Review of "A comprehensive characterization of ice nucleation by three different types of cellulose particles immersed in water: lessons learned and future research directions," by N. Hiranuma et al. 2018

It is an intimidating task to review a manuscript with such an extensive and esteemed authorship and I know most if not all of these scientists to be highly accomplished and dedicated to their scientific endeavors. However, I find the submitted manuscript in its current form to be lacking in multiple aspects. It does not have clear thread or cohesion of a story, lacks motivation from different angles, and suffers from being difficult to read in many places. There are many examples of both run-on sentences which lack clarity and short sentence/thought fragments. I would encourage the authorship to take a heavy editorial hand during any revisions. This said, the summarized work is a very ambitious set of experiments etc. and perhaps the manuscript is penalized by simply trying to collect and summarize such a wide ranging project in one report. Below I try to summarize my areas of major concern and append a section of "specific comments" where, when I have had the time I note specific editorial areas for attention.

From the beginning I am left a bit confused about what is the primary purpose of the manuscript. Immediately in §***1.3 Goals*** the authors say, "The main objective of this study is to examine how different ice nucleation instrument techniques compare when using chemically homogeneous biological material rather than multi mineral systems,..." This type of explicit statement and the general way the manuscript seems to be framed is as a summary of how well ice nucleation tests of a single substance in laboratories around the world can be compared. In this context would AMT not have been a better choice for manuscript submission? For ACP, I would expect the motivations for the research to more clearly focus on the importance of cellulose to the physics and chemistry of the atmosphere. In its current state the single paragraph on page 3 motivating cellulose as important in an atmospheric context is not particularly convincing.

Within §***2. Sample Preparation and Characterization*** the authors spend considerable space discussing the use of Laser Ablation mass spectrometry to characterize samples and also discuss ambient ALABAMA measurements. To me the motivation for this type of characterization is not clear and I am left to surmise that ultimately a demonstration of the laboratory relevance to ambient measurements is the goal. It is unclear what such a hard ionization treatment of cellulose, which in the case presented results in mass spectra of fragmented materials, can really illuminate. Cellulose has a high molecular weight $m/z \geq 160$, which is the weight of its basic building block levoglucosan. Thus it is unsurprising with laser ablation one generates mass spectra with many fragments, why would one expect anything different? To me the only thing that clearly emerges from the mass spectrometry is that the examined substances included have high molecular weight, and thus fragment to yield peaks at many lower molecular weights – therefore I am left wondering how Figures 1, 2 (d) and 3 further the discussion. Do the authors intend to assert that there are clear cellulose fingerprints and that ultimately these are present in both Figure 3 panels? If this is the case then why is the choice made to use "average mass spectra"? Why not present some precise exemplar mass spectra, or perhaps use another technique to highlight peaks (lack of peaks) or peak combinations of interest (e.g., PMF)? Without considering the issue deeply, I think averaging these types of spectra will result in a loss of information. Furthermore, given the strong fragmentation I would think any ambient sample that included biomass materials (e.g., biomass burning) would to the eye look similar.

Overall my impression is that the mass spectrometry approach to particle composition taken within this manuscript contains either too little or too much information. Perhaps it would be better left to an entirely different report to present and discuss links between mass spectra of ambient samples and mass spectra of known cellulose samples? If the authors presume to have a strong case linking their characterizations to ambient measurements and therefore might make some statement about the atmospheric budget of cellulose, it is perhaps an important story beyond the scope of this manuscript. As it stands the link of the mass spectra to ice nucleation is never really revisited in the discussion and conclusions, making its presentation seem to add material without a clear purpose.

This section (***2. Sample Preparation and Characterization***) is also somehow representative of the lack of manuscript cohesion. It was discomfiting to begin reading about the sample specifics in ***2. Sample Specifications***, including introducing some SEM information, only to 12 pages later come

across a section ***3.4 Surface Structure Analyses***, were the writing very much gave the impression it should have led section 2. Likewise this is revisited again a further 20 pages later in ***4.4 Surface Structure of Cellulose Samples*** where Figures 9 – 11 are introduced. These or one of these could potentially have led the entire manuscript as an introduction to the material. Generally, I am uncertain that any part of the material characterization needs to be in the results section. First, it does not match with the stated objectives of the paper that an important result is physical/chemical characterization of cellulose samples. Second, breaking up the discussion of the material of study is one example of how the current manuscript lacks cohesion. That said the analysis in 3.4 is outright confusing, for me primarily due to the introduction of "line structures". Is the statement, "Followed by the background correction, line structures on the particle surfaces were clipped." supposed to mean something? Is this type of image analysis something that is well-known in the SEM lexicon? I am unable to follow the "line structure" analysis, or discern from the cited material whether or not it is simply my ignorance of some standard analysis. Naively, from Figures 9 and 10 I would think that "line structure" simply says something about surface roughness at a length scale concomitant with the measurement wavelength. However, Figures 9 and 10 which seem to relate directly to this section 3.4 are not even introduced until section 4.4.

