Answers to the report by anonymous Referee #2

We thank Referee 2 for reviewing our manuscript and also for useful hints and suggestions. Below, comments from the referee are given in blue while our answers are given in black, with passages including new text given in italic. Additionally, the new text is marked yellow in the revised version of the manuscript.

This paper presents measurements of ice nucleating particles in Beijing, China. The ice nucleation activity of particles sampled on filters was quantified using ice-nucleating droplet arrays, LINA and INDA. This information was supplemented by ion chromatography measurements of the filters and in-situ measurements of black carbon and particle size distributions. The authors find no correlation between filter-based INP concentrations and PM2.5 or black carbon measurements. As the authors correctly state, there are few measurements of ice nucleating particles in urban areas, particularly in China. This paper is therefore of interest to the community. I recommend the publication in ACP after the following concerns are addressed:

1. It would be useful to see a time series of INP concentrations alongside Figure 1.

We included such a time series in the lower panel of what was Figure 2 (now Fig. 7), and, for the flow of the text, made that lower panel an extra figure which now appears as Figure 7. Related necessary changes were made in the text.

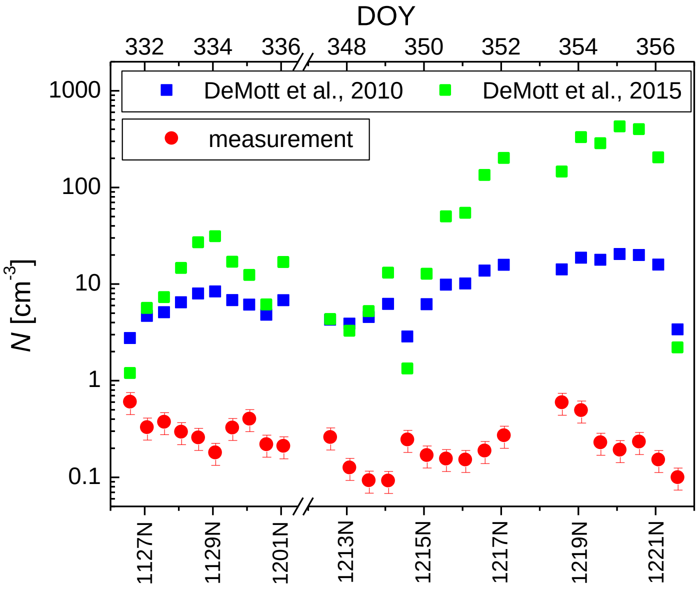


Figure 7. The time series of measured N_{INP} and N_{INP} parameterized according to DeMott et al. (2010, 2015) at -16°C.

2. On p. 10, lines 250-252, the authors mention difficulty in washing particles off of PTFE filters and state that this procedure cannot be recommended in general. Why

was the non-recommended technique used here? Can the authors provide an estimate of the uncertainty that this contributes to LINA measurements? Further, in line 252, the authors mention that they heave used a "subset" of PTFE filter LINA measurements. Which measurements were left off and why?

While doing the sampling, we had planned to focus on the quartz fiber filters, knowing that this will yield results for a restricted temperature range, only. But as we had a four-channel sampler, we thought we could try to sample on additional filter material. Polycarbonate filters did not work out, as they cause such a large pressure drop and the pump that was available was not sufficiently strong to collect a reasonable air volume. Hence the PTFE filters were used. We were not sure if these filters would work, but tried, nevertheless. It turned out that indeed, due to the fibers, particles stick in them even after washing (filters sometimes were still colored after the washing), but we decided to use at least results from those filters for which, in the temperature range where data was obtained from both filters, results were not more than a factor of 4.4 lower for LINA than for INDA data, which left data from ten filters analyzed with LINA.

We edited the text concerning this and added some additional information, so this whole passage now is as follows (with new text in italic) (see line 270):

“Washing particles off from the PTFE filters was more complete for some filters than for others. This showed in differently large deviations in N_{INP} from INDA and LINA measurements in the overlapping temperature range, where results determined from INDA were always similar to or higher than those from LINA, as particle removal by washing the filters was frequently incomplete. *It is mentioned in Conen et al. (2012), that a quantitative extraction of particles from quartz fiber filters was not possible without also extracting large amounts of quartz fibers. We tried to overcome this issue by using PTFE filters, as degradation of the PTFE filter during washing does not occur due to the hydrophobic properties of the filter material. But we observed that not all particles were released into the water during the washing procedure (likely those collected deep within the filter), as filters frequently still looked greyish after washing, independent from the washing procedure (we experimented with different washing times up to 4 hours and with the use of an ultrasonic bath). For our INDA measurements, punches of quartz filters were measured after they were immersed in water, representing the ice nucleating properties of all collected particles (Conen et al., 2012). However, as already mentioned above,* N_{INP} *derived from LINA measurements were lower than those from INDA, due to particles that did not come off during washing. Based on our observations, we cannot recommend the use of sampling on PTFE filters followed by particle extraction in water. But we still decided to select those data from LINA measurements that showed the lowest deviation to the respective INDA results in the overlapping temperature range for use in this study. After calculating the deviation between INDA and LINA results, represented as the factor (*N_{INP} *of INDA /* N_{INP} *of LINA), ten LINA measurements from different days were selected to be used. For these measurements, the factor representing the deviation was in a range from 1.3 to 4.4.”*

