connections between wind-direction and pollution levels in Beijing have been analyzed in detail previously in Wehner et al. (2008).”

Reviewer: The reviewer appreciate the addition of the new plots and new text. This is very useful information for the readers. However, what is still missing is the correlation of the meteorological variables with the INP concentrations. I assume that one of the main goals of this study is to identify the source of the INPs. Meteorology could help the authors to understand this. Is the INPs concentration lower or higher when the air masses were from the north and north-west with low PM<sub>2.5</sub>? Is the INPs concentration lower or higher when the air masses were from the south and south-west with high PM<sub>2.5</sub>? How about wind speed? Does it have any influence in the INP concentration?

Authors: Our main goal was to see if anthropogenically generated particles in the polluted Beijing winter air would contribute to atmospheric INP. Still, following the reviewer's suggestions, two plots are displayed here. The first one shows the relationship between INP concentration and wind-speed. The second one displays the INP concentration-colored backward trajectories. No clear correlation between wind speed and INP concentrations was found (Fig. 1). Fig. 2 displays the backward trajectories colored by INP concentrations. There were no evident dependency of the direction of air masses and INP concentration.

We added R2 and p values for the correlation with wind speed in Table 1, added Fig 2 to the manuscript (Fig.9), and added the following text (line 368):

*“In addition to what we discussed above, also no correlation was observed between  $N_{INP}$  and wind-speed, as can be seen by the respective values for  $R^2$  and  $p$  given in Table 1. Fig. 9 indicates that there was also no correlation with wind-direction. The fact that we find no correlation with either wind-speed or wind-direction agrees with the desert regions towards the north-west not being efficient dust sources in winter, and are a hint that we may have observed average background INP concentrations in Beijing during our measurements.”*

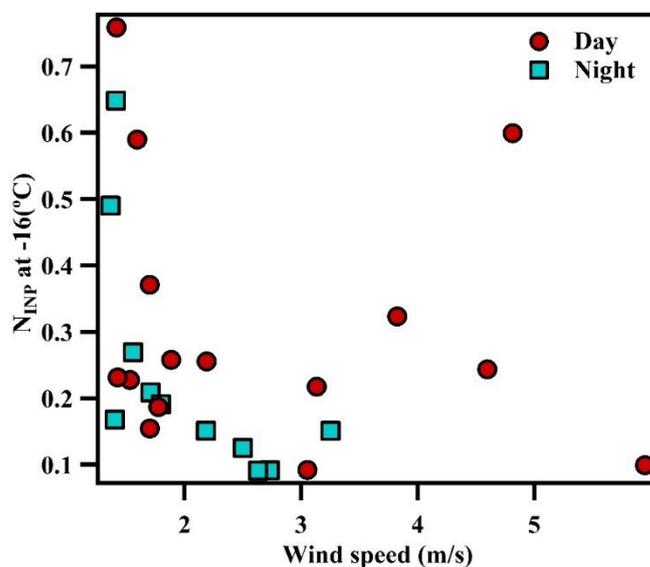


Figure 1: INP concentration vs. wind speed.

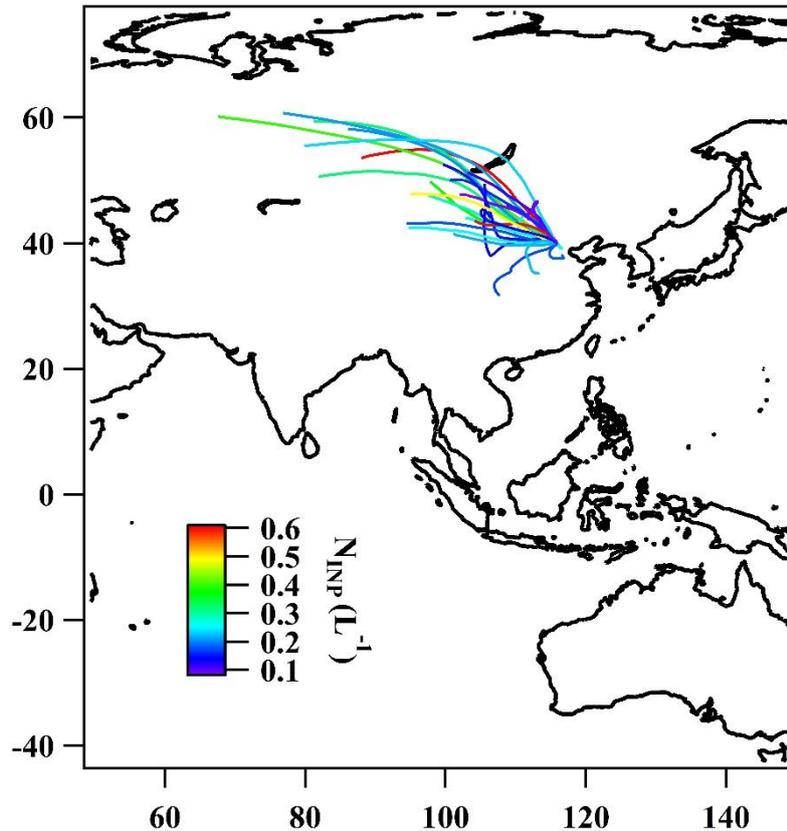


Figure 2: The 2-day back-trajectories obtained by the NOAA HYSPLIT model colored-coded with respect to INP concentration

2. The authors claim that the measured INPs are non-urban and they suggests that the sources of the INPs could be dust or bioparticles which are non-urban. Do the authors think that is it not possible to have urban dust and urban bioparticles?

Authors: Indeed, there may be urban dust and also urban bioparticles. But these are no major contributor to the increase in PM<sub>2.5</sub> mass concentrations during winter times – rather, it is well known that this increase is related to anthropogenic pollution. On the other hand, considering biogenic and dust particles, these particles emitted from urban areas will only contribute little to the overall atmospheric dust and biogenic particle load, as the non-urban sources are much more dominant for these types of particles. Therefore explicitly mentioning that dust and biogenic particles might also be emitted from urban sources does not really make sense. If there is, however, a specific passage in the text that you feel is missformulated, please tell us where this is exactly and why precisely you think this is wrong. For the time being, nothing was changed.

Reviewer: Here I disagree with the response. The authors agree that there are urban dust and bioparticles; however, they provide two arguments to say these particles are not important. It is said that i) they “are no major contributor to the increase in PM<sub>2.5</sub> mass concentrations during winter times” and ii) that “particles emitted from urban areas will only contribute little

to the overall atmospheric dust and biogenic particle load”. First, I agree that they are not a major contributor to PM<sub>2.5</sub>, but this is not a good argument because PM<sub>2.5</sub> was not found to correlate with the INP concentrations. Second, although the concentration of urban bioparticles could be small, if they have good ice nucleating abilities, they can significantly contribute to the INP concentrations. I don’t clearly understand why urban bioparticles are negligible and do not make sense to the authors.

Authors: We cannot determine the contribution of the urban dust and bioparticles to the total aerosol load, and yes, these particles might be efficient INP and could contribute to the observed INP, although particularly biogenic particles might not be present in large amounts due to the season. We adjusted the text in line 425-433 (given in regular script here), with the following (given in italic):

*“Despite the difference among methods and ice nucleating modes, this again suggests that urban pollution aerosol particles might not be efficient immersion freezing INP and that the ice nucleating ability of particles in urban aerosols might originate from the non-urban background aerosol particles that are included in the urban aerosol, i.e., that INP observed in urban environments might have the same sources among bioaerosols and dust particles as non-urban INP. An additional contribution from urban biogenic or dust particles to the INP observed in this study cannot be fully excluded, but the agreement between our data and rural data presented in literature (see Fig. 8 and Table 2) corroborates our assumption that atmospheric INP in general originate from non-urban sources.”*

3. It is unclear how BC was calculated/determined for the PM<sub>2.5</sub> reported in Figure 1.

Authors: The BC was measured by a multi-angle absorption photometer (5012, MAAP, Thermo Fisher Scientific, Waltham, MA, USA) which got the sampled air through an inlet with a 2.5µm cut-off. This had been included in the previous version of the manuscript. The instrument measures the absorption of particles collected on a filter with a time resolution of 5 min and automatically derives BC mass concentration from the measurement while accounting for multiple scattering occurring on the filter. The MAAP is a well known and often used instrument for the measurement of absorption coefficients and BC mass concentrations.

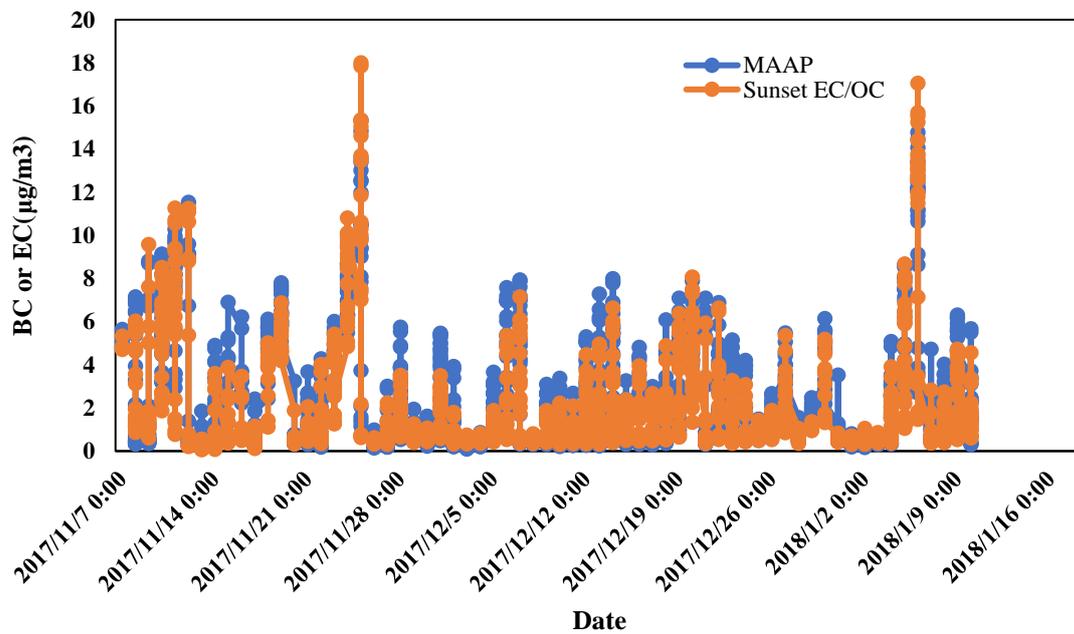
The respective retrieval of BC values is now added in line 143 ff: “The instrument measures the absorption of particles collected on a filter with a time resolution of 5 min and automatically derives BC mass concentration from the measurement while accounting for multiple scattering occurring on the filter.”

Reviewer: The reviewer is very familiar with the MAAP and perhaps my questions was not well formulated. If I understood correctly the concentration of the ions was obtained from the PTEF filters, right? But what it is unclear to me is if the BC concentration reported in Figure 1 is obtained directly from the MAAP or if this was obtained off-line (using other technique), similar to the ions concentrations. If the reported BC data in Figure 1 is from the MAAP, is it directly comparable to ions off-line data?

Authors:

Typically, elemental carbon (EC) concentrations are taken to combine with filter-based ions concentrations. Here, we compared the EC concentration measured by filter-based Sunset EC/OC analyzer with BC concentration measured by MAAP during one recent field campaign. The plot is given below. The comparison showed that the BC measured by MAAP is slightly higher than EC derived from filter-based Sunset EC/OC. The mean ratio of BC/EC is about 1.35. We also added this in the manuscript, see line 147-150:

*“It might be worth noting that a comparison of BC concentrations obtained from the MAAP with concentrations of EC determined by a filter-based SUNSET EC/OC analyzer during a different field campaign showed, that both instruments measured the same trends while the mean ratio of concentrations of BC to EC was about 1.35.”*



1 **Ice nucleating particle concentrations unaffected by**  
2 **urban air pollution in Beijing, China**

3 Jie Chen<sup>1</sup>, Zhijun Wu<sup>1</sup>, Stefanie Augustin-Bauditz<sup>2</sup>, Sarah Grawe<sup>2</sup>, Markus Hartmann<sup>2</sup>,  
4 Xiangyu Pei<sup>3</sup>, Zirui Liu<sup>4</sup>, Dongsheng Ji<sup>4</sup>, Heike Wex<sup>2</sup>

5 <sup>1</sup> State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of  
6 Environmental Sciences and Engineering, Peking University, 100871, Beijing, China.

