Complex plant-derived organic aerosol as ice-nucleating particles – more than a sum of their parts?

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15 **Abstract**

Quantifying the impact of complex organic particles on the formation of ice crystals in clouds remains challenging, mostly due to the vast number of different sources ranging from sea spray to agricultural areas. In particular, there are many open questions regarding the ice nucleation properties of organic particles released from terrestrial sources such as decaying plant material.

20 In this work, we present results from laboratory studies investigating the immersion freezing properties of individual organic compounds commonly found in plant tissue and complex organic aerosol particles from vegetated environments. To characterize the ice nucleation properties of plant-related aerosol samples for temperatures between 242 and 267 K, we used the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber and the Ice Nucleation Spectrometer of the Karlsruhe Institute of Technology (INSEKT), which
25 is a droplet freezing assay. Individual plant components (polysaccharides, lignin, soy and rice protein) were mostly less or similarly ice-active compared to microcrystalline cellulose, which has been suggested by recent studies as a proxy for quantifying the primary cloud ice formation caused by particles originating from vegetation. In contrast, samples from ambient sources with a complex organic matter composition (agricultural soils, leaf litter) were either similarly ice-active or up to two orders of magnitude more ice-active than cellulose.

30 Of all individual organic plant components, only carnauba wax (i.e. lipids) showed a similarly high ice nucleation activity as the samples from vegetated environments over a temperature range between 245 and 252 K. Hence, based on our experimental results, we suggest to consider cellulose as being representative for the average ice nucleation activity of plant-derived particles, whereas lignin and plant proteins tend to provide a lower limit. In contrast, complex biological particles may exhibit ice nucleation activities which are up to two
35 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.

1 Introduction

Ice formation in the atmosphere has a significant influence on the microphysical and radiative properties of clouds. At temperatures above 235 K, atmospheric aerosol particles may act as ice-nucleating particles (INPs) (Pruppacher and Klett, 2010; Vali et al., 2015). In mixed-phase clouds, immersion freezing is often the dominant ice nucleation mode (Hande and Hoose, 2017). Immersion freezing refers to a solid particle initiating ice formation inside a supercooled cloud droplet.

Over the past decades, many different particle types initiating freezing in mixed-phase clouds have extensively been studied (Hoose and Möhler, 2012; Murray et al., 2012; Kanji et al., 2017). Mineral dust particles emitted from desert areas have been identified as ubiquitous INPs which initiate ice nucleation in clouds over a wide range of temperature and humidity conditions (Boose et al., 2016; Ullrich et al., 2017). Cloud-level concentrations of biological aerosol particles, in contrast, are much lower than background concentrations of mineral dust, with differences of up to 8 orders of magnitude in some cases (Hummel et al., 2018). Nevertheless, several laboratory studies, remote sensing measurements, and studies characterizing ice crystal residuals have found evidence for the potential impact of these particles and more numerous nanoscale fragments on ice formation in mixed-phase clouds (e.g. Möhler et al. (2007), Pratt et al. (2009), Kanitz et al. (2011) and O'Sullivan et al. (2015)). Also, recent studies indicate a missing source of INPs beyond mineral dust, with biological particles from terrestrial environments being a likely candidate for initiating freezing in shallow mixed-phase clouds (O'Sullivan et al., 2018).