3. In Figure 4c, the x-axis label is "Ntotal at -16 degC". Should this be just the Ntotal average values from Figure 1? Why is the "at -16 degC" there?

You are right, thanks for the hint. Corrected!

4. Several (a and c, for example) of the plots in Figure 4 arguably show some weak

correlations. Some statistical tests of significance would help to strengthen the authors' case.

We added the following table giving R^2 and p values for the 6 scatter-plots presented in in what was Fig. 4 (now Fig. 6) and added the respective lines to the figure (see below), together with some text. It can clearly be seen by the values given in the newly added table, that there is no correlation.

The following text was added:
"*Linear fits are included in all panels of Fig. 6, and values for R^2 and p for these fits are shown in Table 1.*" (line 305)

"*Also the R^2 and p values given in Table 1 clearly show that there was no correlation between N_INP and any of the examined parameters.*" (line 309)

Table 1 Coefficient of determination (R^2) and a measure for the statistical significance of the assumption of a linear correlation (p) for the comparison of N_{INP} at -16°C with the different parameters shown in Fig. 6.

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°C	0.008	0.67
(e) N_{INP} at -16°C, based on DeMott et al. (2010)	0.005	0.73
(f) N_{INP} at -16°C, based on DeMott et al. (2015)	0.007	0.67