7 <sup>2</sup> Leibniz Institute for Tropospheric Research, 04318, Leipzig, Germany.

8 <sup>3</sup> Department of Chemistry and Molecular Biology, University of Gothenburg, 41296, Gothenburg,  
9 Sweden.

10 <sup>4</sup> State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute  
11 of Atmospheric Physics, Chinese Academy of Sciences, 100029, Beijing, China.

12 *Corresponding author: Zhijun Wu (zhijunwu@pku.edu.cn)*

13 **Key Points:**

14 Ice nucleation

15 Urban aerosol

16 Immersion mode

17 **Abstract**

18 Exceedingly high levels of  $PM_{2.5}$  with complex chemical composition occur frequently in China. It has  
19 been speculated if anthropogenic  $PM_{2.5}$  may significantly contribute ice nucleating particles (INP).  
20 However, few studies have focused on the ice-nucleating properties of urban particles. In this work, two  
21 ice-nucleating droplet arrays have been used to determine the atmospheric number concentration of INP  
22 ( $N_{INP}$ ) in the range from  $-6\text{ }^{\circ}\text{C}$  to  $-25\text{ }^{\circ}\text{C}$  in Beijing. No correlations between  $N_{INP}$  and neither  $PM_{2.5}$  nor  
23 black carbon mass concentrations were found, although both varied by more than a factor of 30 during  
24 the sampling period. Similarly, there were no correlations between  $N_{INP}$  and either total particle number  
25 concentration or number concentrations for particles with diameters  $> 500\text{ nm}$ . Furthermore, there was  
26 no clear difference between day and night samples. All these indicate that Beijing air pollution did not  
27 increase or decrease INP concentrations in the examined temperature range above values observed in  
28 non-urban areas, hence, the background INP concentrations might not be anthropogenically influenced  
29 as far as urban air pollution is concerned, at least in the examined temperature range.

30 **1 Introduction**

31 Formation of the ice phase in clouds can be modulated by aerosols emitted from anthropogenic and  
32 natural sources (Morris et al., 2014; Murray et al., 2012; Rosenfeld et al., 2008) via heterogeneous ice  
33 nucleation (Pruppacher et al., 1998). This results in a significant impact on the cloud extent, lifetime,  
34 formation of precipitation, and radiative properties of clouds (DeMott et al., 2010). Currently, four  
35 mechanisms are proposed for the heterogeneous ice nucleation in mixed-phase clouds: deposition ice  
36 nucleation, condensation freezing, immersion freezing, and contact freezing (Vali et al., 2015; Hoose  
37 and Möhler, 2012). It is under discussion if condensation freezing is different from immersion freezing  
38 on a fundamental level (Wex et al., 2014) and if at least some of the observed deposition ice nucleation  
39 can be attributed to pore condensation and freezing (Marcolli, 2014). For mixed-phase clouds, immersion  
40 freezing has been widely reported to be the most important ice nucleation mechanism (Ansmann et al.,  
41 2008; Murray et al., 2012; Westbrook and Illingworth, 2013). During the past decades, great efforts have  
42 been dedicated to understanding heterogeneous ice nucleation. However, it has become obvious that  
43 many fundamental questions in this field are still unsolved (Kanji et al., 2017).

44 Numerous studies have attempted to quantify the ice nucleation ability of selected aerosol particles  
45 of a specific composition in immersion mode, such as dust (DeMott et al., 2015; Kaufmann et al., 2016;  
46 DeMott et al., 2003), marine (Wilson et al., 2015; DeMott et al., 2016; Alpert et al., 2011) and biological  
47 particles (Pummer et al., 2012; Hartmann et al., 2013; Fröhlich-Nowoisky et al., 2015). Szyrmer and  
48 Zawadzki (1997), Hoose and Möhler (2012), Murray et al. (2012) and Kanji et al. (2017) are all reviews  
49 which give a more extensive overview over materials that can induce ice nucleation. In general, biogenic  
50 particles have been assumed to provide atmospheric ice nucleating particles (INP) which are ice active  
51 in the immersion mode at comparably high temperatures (above  $-15^{\circ}\text{C}$ , Murray et al., 2012; Petters &  
52 Wright, 2015). Ice activity at lower temperatures is attributed to mineral dust particles (Murray et al.,  
53 2012) while the role of soot particles in atmospheric ice nucleation is still debated (Kanji et al., 2017).

54 Biogenic particles in general have long been known to be able to induce ice nucleation at  
55 comparably high temperatures above  $-10^{\circ}\text{C}$  (e.g. Schnell and Vali, 1972). It has been widely accepted  
56 that biological particles can act as efficient INP, with some bacteria and fungi reported to possess the  
57 ability to arouse freezing at temperatures as high as  $-2^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$  (Lundheim, 2002). Fungal spores  
58 (O'Sullivan et al., 2016; Pummer et al., 2015) and lichen (Moffett et al., 2015) are known to nucleate ice  
59 in the temperature range above  $-10^{\circ}\text{C}$ , while pollen (Augustin et al., 2013; Pummer et al., 2012) may  
60 compete with mineral dust particles in terms of their ability to nucleate ice, albeit not in terms of their  
61 atmospheric abundance.

62 Recognized as the dominant INPs in mixed-phase clouds (Kamphus et al., 2010), particles from  
63 various mineral dusts were found to catalyse ice formation effectively in chamber experiments (Murray  
64 et al., 2012; Kanji et al., 2017). Among mineral dust particles, those containing K-feldspar might be  
65 particularly ice active (Atkinson et al., 2013).

66 In general, burning of liquid fuels produces soot particles (i.e., particles that are mostly organic),  
67 while burning of solid material as e.g., biomass or coal will also produce ash particles which contain the  
68 inorganic components that made up the fuel. Umo et al. (2015) and Grawe et al. (2016) examined the ice  
69 activity of ash particles from wood and coal burning in the immersion mode and both find that these  
70 particles are ice active. In Grawe et al. (2016), ash particles with atmospherically relevant sizes of 300 nm  
71 were examined and the most active particles came from a sample of fly ash from a coal burning power  
72 plant, inducing immersion freezing below  $-22^{\circ}\text{C}$ . Both, Umo et al. (2015) and Grawe et al. (2016) suggest  
73 that ash particles might play a role in the atmosphere, however, point to a lack of knowledge of their

74 atmospheric abundance. Also, different ash samples showed different ice activities, and also large  
75 differences in the results between the methods used for the examination were described, i.e., it is still  
76 inconclusive if ash particle might play an important role as atmospheric INP.

77         Although there has been a considerable number of studies aimed at understanding the ability of  
78 black carbon (BC)-containing particles acting as INP, the results are still controversial. Some studies  
79 show that BC-containing particles did not act as good INP (Schill et al., 2016; Chou et al., 2013). Chou  
80 et al. (2013) observed that soot particles from diesel engines and wood burning form ice at  $-40^{\circ}\text{C}$ , and  
81 unrealistically high relative humidity (RH) was needed for freezing initiation above this temperature.  
82 Schill et al. (2016) showed that neither fresh nor aged emissions from diesel engines contributed  
83 appreciably to atmospheric INP concentrations. However, some studies considered BC-containing  
84 particles as possible INPs (Cozic et al., 2008; Levin et al., 2016; Cozic et al., 2007). Observation of  
85 abundant BC in ice particle residuals in field experiments suggested that some BC-containing particles  
86 may preferentially act as INP (Cozic et al., 2008). In the experiments conducted by Levin et al. (2016),  
87 emissions of different types of biomass fuel produced measurable concentrations of INPs ( $0.1\text{-}10\text{ cm}^{-3}$ )  
88 associated with higher BC concentration accounting for about 0-70%. Determination of ice nucleating  
89 properties of physically and chemically aged soot particles suggests that the heterogeneous ice nucleation  
90 activity of freshly emitted diesel soot particles is sensitive to some of the aging processes (Kulkarni et  
91 al., 2016).

92         In the atmosphere of urban areas with dense population, various sources and complex aging  
93 transformations (such as coagulation, condensation of vapor, chemical reaction) of particles can be found.  
94 Particularly, urban aerosol may be rich in BC-containing particles resulting from anthropogenic activities,  
95 such as fossil fuel combustion and biomass burning (Bond et al., 2013), which were speculated to play a  
96 role for the formation of ice in clouds (Kanji et al., 2017). However, the ice nucleating properties of  
97 particles produced in urban regions have rarely been the focus of previous studies. Exceptions are Knopf  
98 et al. (2010) and Corbin et al. (2012), examining the ice nucleation activity of particles in the  
99 anthropogenically influenced atmospheric aerosol in Mexico City and Toronto, respectively. In both  
100 studies the relative humidity at which measurements were made were below water vapor saturation (with  
101 respect to liquid water). Using filter samples, Knopf et al. (2010) state that organic particles included in  
102 their samples might potentially induce ice nucleation at conditions relevant to cirrus formation. Corbin  
103 et al. (2012) used a CFDC (Continuous-Flow Diffusion Chamber) operating at  $-33^{\circ}\text{C}$  together with a

104 particle mass spectrometer. Statistical limitations impeded a statistical sound analysis, but their data  
105 suggests that dust particles, particles from biomass burning and particles containing elemental carbon  
106 might be sources of INP at their experimental conditions. They explicitly encourage further studies of  
107 these particles types concerning their role as possible INP.

108 In the present study, we measured the ice nucleating activity of urban aerosols in parallel with BC  
109 and PM<sub>2.5</sub> mass concentration and particle number concentrations in the atmosphere of the mega-city  
110 Beijing, which is frequently experiencing heavy pollution. During heavy haze episodes, PM<sub>2.5</sub> mass  
111 concentration can be several hundred micrograms per cubic meter and composed of a complex mixture  
112 of different chemical components (organic matter, inorganic ions and black carbon) (Zheng et al., 2016).  
113 The goal of this project is to find out if anthropogenic sources which are dominant in the urban  
114 atmosphere significantly contribute to the local INP concentrations, focusing particularly on the ice  
115 nucleating ability of BC in urban aerosols.

## 116 **2 Materials and Methods**

### 117 **2.1 Sample collection and particle number measurement**

118 The sampling site for particle collection was on the roof of a six-floor building (about 30 m above  
119 ground level) on the campus of Peking University (39°59'20"N, 116°18'26"E), located in the north-  
120 western urban area of Beijing.

121 Particles with an aerodynamic diameter less than or equal to 2.5 micro-meters (PM<sub>2.5</sub>) were collected  
122 on quartz fiber (Whatman, 1851-865) and PTFE filters (Whatman,7592-104) using a 4-channel sampler  
123 with 2.5µm impactors from 27<sup>th</sup> November 2016 to 1<sup>st</sup> December 2016 and 13<sup>th</sup> December 2016 to 22<sup>th</sup>  
124 December 2016. Daytime filters were collected from 8:00 am to 8:00 pm and nighttime filters were  
125 collected from 8:00 pm to 8:00 am with an air flow rate of 16.7 L min<sup>-1</sup>, resulting in a total volume of air  
126 sampled on each filter of ~12000 L. Note that all sample volumes used herein were converted to standard  
127 volumes. The quartz filters were treated before the sampling by heating them to 550 °C for 6 h. After  
128 sampling, all filters were kept at ≤ -18 °C during storage, and the INP analysis was done within 20 days,  
129 starting on 5th February in 2017.

