Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2021-922-RC2, 2022

Referee Comment on acp-2021-922

Anonymous Referee #2

Referee comment on "Ice-nucleating particles from multiple aerosol sources in the urban environment of Beijing under mixed-phase cloud conditions" by Cuiqi Zhang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-922-RC2, 2022

Review of "Ice nucleating particles from multiple aerosol sources in the urban environment under mixed-phase cloud conditions" by Zhang et al.

Zhang et al. report ice nuclei concentrations (N_{INP}) measured under mixed-phase cloud conditions in Beijing over a 19 days that included a variety of aerosol conditions. The authors correlate N_{INP} with several collocated measurements in interpret the sources of INP, including non-refractory composition, black carbon, aerosol mass, and wide-ranging size distributions.

The study reports interesting and relevant results that are important to aerosol-cloud studies in the urban environment. The scientific questions under study are within the scope of ACP. The paper is very well organized and written. Literature references are appropriate and demonstrate a strong understanding of the relevant measurements and the sampling environment. The measurement study appears well conceived and executed.

The authors clearly demonstrate several negative results that are interesting and important, eg, that INP concentrations do not correlate with urban pollution, traffic

emissions, BC, or particles generated by fireworks. However, the role of dust in INP concentrations is more problematic, and the paper needs to address the apparent inconsistencies in the data more clearly.

Below I detail 3 concerns that affect some of the paper's conclusions. I encourage the authors to address the major and minor comments, and in particular consider what robust conclusions can be made regarding mineral dust. Once these issues are addressed, the paper will be appropriate for publication in ACP.

Major comments:

- The data show that N_{INP} has an inverse relationship to several aerosol quantities like N500 and PM10-PM2.5 that the authors suggest are surrogates for mineral dust. In particular, Fig 5a suggests a robust anti-correlation of N_{INP} and large particles during the dust event. This surprising result is lost in the discussion of correlation coefficients, which are arguably less important here than whether the slope of the correlation plot is positive or negative (or essentially zero). The authors should add text when describing Figs 5, 9, C1, and C2 to discuss whether the quantities are directly or inversely correlated, while using the R^2 values as a guide to the strength of that relationship. Or instead of discussing the slope of the fits, replace the R^2 values with the Pearson's correlation coefficient (R), which is negative for an inverse relationship.

Most importantly, the authors should carefully consider these direct and inverse correlations, and lack thereof, in their conclusions regarding dust aerosol. Specifically, line 352 states, "*Our study reveals that mineral dusts, even though present in relatively low number concentration out of the high background particle number concentration, dominate immersion INP population in the urban environment*". This statement is not supported by Fig 5, C1a, nor C2, which show an inverse or no relationship between N_{INP} and the aerosol properties chosen as surrogates for dust. Somewhat confusingly, the two campaign-wide correlation plots (C1b and C2b) disagree in the sign of the correlation. These apparent inconsistencies, and particularly the surprising inverse relationships,

should be more clearly interpreted in the concluding remarks and abstract (line 27-28). Indeed, for this study it seems that the data are generally inconclusive as to dust's (or large particles') role in ice nuclei, particularly outside of clear dust events.

- It most cases it is statistically incorrect to remove negative values from a set of measurements taken near the limit of detection, LOD (or limit of quantification, LOQ), line 146. The authors correctly state that negative values (and some small positive ones too!) are indistinguishable from zero. However, these 'zeros' represent legitimate results, and they must be included in many instances, for example when calculating a mean value or a correlation with another parameter.

Consider the case where an instrument attempts to measure a property that has a true value of zero. Random statistical noise will result in the measured (signal minus background) being small positive for some samples and small negative for others, centered around zero within the instruments LOD. If you removed all the negative values, your calculated mean will always be artificially positive, where it should actually be zero.