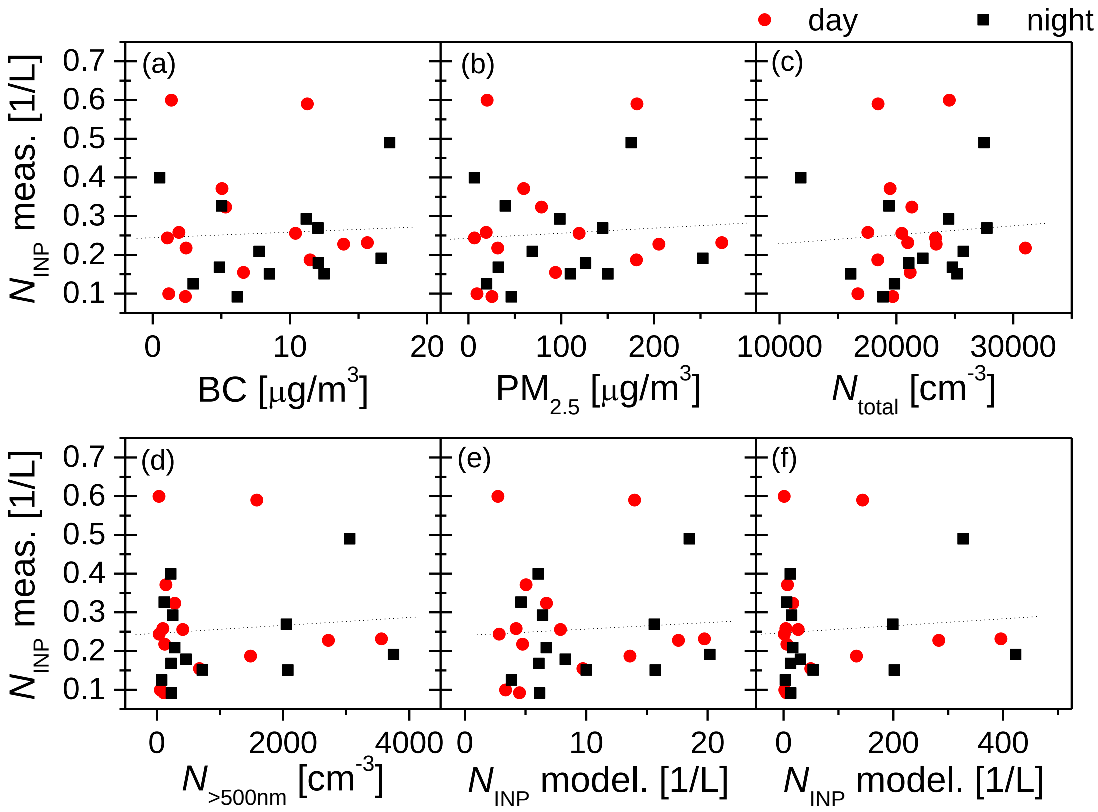


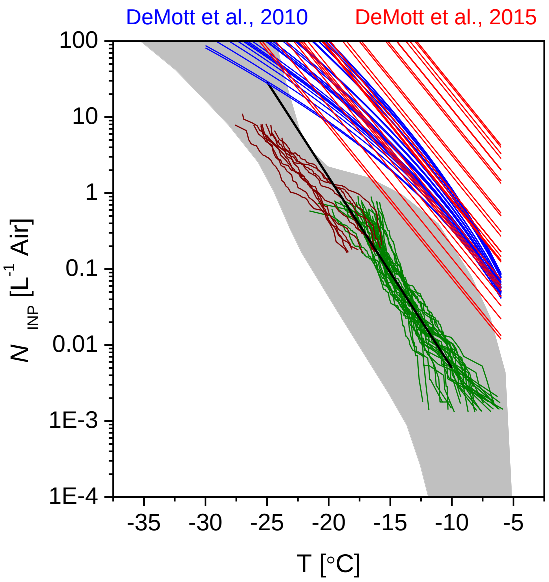
Figure 6. N_{INP} **at -16°C as function of mass concentrations of BC (a) and** $PM_{2.5}$ **(b), and of 12h-average values of** N_{total} **(c). Furthermore, we show** $N_{>500nm}$ **(d), and** N_{INP} **at -16°C derived based on (DeMott et al., 2010) (e) and DeMott et al. (2015) (f) for daytime (red round symbols) and nighttime (green square symbols) samples.**

5. Figure 4 (Now Figure 6) only shows INP concentrations at -16 degC, were there any differences for other temperatures?

No, there were no correlations at other temperatures, either (which can already be seen by the freezing curves not crossing much). This had been said before in the manuscript (previously line 268, now line 306), therefore nothing was changed: “Our results discussed in the following, based on N_{INP} at -16°C, are similarly valid for all other temperatures down to -25°C.”

6. It would be useful to plot DeMott, et al. (2010 and 2015) parametrizations alongside the Fletcher (1962) parametrization in Figure 5.

The DeMott parameterizations were added to the respective figure as shown below. However, we do prefer to not add this to the main manuscript as we do not want to stress it too much that these parameterizations do not fit, as this is caused by the pollution aerosol, which also included pollution particles larger than 500 nm, and not by the parameterizations. It does not say anything about the applicability of the parameterizations. Should you be of a different opinion, please let us know.



7. The authors conclude that the INPs detected here are "background" INPs, likely originating from dust, based on some previous measurements in China, which show enhancements in ice nucleation during dust events. Since the calcium ion is used here as a tracer for dust, do the INP concentrations correlate with it? Do they correlate with any of the chemical constituents measured with ion chromatography?

We did not find a correlation with any single component we looked at, please see the comparison with Ca^{2+} and K^{+} as examples below (this is not included in the new version of the manuscript, we only show it to you here). It has been assumed that the feldspar fraction (and there maybe only the K-feldspar fraction) of dust may be responsible for the ice nucleation activity of atmospheric mineral dust, therefore it is not too astounding that no correlation with Ca^{2+} was found (see both figures below). As for K^{+}, this is also emitted during biomass burning and hence is influenced by anthropogenic pollution (as can be seen in the second figure below, it follows the trends of the pollution), and hence, it also will not serve as a tracer for mineral dust. It should also be mentioned, that we only examined the soluble fractions of these components, while in dust particles, they might occur in non-soluble compounds.

Furthermore, INP make up a very small amount of both, total mass and total number concentration (a general value that is often given is that one in a million particles is ice active at -20°C), so it might be impossible to correlate atmospheric INP with a chemical compound based on the chemical analysis we did here.

And last but not least, the broad temperature range over which INP concentrations in the atmosphere are observed to increase generally suggest that a number of different types of INP participate (it is often assumed that more rarely occurring biological particles cause ice nucleation at higher temperatures (>-15°C) while mineral dust particles are responsible for the observed ice nucleation at lower temperatures), so we might have to look at a combination of different trace components.