130 A scanning mobility particle sizer (SMPS, TSI Inc., USA) system was used to obtain particle  
131 number distribution in the 3-700 nm (electrical mobility diameter) size range during the sampling period

132 while an aerodynamic particle sizer (APS, TSI model 3321, TSI Inc., USA) measured particle number  
133 size distributions between 800 nm and 2.5 $\mu$ m (aerodynamic diameter). The APS results were transformed  
134 from aerodynamic diameter to Stokes diameter with a particle density of 1.5 g cm<sup>-3</sup> which were measured  
135 by a CPMA (centrifugal particle mass analyzer) and combined with the measured and inverted size  
136 distributions obtained from the SMPS. From these combined size distributions, we calculated the total  
137 particle number concentration of particles in the diameter range from 3nm to 2.5 $\mu$ m ( $N_{\text{total}}$ ) and number  
138 concentrations of particles larger than 500nm ( $N_{>500\text{nm}}$ ). When comparing with filter results, we use 12h-  
139 average values of  $N_{\text{total}}$  and  $N_{>500\text{nm}}$ , where the averages were always made from 8:00 am to 8:00 pm for  
140 daytime data and from 8:00 pm to 8:00 am for nighttime data.  $N_{>500\text{nm}}$  was derived, as in general larger  
141 particles are expected to be more efficient INP, and also as this size range was selected in DeMott et al.  
142 (2010, 2015) to serve as a base for parameterizations of INP number concentrations.

143 Concentrations of BC were continuously measured by a multi-angle absorption photometer (5012  
144 MAAP, Thermo Fisher Scientific, Waltham, MA, USA) utilizing a 637 nm LED as a light source (Müller  
145 et al., 2011). The instrument measures the absorption of particles collected on a filter with a time  
146 resolution of 5 min and automatically derives BC mass concentration from the measurement while  
147 accounting for multiple scattering occurring on the filter. It might be worth noting that a comparison of  
148 BC concentrations obtained from the MAAP with concentrations of EC determined by a filter-based  
149 SUNSET EC/OC analyzer during a different field campaign showed, that both instruments measured the  
150 same trends while the mean ratio of concentrations of BC to EC was about 1.35.

## 151 2.2 Chemical analysis

152 Two PTEF filters were always sampled in parallel, and while one was used for INP analysis, the  
153 other was selected for the total mass and water-soluble ion analysis. PM<sub>2.5</sub> mass concentration was  
154 obtained with an analytical balance by the gravimetric method (Mettler Toledo AG285) (Yang et al.,  
155 2011). As for water-soluble inorganic compounds analysis, Guo et al. (2012) described the method for  
156 seven major ions (K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) measured by ion-chromatograph (DIONEX,  
157 ICS-2500/2000) based on the usage of PTEF filters. Post-sampling, all filters were stored in the  
158 refrigerator at -18 °C before analysis.

### 159 **2.3 INDA and LINA analysis**

160 Two devices called INDA (Ice Nucleation Droplet Array) and LINA (Leipzig Ice Nucleation Array)  
161 have been set up at the Leibniz Institute for Tropospheric Research (TROPOS) in Germany following  
162 the design described in Conen et al. (2012) and in Budke & Koop (2015), respectively. INDA was used  
163 to investigate the immersion freezing properties of the quartz fibre filter samples while LINA was used  
164 to test the particles on PTFE filters.

165 INDA consists of a thermostat (JULABO FP40) with a 16 L cooling bath. 96 circles (1mm in  
166 diameter each) of each quartz filter were cut out by a punch and immersed separately in the tubes of a  
167 PCR (Polymerase chain reaction) tray which each contained 50  $\mu\text{l}$  distilled water. While Conen et al.  
168 (2012) originally used separate Eppendorf Tubes®, the use of PCR trays for immersion freezing studies  
169 has been suggested before in Hill et al. (2016) and was adapted in the LINA set-up. The PCR trays were  
170 placed on a sample-holder and exposed to decreasing temperatures with a cooling rate of approximately  
171 1 K  $\text{min}^{-1}$  in the cooling bath down to -30 °C. Real time images of the PCR trays were recorded every 6  
172 seconds by a CCD (Charge Coupled Device) camera. A flat light that was fixed at the bottom of the  
173 cooling bath helped to yield proper contrast between frozen and unfrozen droplets on the recorded  
174 pictures, so that frozen droplets could be identified according to the brightness change during the freezing  
175 process. A program recorded the current temperature of the cooling bath and related it to the real-time  
176 images from the CCD camera. The temperature in the PCR trays had been calibrated previously as  
177 described in section 1.1 of the appendix.

178 For the measurement of ice nucleating particles at lower temperature, LINA was built according  
179 to an optical freezing array named BINARY, which was described in detail by Budke & Koop (2015).  
180 PTFE filters collected during the same period as quartz fibre filters were used for LINA. Half of the  
181 PTFE filter of each day was immersed in 10 ml distilled water and shaken for 1 h to wash particles off.  
182 For each measurement, 90 droplets with the volume of 1  $\mu\text{l}$  were pipetted from the resulting suspension  
183 onto a thin hydrophobic glass slide (diameter 40 mm, thickness 0.13-0.16 mm, obtained from Marienfeld-  
184 superior), with each droplet being contained in a separate compartment. These compartments were round  
185 holes with diameters of 3 mm, drilled into an aluminium plate with a diameter of 40 mm and a thickness  
186 of 14 mm. Both, hydrophobic glass slide and the aluminium plate with the compartments were  
187 surrounded by an aluminium ring with an inner diameter of 40 mm, which acted to keep glass slide and

188 aluminium plate in place. Slide, plate and ring were all arranged before the droplets were pipetted. A  
189 second thin glass slide was put on top of the plate so that the compartments were all separated from each  
190 other and that evaporation of the droplets was prevented. The droplets were cooled on a Peltier element  
191 with a cooling rate of 1 K min<sup>-1</sup>. There was a thin oil (squalene) film between the hydrophobic glass slide  
192 and the Peltier element for optimal heat conductivity. The temperature on the glass slide had been  
193 determined previous to the experiments as described in section 1.2 of the appendix, and the temperature  
194 shift between that set on the Peltier element and that observed on the glass slide was accounted for in the  
195 data presented herein. The freezing process again was recorded by taking pictures with a CCD camera  
196 every 6 seconds and detecting the freezing based on a change in the reflectance of the droplets upon  
197 freezing.

198 As mentioned above, the temperature calibration for these two instruments is described in detail in  
199 the section 1.1 and 1.2 of the appendix. The background freezing signal of pure distilled water and circles  
200 cut from clean filters were tested as well. These results are shown in the section 2 of the appendix.

201 The measurements resulted in frozen fractions ( $f_{ice}$ ) as defined in Eq. (1):

$$202 \quad f_{ice} = \frac{N_{frozen}}{N_t} \quad (1)$$

203 where  $N_{frozen}$  is the number of frozen tubes or droplets at a certain temperature and  $N_t$  is the total number  
204 of tubes in PCR trays (i.e., 96) or droplets on the slides (i.e., 90).

205 The temperature dependent cumulative number concentration of INP ( $N_{INP}$ ) per volume of sampled  
206 air was calculated according to Eq. (2), similarly to Vali (1971) and Conen et al. (2012):

$$207 \quad N_{INP}(T) = -\frac{\ln(1-f_{ice}(T))}{V_{sampled}} \quad (2)$$

208 where  $N_{unfrozen}$  is the number of tubes or droplets still unfrozen (liquid) at a certain temperature, and  
209  $V_{sampled}$  is the volume of air converted to standard conditions (0°C and 1013hPa) from which the particles  
210 were collected that were suspended in each of the droplets in LINA or that were collected on each filter  
211 punch used for INDA measurements, respectively.

212 The chemical ion analysis in section 3.1 and the determination of the PM<sub>2.5</sub> mass concentration was  
213 done at Peking University. The filters used for INP measurements were brought to TROPOS where then  
214 INP measurements were done. Filters were continuously cooled below 0°C in a portable ice box during  
215 transport.

## 216 **3 Results and Discussion**

### 217 **3.1 Severe PM<sub>2.5</sub> pollution in Beijing**

218 Fig. 1 shows the time series of PM<sub>2.5</sub> mass concentrations and chemical composition during the  
219 sampling period. The PM<sub>2.5</sub> mass concentration with a mean value of  $97.30 \pm 77.9 \mu\text{g m}^{-3}$  ranged from  
220  $6.54 \mu\text{g m}^{-3}$  up to  $273.06 \mu\text{g m}^{-3}$ . Here, the cases with PM<sub>2.5</sub> above  $50 \mu\text{g m}^{-3}$  were defined as polluted  
221 days, whereas the rest was defined as clean days. On average, the sulfate, nitrate, and ammonia (SNA)  
222 accounted for around 35% of PM<sub>2.5</sub> during the whole period with an obvious enhancement in polluted  
223 days (53%), indicating that generation of secondary particulate mass is one major contributor to the  
224 formation of particulate pollution, as it has previously been described in Guo et al. (2010) and Zheng et  
225 al. (2016). In this study, when we refer to secondarily formed particulate matter, this will always stand  
226 mainly for SNA and secondary organic substances. Dust particles are in the coarse mode, and only  
227 contribute little to the total PM<sub>2.5</sub> load (Lu et al., 2015; Li and Shao, 2009). In these studies, Ca<sup>2+</sup> as a  
228 tracer for dust particles showed a low proportion in PM<sub>2.5</sub>, suggesting that the dust particles also only  
229 contributed little to PM<sub>2.5</sub> during our observations as well.

230 During the sampling period, BC mass concentrations varied from  $0.50 \mu\text{g m}^{-3}$  on clean days up to  
231  $17.26 \mu\text{g m}^{-3}$  on polluted days. On average, the mean mass concentration of BC,  $7.77 \pm 5.23 \mu\text{g m}^{-3}$ ,  
232 accounted for about 13% of PM<sub>2.5</sub>. During night time, BC concentrations were higher than those during  
233 daytime due to stronger diesel engine emissions and a lower boundary layer (Guo et al., 2012). Our  
234 previous studies showed that secondarily and primarily formed organic particulate matter contributed to  
235 around 36% of non-refractory PM<sub>1</sub> detected by an aerosols mass spectrometer during wintertime in the  
236 atmosphere of Beijing (Hu et al., 2017).

237 Additionally, Fig. 2 shows 2-day back-trajectories obtained by the NOAA HYSPLIT model, with  
238 one trajectory related to each sampled filter, starting at the median sampling time of each filter. Fig. 3  
239 shows minutely recorded data for wind-direction and wind-speed collected by an Auto weather station  
240 (Met One Instruments Inc.) located on the same roof top as the aerosol sampling equipment. Both pictures  
241 are colored-coded with respect to PM<sub>2.5</sub> mass concentrations. The air masses that came from north or  
242 north-western directions were generally coincident with higher wind-speeds. They brought clean air with  
243 lower PM<sub>2.5</sub> mass concentrations. They did cross desert regions, however, Beijing was reported to be  
244 affected by desert dust mainly only in spring (Wu et al., 2009). Typically, the air masses coming from

245 south and south-west of Beijing moved slowly and spent much more time over industrialized regions,  
246 resulting in high particulate matter mass concentrations. This here observed pattern is typical for Beijing,  
247 and these connections between wind-direction and pollution levels in Beijing have been analyzed in  
248 detail previously in Wehner et al. (2008).

### 249 **3.2 Particle number concentrations**

250 Fig. 4 shows the time series of the total number concentration of particles from 3 nm up to 2.5 $\mu$ m  
251 ( $N_{\text{total}}$ ) and the number concentration of particles larger than 500 nm ( $N_{>500\text{nm}}$ ), where  $N_{\text{total}}$  varied from  
252  $3 \cdot 10^3$ - $7 \cdot 10^4$  cm<sup>-3</sup> and  $N_{>500\text{nm}}$  varied from 10 to  $4 \cdot 10^3$  cm<sup>-3</sup>. Obviously, in the atmosphere of Beijing  
253 during the sampling period, small particles less than 500 nm account for a large fraction of the total  
254 particle number concentration, but during strong pollution events, also a large increase in  $N_{>500\text{nm}}$  is seen.  
255

256 Fig. 5(a) and Fig. 5(b) show INP number concentrations ( $N_{\text{INP}}$ ) as a function of temperature for  
257 INDA measurements. The lines are colour coded depending on the PM<sub>2.5</sub> mass concentration (Fig. 5(a))  
258 and 12h-average  $N_{>500\text{nm}}$  (Fig. 5(b)) during the respective filter sampling, where each line (30 in total)  
259 represents an individual result of a filter. Exemplary measurement uncertainties are given in section 3 of  
260 the appendix. All filter samples had INP that were active at -12.5°C and the highest freezing temperature  
261 was observed to be -6°C. Overall,  $N_{\text{INP}}$  varied from 10<sup>-3</sup> to 1 L<sup>-1</sup>. Already at a first glance, there is no  
262 clear trend in  $N_{\text{INP}}$  with PM<sub>2.5</sub> mass concentration and 12h-average  $N_{>500\text{nm}}$ , indicating that the dominant  
263 pollutants of urban atmosphere may not significantly contribute to INPs active down to roughly -16°C  
264 in an urban region.