One of the characteristics of biological INPs is that they include a vast variety of different particle types, ranging from primary biological particles such as bacteria, fungi and pollen to complex organic particles carrying different ice-nucleating agents and originating from biogenic sources (Schnell and Vali, 1973; Hoose and Möhler, 2012; Murray et al., 2012; Augustin et al., 2013; O'Sullivan et al., 2014; Tobo et al., 2014; Conen et al., 2016; Steinke et al., 2016). An example for complex organic particles are agricultural soil dust particles where the observed high ice nucleation efficiency can be linked to microbiological activity and the presence of organic macromolecules (O'Sullivan et al., 2014; Tobo et al., 2014; Hill et al., 2016; Steinke et al., 2016; Suski et al., 2018). The expression of bacterial and fungal ice-active proteins is highly variable, also because environmental stress (e.g. a change in temperature) can change the structure of ice-nucleating proteins, resulting in a loss of functionality (Pummer et al., 2012). In contrast, some of the organic macromolecules found in agricultural soils are very inert as they are able to withstand physical and chemical treatments, e.g. with heat or exposure to enzymes (Hill et al., 2016). With decaying plant material being one of the major sources of these macromolecules (Hill et al., 2016), the need arises to better characterize the ice nucleation properties of plant-derived particles as well as their individual organic components.

Lignin and polysaccharides are integral components of plant cell structures and contribute up to 50 % to plant debris (Williams and Gray, 1974). Proteinaceous components of leaf litter (e.g. enzymes, storage proteins or structure proteins) vary considerably but have been found to account for up to 15 % (Williams and Gray, 1974). Lipids contribute up to 10 % to dry leaf mass (Graça et al., 2005). Note that only 50 % of the organic matter is accessible through chemical degradative techniques which inadvertently impact the structure of the extracted organic matter (Kögel-Knabner, 2002).

In this study, we investigate the immersion freezing properties of commercially available plant-derived organic compounds such as lignin, polysaccharides, plant wax and plant proteins – which are the main components of

decaying plant material – as well as ambient samples rich in plant material. We used commercially available organic compounds as analogues for plant-derived organics because many of the extraction methods for organic matter may cause significant changes in the physicochemical properties of the extracted organic compounds

80 (Kögel-Knabner, 2002). Experiments were conducted at the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) cloud chamber and complemented by drop freezing assay studies using the Ice Nucleation Spectrometer of the Karlsruhe Institute of Technology (INSEKT). From our experimental results we derived temperature dependent parameterizations based on the ice nucleation active surface site (INAS) densities concept (Connolly et al., 2009; Niemand et al., 2012). These parameterizations were then used to estimate upper limits

85 for ambient INP concentrations for complex organic aerosols from vegetated environments.

2 Samples and methods

2.1 Samples

In Table 1 we describe the samples used in this study, which include commercially available plant-derived organic compounds as well as ambient samples from vegetated environments.

90 Note that the agricultural dust from harvesting machines (bulk sample) contains roughly 90 % of biological material, e.g. partially intact plant cells and similar particles (Fig. S1). The soil dust sample from Wyoming has been investigated in a recent study by Tobo et al. (2014) finding that organics contribute signficantly to the ice nucleation efficiency observed for size-selected particles (d = 600 nm). Representative microscopy images of all other samples used in this study are shown in the supplement (Fig. S2).

95 ### 2.2 AIDA immersion freezing experiments

Immersion freezing initiated by plant-related particles was investigated in the AIDA cloud chamber (Karlsruhe Institute of Technology, Germany). The AIDA cloud chamber consists of a cylindrical aluminium vessel (volume 84 m^3) which is enclosed by a thermally insulated box. The ascent of cloud parcels is simulated by lowering the pressure from ambient levels (about 1000 hPa) to around 800 mbar, and by that lowering the

100 temperature and increasing the relative humidity in the expanding air of the chamber volume.

A fan at the bottom of the AIDA chamber ensures homogeneous mixing (also with regard to temperature and humidity) across the whole chamber volume, except for transition zones near the chamber walls. The overall uncertainty of the mean gas temperature is about $\Delta T = \pm 0.3$ K (Möhler et al., 2006). The absolute water vapor partial pressure is measured with a tunable diode laser instrument and converted into humidity values by

105 leveraging the saturation pressure formulation given in the review by Murphy and Koop (2005). The relative humidity values can be measured with an accuracy of $\Delta RH_{ice} = \pm 5$ % (Fahey et al., 2014).