Itemized Scientific and Editorial Comments:

In my estimation the tilde symbol (˜) is repeatedly misused. A low tilde ($\sim$) typically denotes 'similar to' in mathematical terms (or approximately in an informal sense, within an order of magnitude), whereas $\approx$ should be used for 'approximately equal to'. The high tilde symbol ˜ is mathematically meaningless but herein it appears the authors have used it to denote both $\sim$ and $\approx$.

Specific Suggestions by Page and Line Number (page, line):

- (3,27) remove "indeed"
- (3,32) to study heterogeneous ice... (strike "the")
- (4,1) "various yet meticulous" seems like a misuse of *yet*
- (4,10) "remarked the importance" – fragment
- (4,28) What to the authors mean by "concurrent study"?
- (5,1) Should simply be 'in 2015', strike "year"
- (5,2) *the* sensitivity, also suggest ending becomes, '... ice nucleation instruments with respect to immersion...'
- (5,8-9) strike "alphabetical order according to the abbreviations" Order is not relevant.
- (5, 15) many institutions should be preceded by a 'the' e.g., the Pacific Northwest National Laboratory...double check for readability
- (5, 15-20) This is a log run-on sentence. Break apart and/or change.
- (5,21) awkward use of "towards"
- (5, 28) "using" should be *used*
- (7, 10) The "electron micrograph-assessed size of...." What does this mean?
- (8,2) insert *and* before "droplet residuals"
- (8,22) extra)
- (8,34) Use of ˜ . Here is should likely be $\approx$; see above comment.
- (10,13) "or/and" is typically 'and/or'
- (10,27) perhaps use 'in more detail than what is reported by' in place of "in addition to what"
- (11,10) *the* U.S.

• (11,29) suggest: With this methodology, a total of 5637 particles () were analyzed and impurity inclusions of less than 0.25% were identified.

• (11,25) are known *to have* negligible...

• (11,26) strike “for” and “as”

• (11,33) sodium, which possibly ...

• (12,1) strike “up and”

• (12,5) should this be $\leq 3\%$

• (12,6) “wall” should be *walls*, strike “our”

• (12,7) AIDA expansion experiments...

• (12,8) change to: impurities negligibly impact the ice nucleation activity of cellulose at heterogeneous...

• (12,12) Should the $>$ be a $<$? If it is correct then it seems an upper bound should be provided.

• (14,16) differential mobility analyzer should likely be plural, as I presume each partner was using their own unit.

• (14,20) see tilde comment

• (14,24) Units are missing for droplet size in parenthesis.

• (14,33) The discussion of what is activated to droplets versus “activated fraction” is poorly structured. Are the authors using AF to mean droplet activation or freezing? Furthermore, even in systems (e.g., CFDCs) when it is assumed all particles activate, it is likely not true that AF=1(see for example, Garimella et al.[1],[2]). This will be a source of uncertainty in measurements and should be acknowledged. Also perhaps a short statement of where and how such error would enter into the results should be made.

• (15,17) used *in* each

• (15,19) to what are the authors referring when they say “this subset”

• (15,34) Do not begin sentence with mathematical symbol, “$\Delta \log$...

At this point in the text I had largely run out of the time/energy to make careful editorial remarks. However, the need for careful editing remains throughout the text, I continue below primarily with comments I see as scientifically relevant.

• (16,1) see tilda comment

• (16,6) What is meant by “status of the suspension solution...”? Do they intend to say something like a, ‘a description of the suspension...’

• (17,31) *the* Supplemental Information.

• (18,1-5) Have the authors considered the recent comment by Vali (2018) in response to the Polen et al.[3] AMT paper (see the discussion for Vali comment)? If so I think these works should be cited, and furthermore, it seems that C_{INP} should emerge from differential freezing spectra, not simply what is presented in Eq. (4). This links directly to section 4.5.1 and Figure 12. Both of which perhaps should be moved forward to offer a cohesive view of how the active site spectra are generated.

• (19,12-26) The discussion of temperature binning, especially how the moving average is constructed is confusing and needs to be clarified. Typically a moving average reassigns a value for each temperature that is used. Thus some temperature must still be chosen? Depending on the temperature resolution it then seems that a 3-point moving average might be inadequate. More specifics are needed. I understand that perhaps for a 0.5 degree resolution, a 3 point, centered moving average could (generally) be used, with the average for each integer degree then extracted from the moving average and used for the binning. Such a description would be valid for that specific case,

but would not perhaps not make sense for a different T resolution. As it is presented, it is impossible to know what exactly was done for the temperature binning.