265 To verify the results observed in INDA at lower temperatures, PM<sub>2.5</sub> collected by PTEF filters in  
266 the same period were used for LINA which can test the ice nucleating properties of droplets down to  
267 below -20°C. Washing particles off from the PTFE filters was more complete for some filters than for  
268 others. This showed in differently large deviations in  $N_{\text{INP}}$  from INDA and LINA measurements in the  
269 overlapping temperature range, where results determined from INDA were always similar to or higher  
270 than those from LINA as particle removal by washing the filters was frequently incomplete. It is  
271 mentioned in Conen et al. (2012), that a quantitative extraction of particles from quartz fiber filters was  
272 not possible without also extracting large amounts of quartz fibers. We tried to overcome this issue by

273 using PTFE filters, as degradation of the PTFE filter during washing does not occur due to the  
274 hydrophobic properties of the filter material. But we observed that not all particles were released into the  
275 water during the washing procedure (likely those collected deep within the filter), as filters frequently  
276 still looked greyish after washing, independent from the washing procedure (we experimented with  
277 different washing times up to 4 hours and with the use of an ultrasonic bath).

278 For our INDA measurements, punches of quartz filters were measured after they were immersed in  
279 water, representing the ice nucleating properties of all collected particles (Conen et al., 2012). However,  
280 as already mentioned above,  $N_{\text{INP}}$  derived from LINA measurements were lower than those from INDA,  
281 due to particles that did not come off during washing. Based on our observations, we cannot recommend  
282 the use of sampling on PTFE filters followed by particle extraction in water. But we still decided to select  
283 those data from LINA measurements that showed the lowest deviation to the respective INDA results in  
284 the overlapping temperature range for use in this study. After calculating the deviation between INDA  
285 and LINA results, represented as the factor ( $N_{\text{INP}}$  of INDA /  $N_{\text{INP}}$  of LINA), ten LINA measurements  
286 from different days were selected to be used. For these measurements, the factor representing the  
287 deviation was in a range from 1.3 to 4.4. These data are shown in Fig. 5(c) and Fig. 5(d). The LINA data  
288 is represented by the dotted lines and the respective INDA data from the same sampling periods is  
289 represented by solid lines. In the temperature from  $-20^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$ , results of LINA also show no clear  
290 trend in  $N_{\text{INP}}$  with  $\text{PM}_{2.5}$  mass concentration and 12h-average  $N_{>500\text{nm}}$ , even though a lower temperature  
291 has been involved, extending our statement that urban pollution might not contribute to INP down to -  
292  $25^{\circ}\text{C}$ .

### 293 **3.3 Correlation of $N_{\text{INP}}$ with $\text{PM}_{2.5}$ , and BC mass concentration and particle number concentrations**

294 There have been many studies carried out in field and laboratory focusing on the ice nucleating  
295 properties of BC particles, however with inconclusive results. Some held the view that BC is not an  
296 efficient ice nucleation active species (Kamphus et al., 2010; Schill et al., 2016), whereas some described  
297 BC particles as possible INPs (Cozic et al., 2008; Cozic et al., 2007).

298 Here we selected  $N_{\text{INP}}$  derived from INDA measurements at  $-16^{\circ}\text{C}$  and plotted them against BC (Fig.  
299 6 (a)),  $\text{PM}_{2.5}$  mass concentrations (Fig. 6 (b)) and 12h-average values of  $N_{\text{total}}$  (Fig. 6 (c)),  $N_{>500\text{nm}}$  (Fig. 6  
300 (d)), and  $N_{\text{INP}}$  at  $-16^{\circ}\text{C}$  derived from DeMott et al. (2010) (Fig.6 (e)) and DeMott et al. (2015) (Fig.6 (f)).

301 To determine the latter two, the 12h-averages of  $N_{>500 \text{ nm}}$  shown in Fig. 3 were used, following  
302 parameterizations suggested by DeMott et al. (2010, 2015). Linear fits are included in all panels of Fig.  
303 6, and values for  $R^2$  and  $p$  for these fits are shown in Table 1 Our results discussed in the following, based  
304 on  $N_{\text{INP}}$  at  $-16^\circ\text{C}$ , are similarly valid for all other temperatures down to  $-25^\circ\text{C}$ .

305 Fig. 6(a) to (f) show that there was no clear trend between  $N_{\text{INP}}$  and any of the displayed parameters,  
306 be it BC or  $\text{PM}_{2.5}$  mass concentration or any of the 12h-average particle number concentrations. Also the  
307  $R^2$  and  $p$  values given in Table 1 clearly show that there was no correlation between  $N_{\text{INP}}$  and any of the  
308 examined parameters. In the urban region of Beijing during winter, the INP could be assumed to be soot  
309 or ash particles from traffic emissions, biomass burning and coal combustion, or to be dust particles  
310 advected from the desert regions during prevailing northern and north-western wind, or to originate from  
311 the biosphere. While mineral dust and biological particles are generally assumed to be the most abundant  
312 INP in the atmosphere (Murray et al., 2012, Kanji et al., 2017), the role of particles from combustion,  
313 i.e., of soot and ash particles, as INP is still controversial (Kanji et al., 2017). Our results indicate that  
314 BC particles did not correlate with INP concentrations in the urban atmosphere. It is possible that the BC  
315 particles emitted from coal burning, biomass burning, and traffic emissions are not ice active in the first  
316 place, or that they underwent atmospheric aging processes (such as coagulation, condensation upon vapor,  
317 and chemical reaction) resulting in more internally mixed particles after emission (Pöschl, 2005), which  
318 might inactivate their potential to act as INP. In the atmosphere of Beijing, the aging timescale is much  
319 shorter than in cleaner urban environments, which was shown in Peng et al. (2016). For example, to  
320 achieve a complete morphology modification for BC particles in Beijing, the aging timescale was  
321 estimated to be 2.3 h, compared to 9 h in Houston (Peng et al., 2016).  $\text{PM}_{2.5}$  chemical composition  
322 indicated that the BC particles may be aged and coated by secondarily formed chemical components  
323 (SNA and other secondary organic materials) during the heavy haze episodes (Peng et al., 2016), thereby,  
324 resulting in weakened heterogeneous ice nucleation activity of freshly emitted diesel soot particles  
325 (Kulkarni et al., 2016).

326 However, if a possible coating was soluble, it would dissolve both during immersion freezing and  
327 during our experiments and would not impede the ice activity of BC particles, unless it reacted chemically  
328 with an ice active site. It has been observed that a coating did not impede the ice activity of mineral dust  
329 particles coated with nitric acid in Sullivan et al. (2010) and coated with succinic acid or levoglucosan  
330 in Wex et al. (2014).

331 Another study conducted in Ulaanbaatar in Mongolia, a city suffering from severe air pollution,  
332 showed a low ice activity towards heterogeneous ice nucleation when the sulphur content of particles  
333 was highest (Hasenkopf et al., 2016). It is interesting to note that we observe the opposite in our study,  
334 i.e., the increase of  $PM_{2.5}$  mass concentration and percentage of SNA in  $PM_{2.5}$  during haze periods also  
335 seem to have no negative impact on INP concentrations. Not only did increased BC mass concentrations  
336 not increase the observed INP concentrations, but also were INP concentrations not particularly low  
337 during pollution episodes. Furthermore, we conclude that the strong formation of secondary particulate  
338 matter during haze days would not contribute to INP. In addition, there is no clear difference of ice  
339 nucleation between day and night time samples.

340 The size distribution measurements show that the largest fraction of all particles occurred in the size  
341 range below 500 nm. However, during the strongest pollution event towards the end of our measurement  
342 period (Dec. 17 during daytime (1217D) till the night from Dec. 21 to Dec. 22 (1221N)), also  $N_{>500nm}$   
343 increased noticeably to much larger values than before. In general, also particles in this size range were  
344 affected by the pollution, e.g., by an increase in size of pre-existing particles via atmospheric aging  
345 processes (such as coagulation, condensation, chemical reaction) where particles advected from southern  
346 industrial areas of Beijing might also contribute. This is at the base of the explanation why the  
347 parameterizations for  $N_{INP}$  by DeMott et al. (2010, 2015) were not able to describe the measured values,  
348 as seen in Fig. 6 (e) and (f). Additionally, the time series of  $N_{INP}$  at  $-16^{\circ}C$ , based on DeMott et al. (2010,  
349 2015) and are shown as blue and green squares in Fig. 7, respectively. Also shown are values for  $N_{INP}$  at  
350  $-16^{\circ}C$  as measured by LINA (red circles), i.e., the same values used in Fig. 7. Mostly, the  
351 parameterization by DeMott et al. (2015) yields larger values and a larger spread, compared to the  
352 parameterization by DeMott et al. (2010), but naturally both follow the trends in  $N_{>500nm}$ . A correction  
353 factor of 3, as suggested in DeMott et al. (2015), was not applied, as this would simply increase all  
354 respective values by this factor, i.e., it will not change the results. Indeed, during the pollution phase, the  
355 parameterizations overestimate the observed values by more than two orders of magnitude. But also  
356 during clean phases, neither  $N_{>500nm}$  nor the parameterizations by DeMott et al. (2010, 2015) correlate  
357 with  $N_{INP}$ . Summarizing, this shows that pollution events not only did not add INP, but also that for the  
358 aerosol observed during our study, a parameterization of  $N_{INP}$  based on particles in the size range  $> 500$   
359 nm is not feasible. Interestingly, as will be shortly discussed in the next section, a much older  
360 parameterization by Fletcher (1962) captures  $N_{INP}$  as measured in this study rather surprisingly well, at

361 least within one order of magnitude (Fig. 8). In summary, during polluted days, the increase of BC  
362 concentration, secondary components (SNA) and other compounds contributing to PM<sub>2.5</sub>, as well as  
363 particle concentrations have no impact on INP concentrations down to -25°C in the urban region we  
364 examined in our study. This means that anthropogenic pollution did not contribute to the INP  
365 concentration. But it also indicates that that anthropogenic pollution in Beijing did not deactivate the  
366 present INP, as polluted periods did not show particularly low INP concentrations, although aging and  
367 formation of secondary particulate matter typically are intense during times of strong pollution.

368 In addition to what we discussed above, also no correlation was observed between  $N_{\text{INP}}$  and wind-  
369 speed, as can be seen by the respective values for  $R^2$  and  $p$  given in Table 1. Fig. 9 indicates that there  
370 was also no correlation with wind-direction. The fact that we find no correlation with either wind-speed  
371 or wind-direction agrees with the desert regions towards the north-west not being efficient dust sources  
372 in winter, and are a hint that we may have observed average background INP concentrations in Beijing  
373 during our measurements.

374 Additionally, also no correlation was found between any of the water-soluble constituents that were  
375 analyzed with ion chromatography and INP concentrations. This is not too astounding, as INP make up  
376 only a small fraction of all particles, as can be seen when comparing number concentrations from Fig. 4  
377 and Fig. 7, and hence they make up only a small fraction of the mass, likely too small to be detected.  
378 Furthermore, a number of different components might contribute to INP, e.g., biological INP that are  
379 generally ice active at higher temperatures ( $> -15^\circ\text{C}$ ) and mineral dusts which are ice active at lower  
380 temperatures, therefore one common tracer for INP might not be applicable. As far as K is concerned,  
381 which might be connected to K-feldspar containing mineral dust particles with high ice activity (Atkinson  
382 et al., 2013), we only analyzed the water soluble fraction, i.e., K related to feldspar would not have been  
383 analyzed. Moreover, K is also emitted by biomass burning and hence influenced by anthropogenic  
384 pollution. It remains to be seen if a simple correlation between chemical constituents of the atmospheric  
385 aerosol and INP concentrations can be established at all.