Particle background concentrations within the cloud chamber are typically below 0.1 cm^{-3}. For the immersion freezing experiments presented in this work, aerosol samples were injected into the cloud chamber by using a rotating brush generator (RBG-1000, Palas GmbH) for dry dispersion. Additionally, impactor stages were used

110 to eliminate particles larger than 3 to 5 μm. The aerosol size distribution at the beginning of each experimental run was measured by combining data from an Aerodynamic Particle Sizer (APS, TSI, Model 3321) and a Scanning Mobility Particle Sizer (SMPS, TSI, Model 3076).

Upon reaching water saturation during an expansion experiment, aerosol particles within the cloud chamber are activated to droplets and may freeze subsequently. Ice crystal number concentrations are measured with two

115 optical particle counters (WhitE-Light Aerosol Spectrometer, welas1 and welas2, series 2300 and 2500, PALAS

GmbH) with size ranges of 0.7 – 46 and 5 – 240 μm in optical particle diameter, respectively (Wagner and Möhler, 2013).

2.2 Droplet freezing assay studies

To investigate the freezing of suspensions created with the bulk samples and hence to account for freezing

120 caused by particles larger than 5 μm, a droplet freezing technique was employed. The Ice Nucleation Spectrometer of the Karlsruhe Institute of Technology (INSEKT) setup (Schiebel, 2017) is based on the droplet freezing assay originally developed at Colorado State University (Hill et al., 2014).

Suspensions were created from bulk samples, combining 2 mg of material with 20 ml of deionized water (resistivity about 18 MΩ) which has been passed through a filter with a pore diameter of 0.1 μm (Whatman

125 Puradisc 25). Suspensions were shaken by hand (about 1 min) and the suspension tube was then submerged in an ultrasonic bath (5 min) to promote dispersion of the particles. In addition to the original suspensions, we also created suspensions with a dilution factor of 15 and 225 by adding filtered deionized water in proportion. Original and diluted suspensions were partitioned into 192 wells (aliquot volume: 50 μL) of a sterile polypropylene polymerase chain reaction (PCR) tray, with 32 wells set aside for blank measurements, i.e.

130 freezing of particle-free filtered deionized water. These blank measurements are used for determining the background which is then subtracted from the observed freezing curves. In this study, droplet freezing was measured at a cooling rate of 0.33 K/min. Cooling is achieved by flowing chilled ethanol through a custom-made aluminium block which encloses the bottom part of the PCR tray. The overall temperature uncertainty is $\Delta T = \pm 0.3$ K (Schiebel, 2017).

135 ### 2.3 Ice nucleation active surface site densities

For all experiments, the ice nucleation efficiency was quantified by calculating the ice nucleation active surface site (INAS) density n_s. The n_s values were derived by scaling the observed ice crystal number concentration n_{ice} with the available aerosol surface A_{aer} (Connolly et al., 2009; Niemand et al., 2012).

For the cloud chamber experiments, the aerosol surface A_{aer} [μm²/cm³] was calculated from the APS and SMPS

140 size distribution data using volume-equivalent sphere diameters (Möhler et al., 2006). In this study, it was assumed that all aerosol particles are activated to droplets upon reaching water saturation. Hence, the full aerosol surface area was considered to be available for immersion freezing. The ice crystal number concentration n_{ice} was derived from particle size distributions measured with the optical particle counters welas1 and welas2, in conjunction with a size threshold above which particles are counted as ice crystals. Based on the measurement

145 uncertainties of the observed ice crystal concentration $\Delta n_{ice}/n_{ice} = 0.2$ and the aerosol surface area concentration $\Delta A_{aer}/A_{aer} = 0.35$, the resulting uncertainty of the INAS density is $\Delta n_s/n_s = 0.4$ (Ullrich et al., 2017).