Alternately, if a measurement has a clearly defined LOD (eg, a set of filtered-air HINC runs), it is also correct to replace all values <LOD with the value zero. A third option is to replace all values <LOD with the LOD value or LODx0.5. This is a typical solution when logarithm of the data is required. If the authors continue to use correlations in log-space, some variation of this third option is acceptable. Depending on what fraction of the data was removed, including this low/negative/zero measurements may significantly affect the reported correlations.

- In line 260, the authors consider ammonium secondary material on dust particles acting as a nucleating agent. Although Fig 6 indeed shows a mild correlation between N_{INP} and m_{ammo}, "*…suggesting that N_{INP} might be associated with m_{ammo} during dust events in the urban environment*." However, the authors do not demonstrate that this correlation is specific to ammonium compared to other secondary aerosol material or to

PM0.5 as a whole. The authors should plot or at least report correlations (R or slope and R^2, etc) with sulfate, organic material, and nitrate. If those correlations are noticeably weaker, then this supports the authors' assertion about ammonium. However, if those correlations are similar to m_{ammo}, then the conclusion about ammonium salts enhancing nucleation activity is not strongly supported by the data, unless the authors can otherwise demonstrate ammonium's role separate from other chemical components.

Minor comments:

Title. Consider specifying, eg, "…the *Beijing* urban environment…"

Fig 1/line 105. Describe the TEOM sampling arrangement, or add TEOMs to the figure. Particularly for the TEOMs, were any efforts made to reduce aerosol losses in sampling tubing (gravitational, impaction)? For instance, were driers or transport tubing oriented vertically?

Line 120. Typically, a TSI APS has a total inlet flow of ~1 vlpm. The sheath flow is a closed internal loop. Please correct your text as necessary.

Section 2.2.2. Although the Aerodyne ACSM is often marketed as a "PM1" instrument, the actual sampling range for their standard inlet range as reported by Ng et al., 2011in the original ACSM instrument paper is dva=75-650nm (the 50% transmission limits). This is equivalent to da<530nm or about "PM0.5", not PM1. The distinction is sometimes irrelevant and is often ignored since submicron aerosol mass is often be restricted to da<530nm. However, for this study Fig2b suggests that much of the true PM1 mass

during pollution events is far outside the ACSM size range. Report the actual size range for your ACSM inlet, and replace the "PM1" notation throughout the document with an accurate label.

Ng et al., 2011: https://doi.org/10.1080/02786826.2011.560211

Line 149. State CPC size range. The ice-active fraction strongly depends on the minimum size of the reference measurement.

Fig 2b. Add more tick labels to left axis.

Table 1. N1000 is missing. Define typical start/stop times for noted dates.

Line 190. Clarify that you are inferring dust composition and therefore the dust event. Specifically, PM10>>P2.5 *indicates* that large particles are present. What is actually *implied/inferred* is that PM10>>PM2.5 is due to mineral dust aerosol. Reference an appropriate Asian dust PM10/PM2.5 if that is helpful.

Line 217. Delete “an”

Line 235. Reword or delete the sentence "It would be worthwhile...". The suggested course of action is confusing because the authors actually go on to explore this.

Line 278-281. Why might the DeMott 2015 dust INP parameterization vastly overestimate the measured INP here? Might “large” particles be something other than dust? Would dust likely be coated with secondary material like sulfate and organics (in addition to ammonium salts)? Will these coatings deactivate dust to the nucleation mechanism under study (add any appropriate refs)?

Line 304. As written, it is unclear if this is a valid comparison since total BC concentrations might be very different in Schill. State the BC concentrations or the active fractions for both studies.

Line 321. Unclear wording "with R2 between...". Again, it is important that 5b shows anti-correlation.

Line 344. Awkward phrase “synchronized variation”. Suggest replacing with “"a weak positive correlation" or similar.

Line 344. “…and NINP exhibited slight dependence on PM10-2.5.” Clarify that it’s an *inverse* dependence!

Fig A1. Clarify the “BG” measurement period. (Is it the same as “clean” in Table 1?)

Fig A3. Show altitudes of the trajectories as colors or as a separate graph. (Is the air over the desert near the surface or aloft?)