### 386 3.4 Comparison with literature

387 First, we compare our results with results of  $N_{\text{INP}}$  derived from precipitation samples as collected  
388 in Petters and Wright (2015) as shown in Fig. 8. These literature data were collected in various locations

389 in North America and Europe, and none of these locations was one with strong anthropogenic pollution,  
390 different from the sample location in the present study. The  $N_{\text{INP}}$  in our study varied from  $10^{-3}$ - $10 \text{ L}^{-1}\cdot\text{air}$   
391 at the temperature range of  $-10^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$ . The data of this study (dark green and brownish lines) are  
392 within the range of values given in Petters and Wright (2015), in the whole temperature range for which  
393 INP concentrations were derived here. A comparison with Corbin et al. (2012) and Knopf et al. (2010),  
394 who both examined INP also in urban air in Toronto and Mexico City, respectively, is not possible due  
395 to different examined ice nucleation modes, and also because they only measured at  $-34^{\circ}\text{C}$  (Corbin et al.,  
396 2012), i.e., outside of the temperature range examined in this study, or only reported ice onset  
397 temperatures (Knopf et al., 2010). But we want to point towards the fact that an older parameterization  
398 based on Fletcher (1962), which has been used for large scale modelling, agrees well with our data (see  
399 Fig. 8) down to  $-20^{\circ}\text{C}$ . It should, however, also be pointed out that the occurring variability in the data  
400 certainly cannot be captured by such a single line. But the increase in  $N_{\text{INP}}$  towards lower temperatures  
401 as parameterized in Fletcher (1962) is similar to that of our data, where it should also be said that this  
402 parameterization is known to overestimate atmospheric observations at lower temperatures (roughly  
403 below  $-25^{\circ}\text{C}$ , see e.g., Meyers et al., 1992). A similar observation was recently described in Welti et al.  
404 (2017), where down to  $-20^{\circ}\text{C}$  the temperature trend of  $N_{\text{INP}}$  derived from filter samples taken on the Cape  
405 Verde islands also agreed well with the parameterisation by Fletcher (1962), while at lower temperatures,  
406 the parameterization exceeded the measurements. In general, for the case of the Beijing air masses  
407 examined in this study, both the range of  $N_{\text{INP}}$  given in Petters and Wright (2015) as well as the  
408 parameterization by Fletcher (1962) agree better with our measurements than the parameterizations by  
409 DeMott et al. (2010, 2015).

410 All of this is again indicative for the fact that Beijing severe air pollution did not increase or decrease  
411 INP concentrations above or below values typically observed in other, non-urban areas on the Earth, and  
412 hence, that the background INP concentrations, at least down to  $-25^{\circ}\text{C}$  might in general not be directly  
413 anthropogenically influenced.

414 Measurements of  $N_{\text{INP}}$  in China have been done as early as 1963 by You and Shi (1964), and a few  
415 further studies listed in Table 2 have been carried out in recent years. Table 2 includes some campaigns  
416 finished in different regions of China including mountains, plateaus and suburban districts with low  $\text{PM}_{2.5}$   
417 concentration and BC-containing particles. In contrast to these observations, our study shows  $N_{\text{INP}}$   
418 detected in an urban region during highly polluted days with complex particle sources. In our study,

419 immersion freezing was examined, while not all studies listed in Table 2 examined this ice nucleation  
420 mode. But due to the scarcity of data, we include the results from all these studies in our discussion here.  
421 Apparently, compared with results in Table 2,  $N_{\text{INP}}$  determined for the urban site of this study ( $1 \text{ L}^{-1} \text{ Air}$   
422 at  $-20^\circ\text{C}$ ) was on the lower end of reported values, which were up to roughly  $20 \text{ L}^{-1} \text{ Air}$  at  $-20^\circ\text{C}$  for non-  
423 dust events. Highest concentrations were observed for dust events with values up to  $604 \text{ L}^{-1} \cdot \text{Air}$  at  $-20^\circ\text{C}$   
424 detected at a suburban site in Beijing, showing that INP from mineral dust contribute to the overall  $N_{\text{INP}}$   
425 already at this temperature (You et al., 2002). Despite the difference among methods and ice nucleating  
426 modes, this again suggests that urban **pollution** aerosol particles might not be efficient immersion  
427 freezing INP and that the ice nucleating ability of particles in urban aerosols might originate from the  
428 non-urban background aerosol particles that are included in the urban aerosol, i.e., that INP observed in  
429 urban environments might have the same sources among bioaerosols and dust particles as non-urban INP.  
430 **An additional contribution from urban biogenic or dust particles to the INP observed in this study cannot**  
431 **be fully excluded, but the agreement between our data and rural data presented in literature (see Fig. 8**  
432 **and Table 2) corroborates our assumption that atmospheric INP in general originate from non-urban**  
433 **sources.**

#### 434 **4 Conclusions**

435 INP concentrations down to  $-25^\circ\text{C}$  determined from  $\text{PM}_{2.5}$  samples collected at an urban site of the  
436 megacity Beijing, China, in winter were found to not be influenced by the highly variable amount of air  
437 pollution, both in mass and particle number concentrations, that was present during the sampling period.  
438 Therefore, we conclude that neither BC nor other pollutants contributed to INP, including secondarily  
439 formed particulate mass. On the other hand, we also conclude that the present INP were not noticeably  
440 deactivated during strong pollution events. Particle number concentrations for particles with diameters  $>$   
441  $500\text{nm}$  were affected by pollution events, and INP concentrations did not correlate with these  
442 concentrations. Therefore, as can be expected, parameterizations based on these concentrations (DeMott  
443 et al., 2010, 2015) do not reproduce the INP concentrations under these extreme conditions and yield  
444 values which are up to more than two orders of magnitude higher than the measured values. On the other  
445 hand, INP concentrations were in the middle of the range reported for atmospheric, non-urban,  
446 concentrations in Petters and Wright (2015), and on the lower end of reported values collected from  
447 previous atmospheric observations in China, while they were much lower than observations during dust

448 events in China. From this, we conclude that INP concentrations might not be influenced directly by  
449 anthropogenic activities, at least not down to roughly  $-25^{\circ}\text{C}$  and maybe even below, and that particularly  
450 natural mineral dust sources might effect INP concentrations observed in China. It should be noted that  
451 ice nucleation observed at high freezing temperatures (particularly above  $-10^{\circ}\text{C}$ , but maybe as low as  $-$   
452  $20^{\circ}\text{C}$ ) is typically attributed to biogenic ice activity. But while identifying the nature of the INP detected  
453 here is beyond the reach of our study, we assume that they originated from natural sources and not from  
454 anthropogenic combustion sources. However, it should be kept in mind that an indirect anthropogenic  
455 influence on INP concentrations is still possible due to land use changes and related changes in  
456 atmospheric dust loadings as well as due to vegetation changes and related changes in the biosphere.

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## 478 **Appendix**

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### 480 **1. Temperature calibration and background of INDA and LINA**

481

#### 482 **1.1 Temperature calibration of INDA**

483 The bath of the thermostat was well mixed during the cooling cycle, and the cooling rate was at 1  
484 K min<sup>-1</sup>. PCR trays were immersed into the cooling liquid such that the water level in the tubes was  
485 below the level of the liquid in the thermostat. The temperature inside the tubes was determined before  
486 the experiments by putting a temperature sensor into a tube during cooling. This was repeated for tubes  
487 in several locations. This worked down to -7°C, below which the sensor induced freezing. In this  
488 temperature range, generally a small constant shift of 0.2 K was observed which was assumed to be  
489 overall valid and was incorporated in the data at all temperatures. A comparison of data obtained for  
490 suspensions of Snomax with previous work done at TROPOS with LACIS (Leipzig Aerosol Cloud  
491 Interaction Simulator) and within INUIT (Ice Nuclei Research Unit, (Wex et al., 2015)) showed good  
492 agreement down to the lowest temperature at which the experiments for the comparison were run, which  
493 was -16°C.

494

#### 495 **1.2 Temperature calibration of LINA**

496 The temperature on the glass slide in LINA was obtained by feeding an air flow with a known dew  
497 point temperature through the instrument, while the instrument cooled down with 1 K min<sup>-1</sup>, i.e., with  
498 the same freezing rate used in the experiments. The humidified air flow was obtained by mixing a dry  
499 air flow with an air flow that was humidified in a Nafion humidifier (Perma Pure MH-110-12S-4, Perma  
500 Pure, Toms River, New Jersey, USA) which was connected to a thermostat (HAAKE C25P, HAAKE  
501 GmbH, Karlsruhe, Germany) that kept the temperature in the humidifier at 10°C. By mixing the two air  
502 streams, dew point temperatures below 0°C were obtained. The dew point temperature was measured  
503 with a dew point mirror (Dew Prime I-S2, Edge Tech, Milford, Massachusetts, USA). The overall setup  
504 is based on the principle of a dew point mirror, i.e., the glass slide on the Peltier element in LINA started  
505 to fog when its temperature reached the dew point temperature adjusted in the air flow. Optical detection  
506 by the CCD camera was deployed similar to how it is used during measurements, i.e., taking a picture  
507 every 6 s. Subsequently detected greyscale images were compared to an image that was taken well before  
508 fogging began. Brightness differences between this original picture and the following pictures were taken  
509 and resulted in a S-shaped curve, reaching the maximum plateau once the glass slide was fogged over

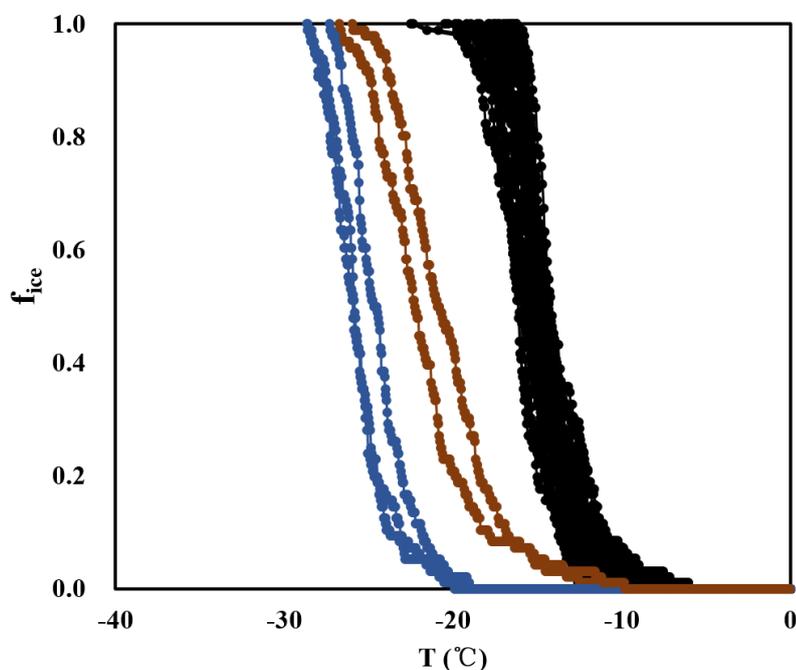
510 completely. A fit was applied to the curve in order to find the temperature where 50% are fogged, which  
511 was taken to represent the actual temperature. Using this principle, the temperature on the glass plate in  
512 LINA was calibrated repeatedly at 5 different temperatures in the range from -2.3°C to -22.3°C. A  
513 comparison of data obtained for suspensions of pollen washing water with previous work done at  
514 TROPOS with LACIS (Augustin et al., 2013) showed good agreement down to the lowest temperature  
515 at which the experiments for the comparison were run, which was -25°C.