For the droplet freezing studies, the INAS density values were derived from normalizing the cumulative INP concentration n_{ice} with the specific aerosol surface A_{aer} [m²/g] derived from Brurnauer-Emmett-Teller (BET) surface measurements. For our INAS density uncertainty analysis, we took into account only the uncertainty of

150 the cumulative INP concentrations. Confidence intervals (at 95 %) have been estimated according to the improved Wald interval which implicitly assumes a normal approximation for binomially distributed measurement errors (Agresti and Coull, 1998). Hence, in our INAS density analysis, we neglected the uncertainties of the BET surface measurements which are in most cases considerably smaller than the previously described uncertainties of the cumulative INP concentrations (Hiranuma et al., 2015a). Another source of

155 uncertainty – which is considerably more difficult to quantify – was the contribution of larger particles. These

larger particles may sediment quickly within the suspension and were probably under-represented in the sampled aliquots. Thus, the particle surface area available for freezing was most likely overestimated in some cases. This effect seems to be negligible, but should be investigated in more detail in future studies.

3 Results and discussion

160 In Fig. 1 we present results from AIDA cloud chamber experiments with commercially available plant-related organic compounds and natural samples (see Table 1). For comparison, we show the ice nucleation activity of microcrystalline cellulose (Hiranuma et al., 2015b), which is a prevalent natural polymer deriving from plant fragments, leaf litter, wood fiber, non-wood fiber and/or even microbes (Quiroz-Castañeda and Folch-Mallol, 2013; Vlachou et al., 2018). We also show the ice nucleation efficiency of agricultural soil dusts investigated in a

165 study by Steinke et al. (2016) as well as an estimate for leaf litter from a study by Schnell et al. (1972). The ice nucleation activity of each sample is expressed as the INAS density n_s.

Figure 1 shows that the observed ice nucleation efficiencies of most individual plant-related organic compounds tend to be lower in comparison to samples from natural environments. However, there is a large spread in INAS density values when comparing between different plant-related organic compounds. Particularly noticeable is the

170 low ice nucleation efficiency observed for plant protein for which freezing was observed only below 248 K. In this study, we tested two different types of plant proteins (PROT_R, PROT_SOY), derived from soy or rice (not differentiated in Fig. 1). Only lignin (LIG) shows an ice nucleation activity as low as the plant protein samples. Alginate, pectin, and starch (which mainly consist of highly complex polysaccharides) are similarly ice-active as microcrystalline cellulose (Hiranuma et al., 2015b) and desert dusts (Ullrich et al., 2017). Above 250 K, the

175 complex polysaccharides investigated in this study (ALG, PEC, STAR_P, STAR_C) tend to be more ice-active than cellulose and exhibit a weaker dependence on temperature.

Of all plant-related compounds, carnauba wax (LIP) shows the highest ice nucleation efficiency, comparable to decaying leaves and two agricultural samples, i.e. dust from a sugar beet field (AGDUST_WYO) and material collected from harvesting machines (AGDUST_HARV). Carnauba wax is a mixture of hydrocarbons, aliphatic

180 esters and fatty alcohols (Vandenburg and Wilder, 1970) with an average chain length of 50 carbon atoms (Basson and Reynhardt, 1988). Crystalline fatty alcohols (C16 - C18) have been highlighted recently in a study by DeMott et al. (2018) with regard to their ability to nucleate ice at 261 K via condensation freezing. Based on theoretical considerations, hydrocarbons with long chains are potentially very good at initiating ice formation (Qiu et al., 2017) but conclusive experimental evidence is still missing. Hence, these theoreretical considerations

185 might provide an explanation for the high ice nucleation ability of carnauba wax.

For ambient samples like the agricultural soil dusts and the leaf litter investigated in this study, some studies (e.g Schnell and Vali (1973) and Steinke et al. (2016)) have found similarly high ice nucleation efficiencies. In contrast, leaf litter from the Arctic consisting mainly of grass leaves has been observed to show relatively low ice nucleation efficiencies (Conen et al., 2016), resulting in INAS density values of $n_s \sim 10^8$ m^{-2} at 258 K when

190 assuming a specific surface area of 2 m^2/g (Fraysse et al., 2010). Hence, the high INAS density values observed in our cloud chamber studies can be interpreted as upper limits for the ice nucleation efficiency of ambient plant-related aerosol particles. Note that for our leaf litter samples we did not differentiate between samples collected at different points in time and for different species. Due to the high variability it was not possible to clearly derive a seasonal trend from the observed ice nucleation efficiencies.