But all this was not the aim of this study. We wanted to see if anthropogenic pollution might add INP, which we showed is not the case. Still, we added a paragraph summarizing what we answered to you above, which can be found at the end of section 3.3, from line 371 onward:

“Additionally, also no correlation was found between any of the water-soluble constituents that were analyzed with ion chromatography and INP concentrations. This is not too astounding, as INP make up only a small fraction of all particles, as can be seen when comparing number concentrations from Fig. 4 and Fig. 7, and hence they make up only a small fraction of the mass, likely too small to be detected. Furthermore, a number of different components might contribute to INP, e.g., biological INP that are generally ice active at higher temperatures (> -15°C, Murray et al., 2012) and mineral dusts which are ice active at lower temperatures, therefore one common tracer for INP might not be applicable. As far as K is concerned, which might be connected to K-feldspar containing mineral dust particles with high ice activity (Atkinson et al., 2013), we only analyzed the water soluble fraction, i.e., K related to feldspar would not have been analyzed. Moreover, K is also emitted by biomass burning and hence influenced by anthropogenic pollution. It remains to be seen if a simple correlation between chemical constituents of the atmospheric aerosol and INP concentrations can be established at all.”

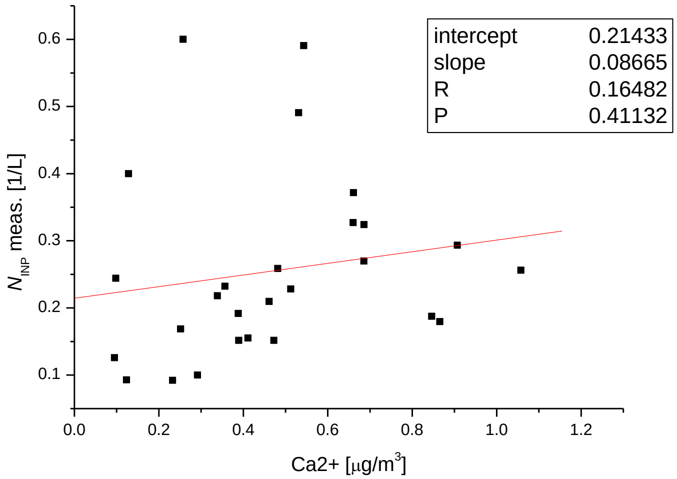


Figure above: Measured INP number concentrations at -16°C plotted versus Ca^{2+} mass concentrations derived from ion chromatography analyzing water soluble ions.

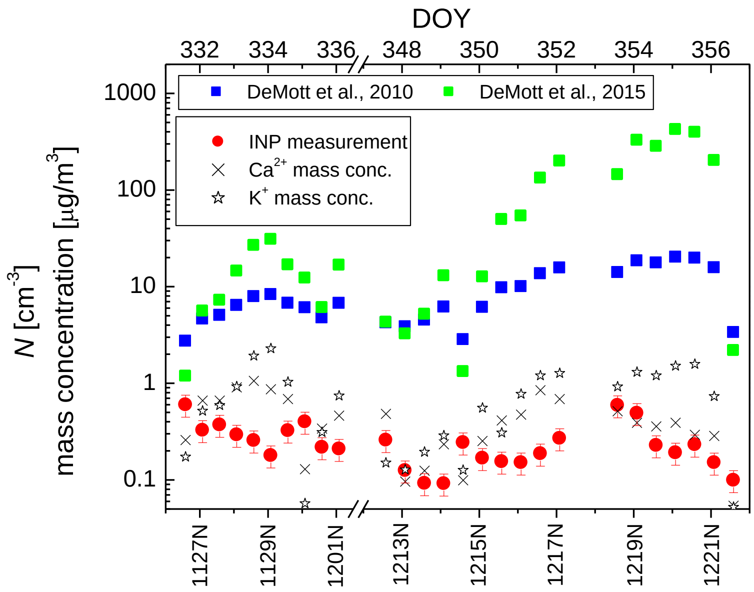


Figure above: The time series of measured N_{INP} and N_{INP} parameterized according to DeMott et al. (2010, 2015) at -16ºC, together with Ca^{2+} and K^+ mass concentrations derived from ion chromatography analyzing water soluble ions.

Literature:

Atkinson, J. D., B. J. Murray, M. T. Woodhouse, T. F. Whale, K. J. Baustian, K. S. Carslaw, S. Dobbie, D. O'Sullivan, and T. L. Malkin (2013), The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds, Nature, 498(7454), 355-358, doi:10.1038/nature12278.

Conen, F., Henne, S., Morris, C. E., and Alewell, C.: Atmospheric ice nucleators active>=12°C can be quantified on PM10 filters, Atmos. Meas. Tech., 5, 321-327, doi:10.5194/amt-5-321-2012, 2012.

Murray, B. J., O'Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, Chem. Soc. Rev., 41, 6519-6554, doi:10.1039/c2cs35200a, 2012.