516

## 517 2. Background measurement of INDA and LINA

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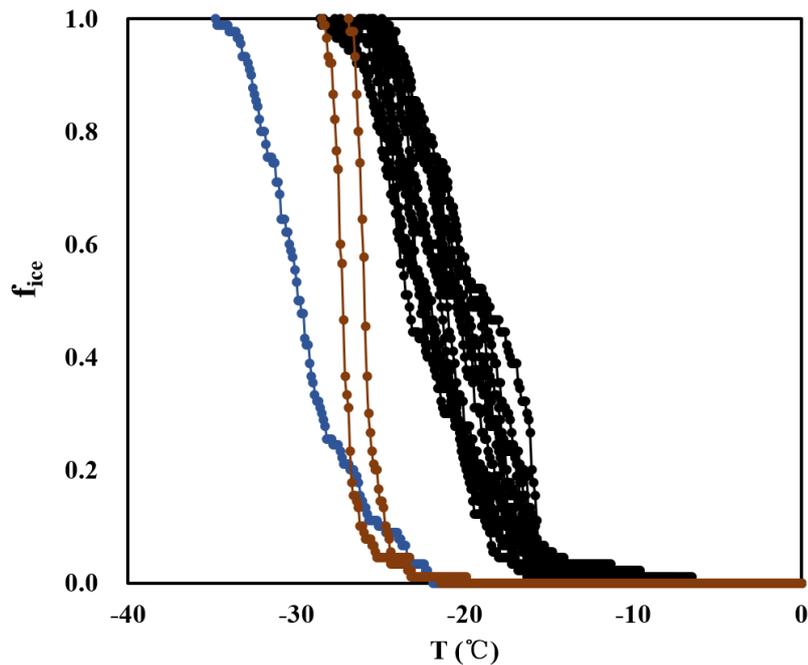
519 In the background experiments of INDA, clean filters in distilled water froze from -17°C to -26°C,  
520 while filters with atmospheric particles froze from -6°C to -22°C. The  $f_{ice}$  of the clean filters was 5 to 14  
521 times lower than that of atmospheric samples at the same temperature, showing a low impact. In LINA  
522 measurements, the background of clean filters washed with distilled water was even lower, as droplets  
523 started to freeze at -22°C. Figure A1 and A2 show the measured frozen fractions of the samples and the  
524 background from pure water and the water with clean filters for both INDA and LINA, to corroborate  
525 that the measurements were well separated from the background.



526

527 Fig. A1 Frozen fractions determined from INDA (black lines), together with background signals determined  
528 for pure water (blue lines) and for pure water containing punches of a clean filter (brown lines).

529



530

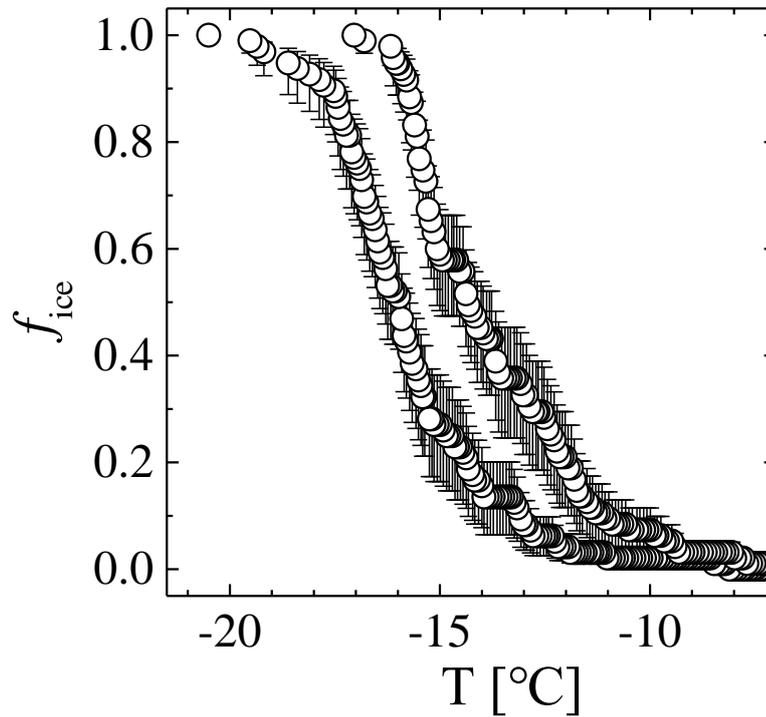
531 **Fig. A2 Frozen fractions determined from LINA, together with background signals determined for pure water**  
 532 **and for pure water in which a clean filter was put and washed, similar to the procedure for the samples.**

533

### 534 **3. Measurement uncertainty for INP measurements**

535

536 The highest and lowest freezing curves detected with INDA are shown exemplarily in Fig. A3  
 537 together with the measurement uncertainty. The derivation of the uncertainty was based on the fact that  
 538 at each temperature, all INP that are ice active at that or any higher temperature are Poisson distributed  
 539 to the examined droplets. It followed a method described in Harrison et al. (2016). For LINA, no  
 540 uncertainties are given, as we know that washing off from the filters was incomplete, and the fraction of  
 541 particles that was retained on the filters cannot be determined. The largest deviation that we allowed  
 542 between LINA and INDA, i.e., a factor of 4.4 (see Sec. 3.2), is the base for the maximum uncertainty for  
 543 f<sub>ice</sub> detected with LINA. For both, INDA and LINA, the temperature uncertainty is 0.5K.



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545 **Fig. A3. The highest and lowest freezing curved detected with INDA together with the measurement**  
 546 **uncertainty.**

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825 **Table and Figures:**

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827 **Table 1 Coefficient of determination ( $R^2$ ) and a measure for the statistical significance of the assumption of a**  
 828 **linear correlation ( $p$ ) for the comparison of  $N_{INP}$  at  $-16^\circ\text{C}$  with the different parameters shown in Fig. 5.**

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parameter	$R^2$	$p$
(a) BC concentration	0.003	0.79
(b) $PM_{2.5}$ concentration	0.006	0.71
(c) $N_{total}$	0.005	0.73
(d) $N_{>500nm}$ at $-16^\circ\text{C}$	0.008	0.67
(e) $N_{INP}$ at $-16^\circ\text{C}$ , based on DeMott et al. (2010)	0.005	0.73
(f) $N_{INP}$ at $-16^\circ\text{C}$ , based on DeMott et al. (2015)	0.007	0.67
<b>(g) Wind speed</b>	<b>&lt;0.001</b>	<b>0.99</b>

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856 **Table 2. Comparison of INP measurements in different regions of China, including  $N_{INP}$  (i.e., INP number**  
 857 **concentrations) and corresponding temperature**

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Sampling site	Citation	Sampling Date	Instruments	Temperature (°C)	Average INP (L <sup>-1</sup> ·Air)	Mode
<b>Huangshan</b> (mountain site)	(Jiang et al., 2015)	September- October,2012	Vacuum water vapor diffusion chamber	-15~-23	0.27~7.02	Deposition
<b>Huangshan</b> (mountain site)	(Jiang et al., 2014)	May- September,2011	Mixing cloud chamber The static diffusion cloud chamber	-20	16.6	Deposition/ Condensation
<b>Huangshan</b> (mountain site)	(Hang et al., 2014)	May- September,2011; September- October,2012	Static vacuum water vapor diffusion cloud chamber	-20	18.74	All modes
<b>Tianshan</b> (mountain site)	(Jiang et al., 2016)	14-24 May, 2014	Vacuum water vapor diffusion chamber; Mixing cloud chamber;	-20	11(non-dust) Hundreds(dust)	Deposition
<b>Nanjing</b> (suburban site)	(Yang et al., 2012)	May-August,2011	The statistic diffusion chamber;	-20	20.11	All modes
<b>Qing Hai</b> (plateau site)	(Shi et al., 2006)	5-26 October, 2003	The Bigger mixing cloud chamber	-15, -20, -25	23.3~85.4	Deposition
<b>Beijing</b> (suburban site)	(You and Shi, 1964)	18 March- 30 April,1963	Mixing cloud chamber	-20	3.9~4.8	All modes
<b>Beijing</b> (suburban site)	(You et al., 2002)	18 March- 30 April,1995	The Bigger mixing cloud chamber	-15, -20	21,78.9(non-dust) 604(dust)	All modes
<b>Beijing</b> (urban site)	This study	27 November- 22 December, 2016	Ice Nucleation droplets Array	-10 ~ -28	0.001~10	Immersion

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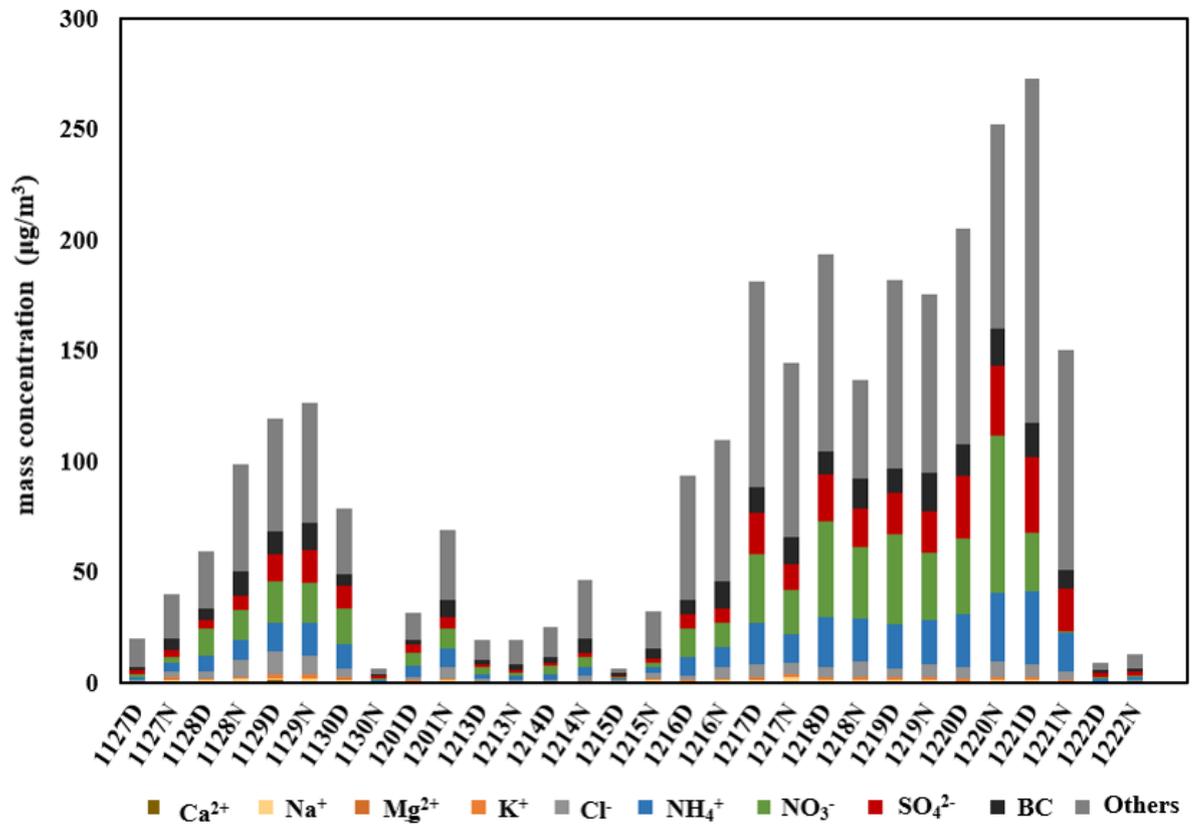
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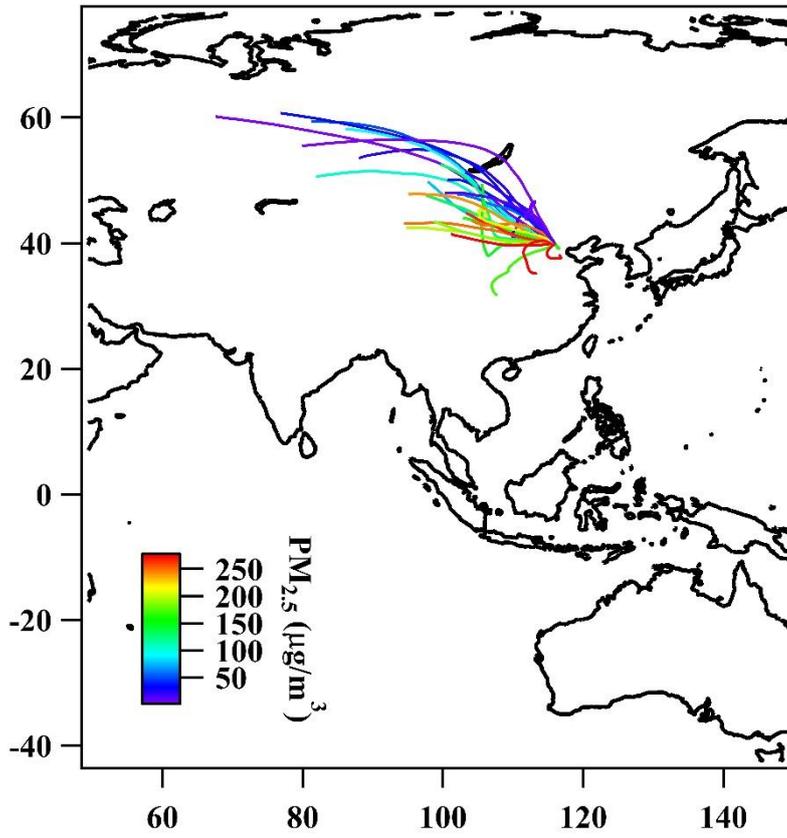