195   In Fig. 2, we show INSEKT-derived INAS density values for selected samples investigated in the previously described AIDA cloud chamber studies. For every sample at least two experimental runs were conducted, using freshly prepared suspensions for each run. The PROT_S sample was investigated to establish the lower boundary of ice nucleation activity observed for plant components whereas the AGDUST_HARV and the LEAF samples were used to represent ambient samples. Note that for the droplet freezing experiments, the INAS densities are

200   evaluated based on the specific surface areas derived from BET measurements rather than the geometric surface areas which were used for analyzing the AIDA experiments. The droplet freezing experiments are complementary to the cloud chamber studies as they deliver insights regarding the freezing properties of the bulk material, in particular with regard to including particles larger than 5 μm which are largely eliminated by impactor stages in our AIDA experiments. Also, observing the freezing of bulk suspensions allows for

205   quantifying the immersion freezing efficiencies at a lower supercooling which are more difficult to quantify in AIDA cloud chamber studies. For leaf litter we observe that INAS density values agree well between INSEKT and AIDA experiments. Similarly for plant protein (PROT_S), the agreement is reasonably. For AGDUST_HARV, there is a difference of approximately more than one order of magnitude which is possibly caused by larger particles being undersampled due to sedimentation within the suspensions.

210   Figure 2 shows that the hierarchy in ice nucleation activities is similar as observed in the AIDA cloud chamber experiments, with leaf litter and agricultural dust being the most ice-active samples. The steep onset of ice nucleation observed for the agricultural dust at 267 K suggests a contribution from biological particles (Suski et al., 2018). In contrast, the reason for the steep onset observed for the leaf litter sample in unclear. Soy protein particles initiate ice formation at higher temperatures (i.e. already below 258 K) than observed in AIDA cloud

215   chamber experiments, but the overall ice nucleation efficiency is still lower than for the complex organic samples from natural environments. Unfortunately, it was not possible to reliably determine INAS density values for carnauba wax (LIP) due to its very low dispersibility. Figure 2 also shows the INAS density values observed for illite as a proxy for freezing induced by mineral dust.

In conclusion, the results from the droplet freezing studies confirm the trend observed in our AIDA cloud

220   chamber experiments, with particles from ambient environments being highly ice-active, whereas individual organic compounds tend to be lower in their ice nucleation efficiencies. It should be noted that the organic compounds investigated in this study may not fully represent the complexity of real organic compounds in plants which often include mixtures, e.g. ligno-polysaccharide complexes with unknown chemical structures (Kögel-Knabner, 2002). At temperatures above 260 K, the gap between individual plant-related compounds and particles

225   from natural environments may be attributed to primary biological particles (e.g. fungi and bacteria) according to our droplet freezing measurements of harvesting dust. For example, ice nucleation efficiencies observed for particles generated from leaf litter fall within the lower range of values observed for bacteria (Hoose and Möhler, 2012).

There are, however, also differences between the ice nucleation efficiencies derived from AIDA cloud chamber

230   experiments and droplet freezing studies, which strongly dependent on the aerosol type. Some of these differences might be explained by differences in the evaluation of the INAS density values which are either related to the geometric surface or the specific surface area. For illite, normalizing by BET surface area results in INAS density values which are one order of magnitude lower compared to values derived by using geometric surface estimates (Hiranuma et al., 2015). Also, for some samples there are possibly differences in the effective

235   size distribution due to agglomeration or low dispersibility in the suspensions. In contrast, the dry dispersion

method (i.e. the rotating brush generator) is more likely to encourage disaggregation of particle agglomerates. Similar differences regarding the freezing of aqueous suspensions in comparison to dry dispersion experiments have been observed in other studies as well (Hiranuma et al., 2015a; Hiranuma et al., 2019).