• (20, 25) “Complementally” is not a word

• (21, 4-10) Figure 4 is introduced and the next figure introduced is Figure 6? Figures should be numbered and introduced in order of appearance within the text. See the more general comment also regarding Figures 9-11.

• (22,11) ratio of the *log of* individual...$n_{s,geo}$ *e*xpressed as $n_{s,avg}$

• (23,4) What is meant by, “across the heterogeneous freezing T”? I suggest giving a range of T, or in someway being more specific.

• (23, 5-6) “each portion of techniques”? do the authors mean, ‘each suspension technique’

• (23, 10) *the* two subsets...

• (23,13) indicates *a* fundamental

• (23, 15) The way in which Figure S2 is currently introduced and repeatedly referred to it would seem like it should be part of the main manuscript.

• (§4.3) Initially reading section 4.3 I thought that it would contain notable results from individual instruments. However, reading onward it seems details of measurements from every utilized instrument are included. In my mind if this approach is taken the individual instruments should be reported prior to the collective results present in sections 4.1 and 4.2, such that the collective results build from the individual results. Another choice could be made which would be to simply highlight particularly notable results from individual instruments and relegate the remainder to supplementary material. In the current form, given the primary stated purpose of the paper, the most important message is buried deep in the middle of the paper (Figure 4-5), and was easy to forget by the time I had finished reading to the end.

• (40, 2-4) The first 2 sentences of section 4.5.2 seem to be extraneous, and can be struck.

• (Section 4.5.2) Perhaps this would be better integrated into other parts of the text. It lacks motivation or connection to descriptions of the experiments and ends with an incomplete thought.

• (41, 2) strike“giant and submicron” These are disparate size scales which seem to suggest a full range of size.

• (41, 9-11) “...fibrous structures that may act as the ice nucleation active site...” seems completely speculative. This is not observed and no convincing link between surface structure and IN activity was established. It would be better to stick to concrete conclusions.

• (41, 22) “deviations in T...” What T? Specify.

• (Figure 1, caption) I think it should read ‘therefore *not* useful...’

• (Figures 4-8) Mostly very nice figures, but I wonder if the plot areas could be optimized a bit to improve visibility? Shorter hash marks? Begin y-axis with 10^2? Anything to improve the data visibility would be good.

• (Figure 6, caption) 19 panels/measurement methods? The caption states 20, what do I miss?

• (Figure 10) It is very unclear from the caption and text what is plotted here. Is it in fact a continuous data set, or do the lines represent connected data points? What was done to generate this plot? Can it be related to Figure 9?

• (Figure 12) See previous comment regarding frozen fraction and differential spectra etc.

Summation: The Hiranuma manuscript is an impressive effort to summarize and present an enormous amount of work by many research groups. However, in its current state the manuscript lacks focus and does not present a clear and cohesive picture that matches with its stated intent. I suggest that the manuscript should be heavily altered in such a way that a clear research trajectory is

presented. Furthermore, the inclusion of complementary information should be motivated by how it helps grow the intended understanding. The links between things like physical and chemical characterization of particles and the ice nucleation should be made explicit. If clear connections are lacking, perhaps it is better to leave certain things broadly descriptive with detailed supplementary material available. Finally, for ACP the entire scope of the work would benefit from stronger grounding in its atmospheric relevance – beyond the innumerable and complicated issues that abound from such a multifarious measurement comparison.

It is my hope that with the necessary work the manuscript can proceed to full publication, given that this is an impressive and important data set. However, the effort might require a significant distillation of the discussion manuscript.

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[1] Garimella, S., Rothenberg, D. A., Wolf, M. J., David, R. O., Kanji, Z. A., Wang, C., Rösch, M., and Cziczo, D. J. (2017). Uncertainty in counting ice nucleating particles with continuous flow diffusion chambers. *Atmospheric Chemistry and Physics*, 17(17):10855–10864.

[2] Garimella, S., Rothenberg, D. A., Wolf, M. J., Wang, C., and Cziczo, D. J. (2018). How uncertainty in field measurements of ice nucleating particles influences modeled cloud forcing. *Journal of the Atmospheric Sciences*, 75(1):179–187.

[3] Polen, M., Brubaker, T., Somers, J., and Sullivan, R. C. (2018). Cleaning up our water: reducing interferences from nonhomogeneous freezing of “pure” water in droplet freezing assays of ice-nucleating particles. *Atmospheric Measurement Techniques*, 11(9):5315–5334.