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877 **Figure 1. The time series of PM<sub>2.5</sub> concentrations and chemical composition. Data are shown for 15 different**

878 **days where the dates are indicated in the x-axis-labeling and “D” and “N” stand for daytime and nighttime,**

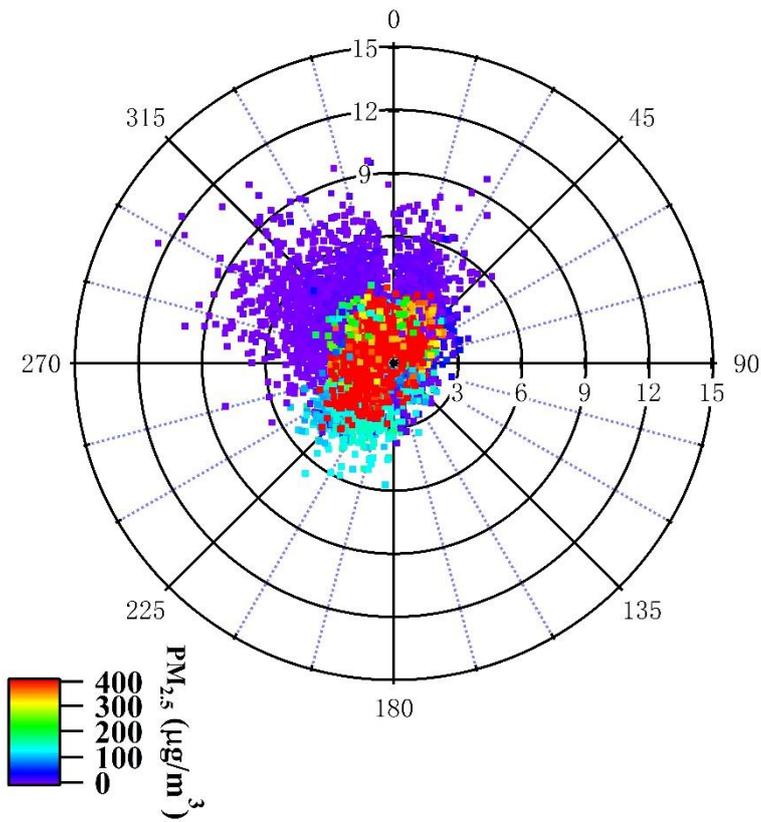
879 **respectively.**



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881 **Figure 2. The 2-day back-trajectories obtained by the NOAA HYSPLIT model colored-coded with respect to**

882 **PM<sub>2.5</sub> mass concentration determined by PTEF filter.**

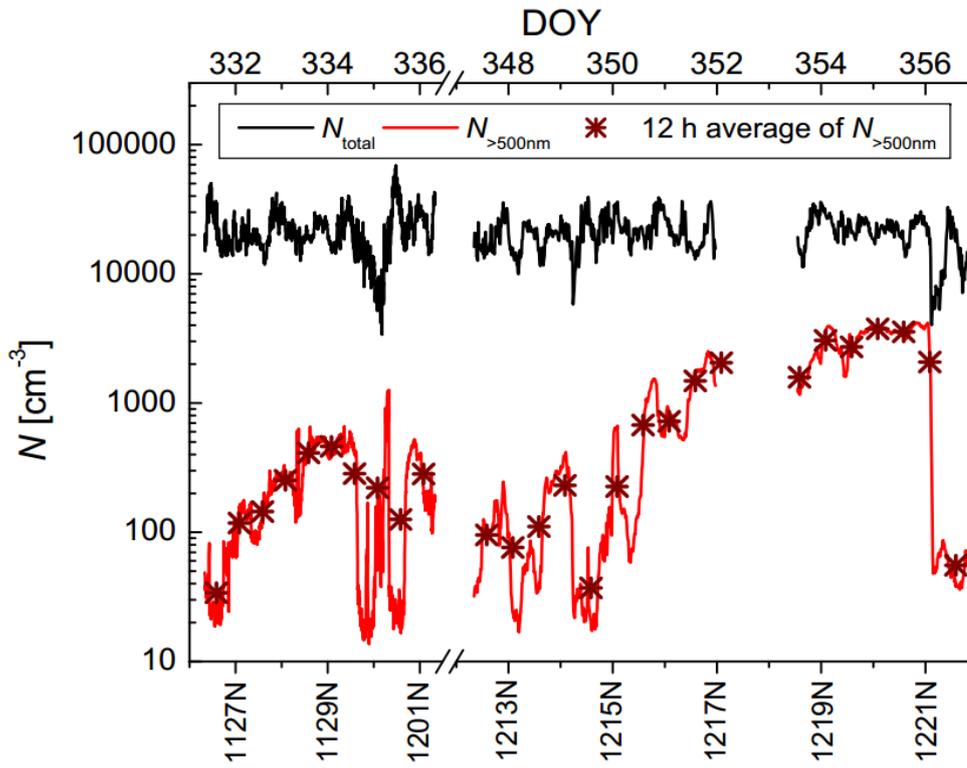


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884 **Figure 3. Minutely recorded data for wind-direction and wind-speed colored-coded with respect to PM<sub>2.5</sub> mass**  
 885 **concentration.**

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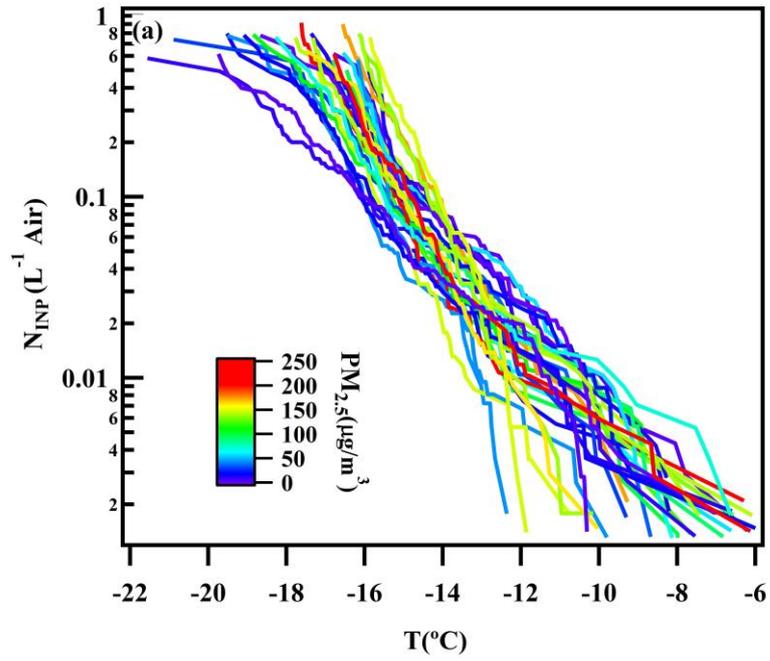
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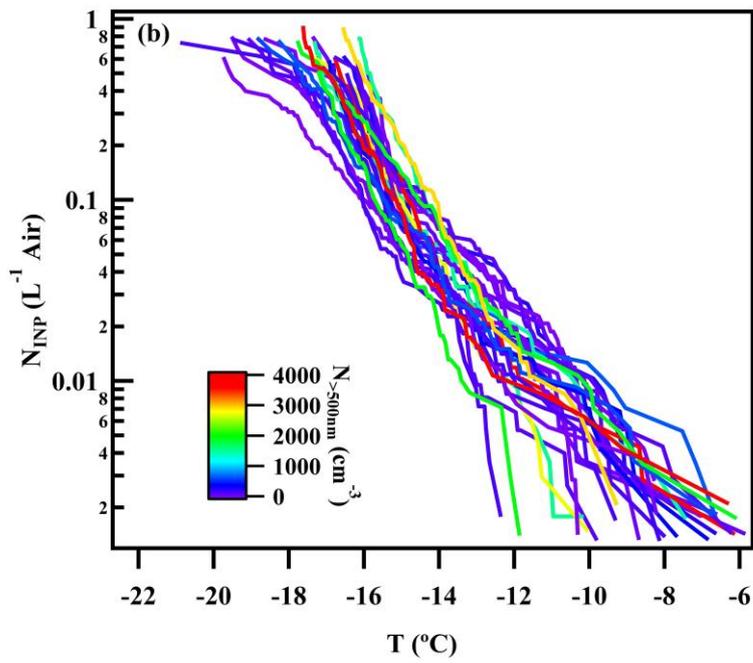
Figure 4. The time series of  $N_{\text{total}}$ ,  $N_{>500\text{nm}}$  and 12-h average  $N_{>500\text{nm}}$  at  $-16^{\circ}\text{C}$ .