Our experimental results suggest that the main components of decaying plant material (i.e. cellulose and lignin)

240 are not very good predictors of ice nucleation by ambient plant-related particles. However, the INAS density values observed for leaf litter and agricultural dust may help to constrain the upper limits of their respective ambient INP concentrations. The INAS density values for leaf litter and agricultural dust can be described by temperature-dependent functions, with

$$n_{s,leaf} = \exp(-0.246 \cdot T_{leaf} + 84.681) \qquad\qquad r^2 = 0.70 \qquad\qquad (1)$$

245 and

$$n_{s,agri} = \exp(-0.541 \cdot T_{agri} + 157.471) \qquad\qquad r^2 = 0.84 \qquad\qquad (2)$$

Note that these functions are only valid within certain temperature ranges, i.e. $T_{leaf} = [243, 258]$ and $T_{agri} = [245, 255]$, with all temperatures given in [K]. Equations 1 and 2 have been derived from the cloud chamber experiments exclusively and are represented in Fig. 2. Note that based on our droplet freezing experiments, both

250 of these aerosol types may have relatively sharp ice nucleation onsets at 257 K (leaf litter) and 267 K (agricultural dusts).

Figure 3 shows a comparison between ambient INP concentration derived from precipitation samples from several sites in the United States and Europe (Petters and Wright, 2015) and estimates for INP concentrations from leaf litter (eq.1) and agricultural dust (eq.2). Note that ambient INP measurements may scatter significantly

255 more than found in the study by Petters and Wright (2015), with deviations of up to four orders of magnitude between different studies (Kanji et al., 2017).

Ground-based measurements for leaf litter concentrations range between 30 ng/m^3 to 1 µg/m^3 (Hildemann et al., 1996; Sánchez-Ochoa et al., 2007). For agricultural dust, ground-based concentration vary between <10 and 100 µg/m^3, with up to 800 µg/m^3 observed occasionally for very strong wind erosion events (Gillette et al., 1978;

260 Sharratt et al., 2007; Hoffmann and Funk, 2015). Annually averaged boundary layer concentrations for desert dust vary between 0.1 and 30 µg/m^3 (Ginoux et al., 2001) which is comparable to the aforementioned concentrations of complex organic particles. Using eqs. 1 and 2 and assuming an aerosol surface area of 1 m^2/g, we can derive order-of-magnitude estimates for the expected atmospheric INP contribution from leaf litter and agricultural dust.

265 The estimates presented in this study should be considered as upper limits, with emission fluxes of organic particles acting as INPs being poorly constrained and more detailed modelling case studies needed. We find that plant-derived organic INPs from leaf litter and agricultural areas are within the same order magnitude as INP concentrations derived from precipitation measurements and field campaigns (Petters and Wright, 2015; Kanji et al., 2017). This finding further emphasizes the potential of plant-related sources to contribute to ambient INPs.

270 **Section 4: Conclusions**

Complex organic particles are emitted from terrestrial sources, with wind erosion, soil cultivation and harvesting crops as potential main drivers for emissions of organic matter associated with plant debris and decomposed residues (Hoffmann et al., 2008; Iturri et al., 2017). These sources are becoming increasingly important in the

275 global view, as climate change, soil degradation and excessive land use will promote dust emissions from agriculturally used areas. The global extent of the affected areas is comparable with the Sahara, the worldwide largest source of mineral dust, which covers 9.2 million km². Temperate grasslands, susceptible to wind erosion, cover an area of 9 million km², and the total area of grown cereals is 5.6 million km², contributing several times a year to dust emissions by diverse tillage and harvest operations. In this study, we investigated the immersion freezing properties of plant-related organic particles and samples from vegetated environments. We used a

