Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-869-RC2, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Complex plant-derived organic aerosol as ice-nucleating particles – more than a sum of their parts?" *by* Isabelle Steinke et al.

Anonymous Referee #2

Received and published: 20 January 2020

The authors present an interesting study aimed at isolating the ice nucleating (immersion freezing) active components of vegetation (e.g., leaf litter and harvesting debris). Particles were generated from commercially-available compounds, such as lignin and carnauba wax, and ice nucleating number concentrations measured as a function of temperature. For comparison to prior work and to normalize the findings, ice nucleating activity was converted to a per-unit-surface-area basis (ice nucleation active surface site density, INAS). To cover the full range of temperatures, two methods – a micro-droplet assay and an expansion cloud chamber – were applied.

The idea of a systematic study to develop more basic understanding of how complex

Printer-friendly version

Discussion paper

atmospheric particles behave in clouds is commendable, and this group is well known for their expertise and impressive laboratory capabilities in probing ice nucleating properties of aerosols. Nevertheless, this study has some important gaps in the presented work that limit the conclusions that can be drawn and the applicability of this work toward improving understanding. I recommend major revision before publishing.

First, ice nucleating active (INA) bacteria were identified decades ago and it is well known that vegetation and leaf litter – depending on type – can host dense populations of these bacteria. This component is discussed in the introductory materials, but not brought up again in comparison with the results for vegetation samples. Why not study P. syringae (as a model for this component) with the same systems and compare to that? Further, the INA component in bacteria is a lipoglycoprotein (with a particular structure that enables its activity), which presumably inspired some of the choices in Table 1. But this is not explained; and in any case, this is also already well known, so it is not clear what was to be accomplished through the selections made for study unless it is implied that other proteins, lipids, etc. might have IN activity as well (if so, why?). The idea of other "unknown" organic constituents being important (e.g., the macromolecules proposed in earlier work by other groups) is certainly raised, but is not explicitly investigated here – except perhaps by ruling out activity from larger particles composed of the selected compounds.

Second, the argument is made that using commercially-available components is preferable because "many of the extraction methods for organic matter may cause significant changes in the physicochemical properties of the extracted organic compounds". Why is this not true also for the commercial products? There is no discussion of how these are manufactured, which seems to be important for the proteins in particular if they are to be considered analogs for natural components. I also have questions regarding the process for generating particles of carnauba wax, which was the only component identified as having significant IN activity: on line 216 it is stated that, "Unfortunately, it was not possible to reliably determine INAS density values for carnauba wax (LIP)

Printer-friendly version

Discussion paper

due to its very low dispersibility." It is appreciated that generating reproducible particles from solid samples is very difficult, but the uncertainties associated with this should be quantified and carried through the analyses. The results for carnauba wax are noted to be surprising (lines 284-285) but few fully satisfying reasons for this result can be deduced from the present study (some ideas are presented in lines 177-185).

A third major point with regard to atmospheric implications is that while soils, leaf litter, harvest debris, etc. can have high densities of INA bacteria or other ice-active components, the mobilization of particles containing those components into the boundary layer, and further, to altitudes where they can impact cloud formation, is a different matter. Limited prior studies suggest there is no direct relationship between surface concentrations and atmospheric concentrations and the atmospheric concentrations become relevant only under conditions where the surface is strongly disturbed (as alluded to in the text). Thus the implications of any findings with respect to atmospheric processes have to be tempered by this consideration. In particular, the concluding sentence of the Abstract, "In contrast, complex biological particles may exhibit ice nucleation activities which are up to two orders of magnitude higher than observed for cellulose, making ambient plant-derived particles a potentially important contributor to the population of ice-nucleating particles in the troposphere" is not a unique conclusion from this work but has been suggested previously, and needs to be modified to acknowledge that the relationship between the surface and ambient concentrations needs to be better understood before quantifying the importance of this source on regional and global scales.

I have additional comments for consideration, as follows.

It is stated that for some of the tested samples, the AIDA and microdroplet methods agree (lines 206-208). However, there is no overlap between these methods, and the surface area determinations use very different approaches, calling this agreement into question. The particle background concentrations for AIDA are stated (line 107) as 100 L-1. Comparing to Figure 3, I'm unclear how this is taken into account; the x-axis

scales on Figures 1 and 2 are different, indicating that AIDA is limited at the warmer temperatures, presumably due to this background?

Prior work by Hiranuma et al. (2015b) is cited for data on cellulose for comparison to the present work. The intercomparisons published by Hiranuma et al (2019) are also cited, however, in that study, it is noted that "While the diverse instruments employed in this study agree in that cellulose has the capacity to nucleate ice, their quantitative agreement is poor. Unfortunately, it is not possible yet to say what the cause of this disagreement is." Does this statement apply to the two techniques used in the manuscript? Hiranuma et al. (2019) also call for "comprehensive studies on the ice nucleation activity of other important plant structural materials, such as cellulose polymorphs, lignin materials, lipids, carbohydrates and other macromolecule saccharides", so the present study is a nice follow-on to that recommendation. However, the issue of whether follow-on studies are premature at this point, if there are fundamental questions regarding the measurements and their interpretation, needs to be addressed.

Line 89: "ambient samples from vegetated environments": my comments above assume these are bulk samples and not obtained by filtering of ambient air. If my interpretation is correct, perhaps the language here needs to be clarified.

Line 148: Brunauer is misspelled. The uncertainties introduced by the different estimates of surface area should be more thoroughly discussed and represented in the figures (how are the uncertainty bars in the figures computed – is this from the variation in the repeat experiments, or does it include other considerations such as surface area?)

Line 174: Desert dust (Ullrich et al., 2017) is mentioned for comparison, but not shown?

Line 204: Is the background for the microdroplet method shown here or in another publication?

Line 110, 148: could these aerosol size and surface area distributions be shown in the

Supplementary Material? This is potentially useful information for other studies that might seek to explore similar science questions with other techniques.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-869, 2019.

Printer-friendly version

Discussion paper