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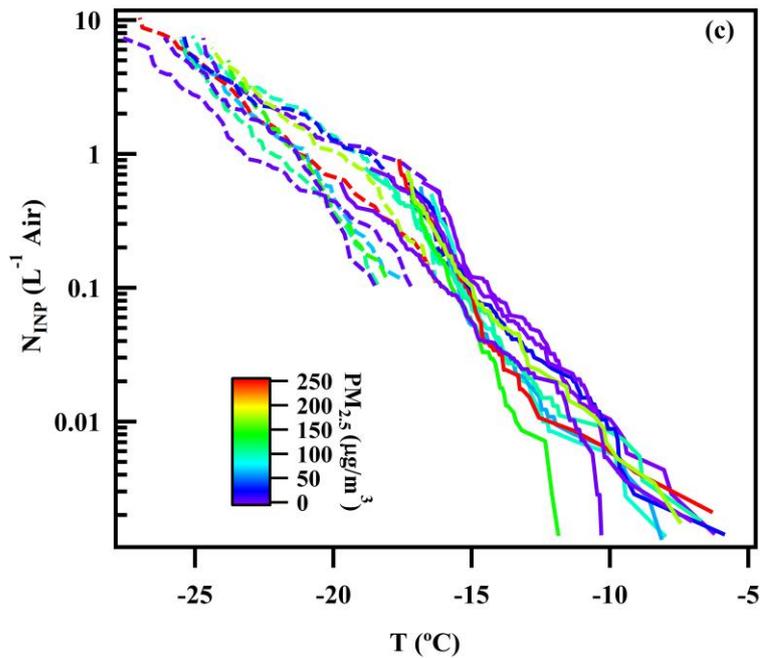
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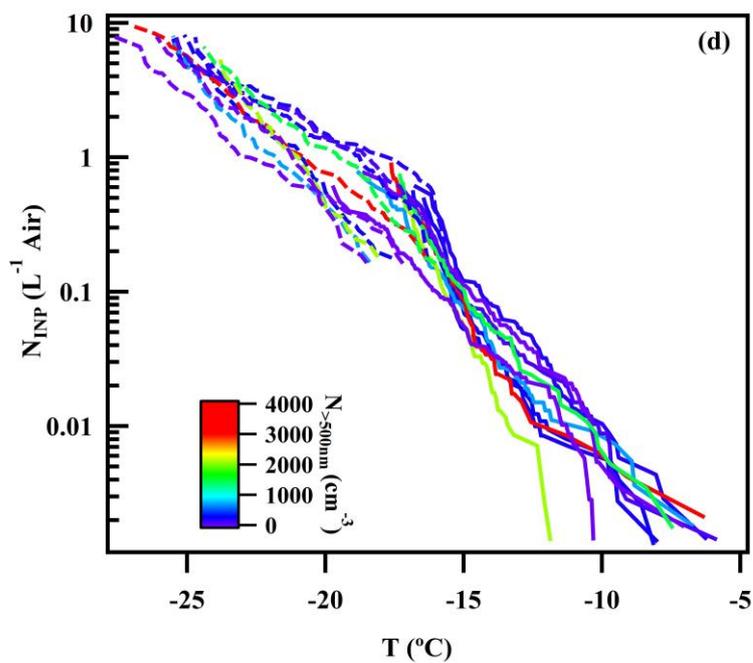
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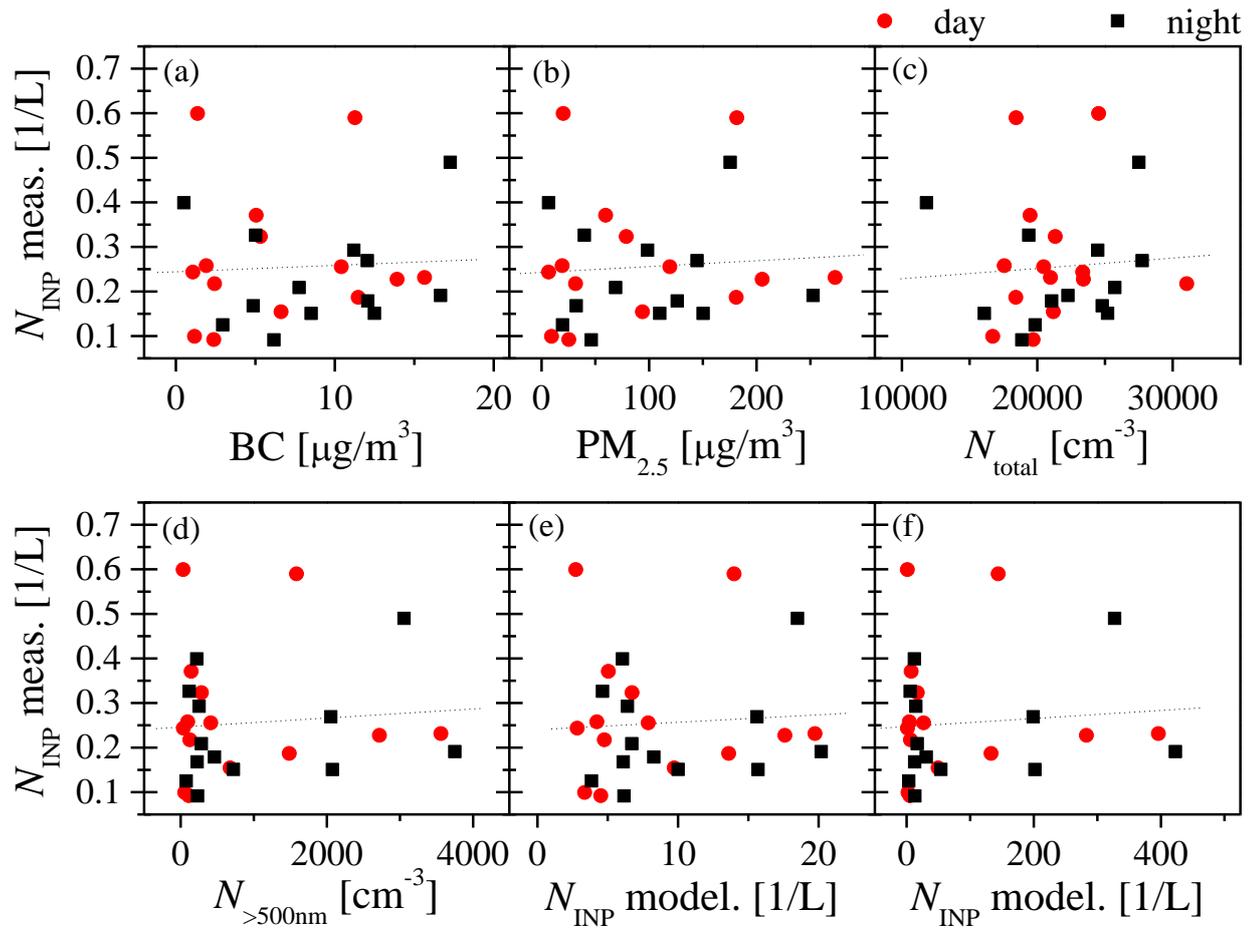


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898 Figure 5.  $N_{\text{INP}}$  as function of temperature, panel (a) and (b) show INDA results coloured by  $\text{PM}_{2.5}$  mass  
 899 concentration and 12h-average  $N_{>500\text{nm}}$ , (c) and (d) for 10 comparable results of INDA and LINA coloured by  
 900  $\text{PM}_{2.5}$  mass concentration and 12h-average  $N_{>500\text{nm}}$ , dotted lines represents LINA results while solid lines  
 901 represents INDA results.

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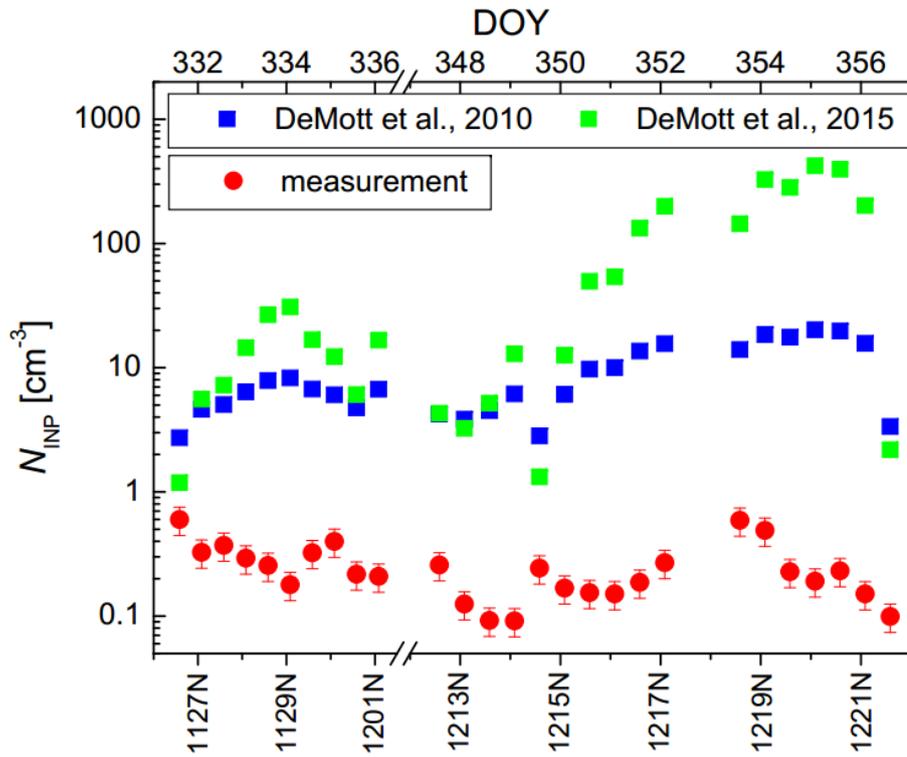
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905 **Figure 6.  $N_{\text{INP}}$  at  $-16^\circ\text{C}$  as function of mass concentrations of BC (a) and  $\text{PM}_{2.5}$  (b), and of 12h-average values**

906 **of  $N_{\text{total}}$  (c). Furthermore, we show  $N_{>500\text{nm}}$  (d), and  $N_{\text{INP}}$  at  $-16^\circ\text{C}$  derived based on (DeMott et al., 2010) (e)**

907 **and DeMott et al. (2015) (f) for daytime (red round symbols) and nighttime (green square symbols) samples.**



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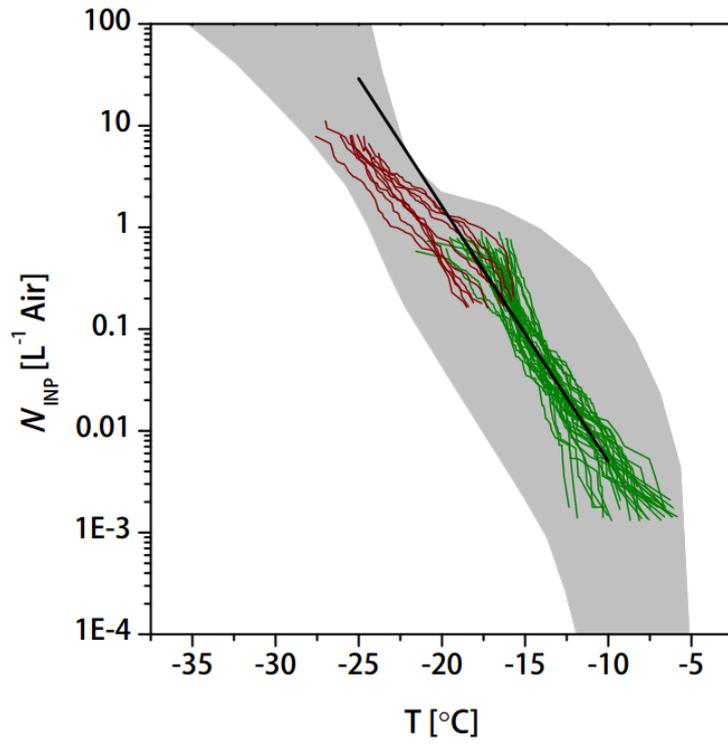
909 **Figure 7. The time series of measured  $N_{\text{INP}}$  and  $N_{\text{INP}}$  parameterized according to DeMott et al. (2010, 2015) at**  
 910  **$-16^{\circ}\text{C}$ .**

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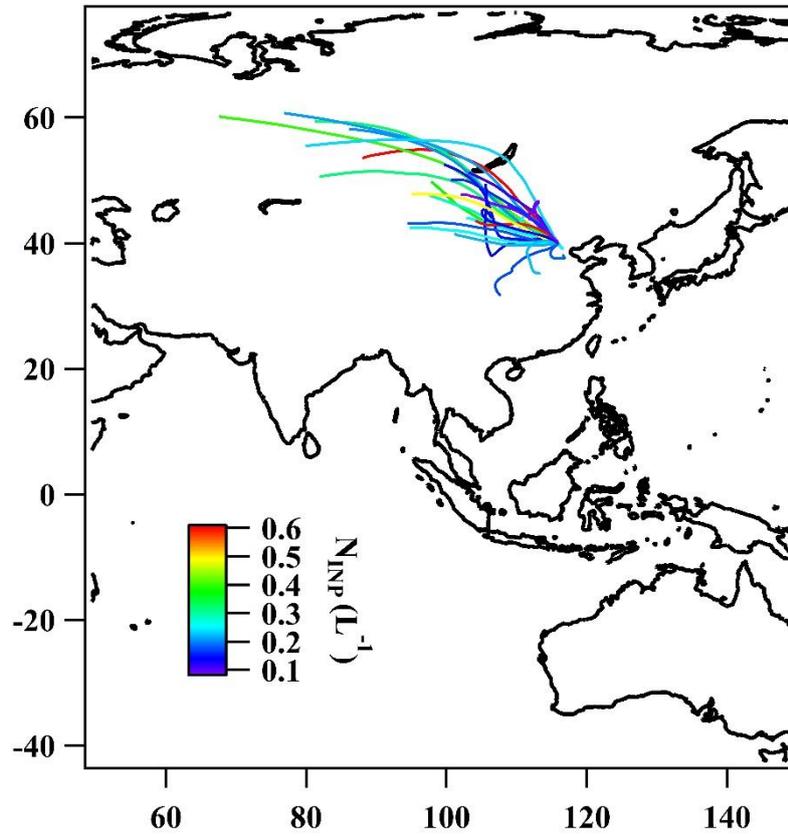
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916 **Figure 8.**  $N_{\text{INP}}$  as derived from precipitation samples collected in Petters and Wright (2015) (grey area) and a  
 917 parameterization based on Fletcher (1962) (black line), together with our results (dark green and brownish  
 918 lines from INDA and LINA measurements, respectively).

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921 **Figure 9. The 2-day back-trajectories obtained by the NOAA HYSPLIT model colored-coded with respect**

922 **to INP concentration**

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