280 combination of AIDA cloud chamber and INSEKT droplet freezing experiments to cover a temperature range between 242 and 267 K. Our experiments show that ambient samples with a complex organic composition are equally or more ice-active than individual plant-related compounds. Lignin and plant protein samples are inefficient INPs, whereas starches, alginate and pectin show moderate to high ice nucleation efficiencies. Surprisingly, carnauba wax – which is a mixture of aliphatic esters and fatty acids – shows the highest ice

285 nucleation activity of all organic compounds investigated in this study. INP estimates based on our cloud chamber experiments lend themselves to the hypothesis that aerosolized particles from leaf litter and agricultural areas are potentially important contributors to atmospheric INPs. However, the high ice nucleation efficiency of these particles could not be fully explained by the ice nucleation activity of individual organic compounds commonly found in plant tissue. Thus, further future studies are indeed demanded and warranted.

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Author contributions

IS and NH designed and conducted the experiments, with contributions from KH, OM and NSU. PGW conducted the BET surface measurements and NT provided the SEM images. IS and NH analyzed the data. IS

295 prepared the manuscript with input from all co-authors.

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Competing interests

The authors declare no competing financial interests.

310 **Data management**

All data in this manuscript will be made available as part of a KITopen data repository.

References

Agresti, A., and Coull, B. A.: Approximate Is Better than "Exact" for Interval Estimation of Binomial Proportions, The American Statistician, 52, 119-126, 10.1080/00031305.1998.10480550, 1998.

315

Augustin, S., Wex, H., Niedermeier, D., Pummer, B., Grothe, H., Hartmann, S., Tomsche, L., Clauss, T., Voigtländer, J., Ignatius, K., and Stratmann, F.: Immersion freezing of birch pollen washing water, Atmos. Chem. Phys., 13, 10989-11003, 10.5194/acp-13-10989-2013, 2013.

320   Basson, I., and Reynhardt, E. C.: An investigation of the structures and molecular dynamics of natural waxes. II. Carnauba wax, Journal of Physics D: Applied Physics, 21, 1429-1433, 10.1088/0022-3727/21/9/017, 1988.

Boose, Y., Welti, A., Atkinson, J., Ramelli, F., Danielczok, A., Bingemer, H. G., Plötze, M., Sierau, B., Kanji, Z. A., and Lohmann, U.: Heterogeneous ice nucleation on dust particles sourced from nine deserts worldwide – Part 325   1: Immersion freezing, Atmos. Chem. Phys., 16, 15075-15095, 10.5194/acp-16-15075-2016, 2016.

Conen, F., Stopelli, E., and Zimmermann, L.: Clues that decaying leaves enrich Arctic air with ice nucleating particles, Atmospheric Environment, 129, 91-94, 10.1016/j.atmosenv.2016.01.027, 2016.

330   Connolly, P. J., Möhler, O., Field, P. R., Saathoff, H., Burgess, R., Choularton, T., and Gallagher, M.: Studies of heterogeneous freezing by three different desert dust samples, Atmos. Chem. Phys., 9, 2805-2824, 10.5194/acp-9-2805-2009, 2009.

DeMott, P. J., Mason, R. H., McCluskey, C. S., Hill, T. C. J., Perkins, R. J., Desyaterik, Y., Bertram, A. K., 335   Trueblood, J. V., Grassian, V. H., Qiu, Y., Molinero, V., Tobo, Y., Sultana, C. M., Lee, C. T., and Prather, K. A.: Ice nucleation by particles containing long-chain fatty acids of relevance to freezing by sea spray aerosols, Environmental Science: Processes & Impacts, 20, 1559-1569, 10.1039/c8em00386f, 2018.

Fahey, D. W., Gao, R. S., Möhler, O., Saathoff, H., Schiller, C., Ebert, V., Krämer, M., Peter, T., Amarouche, 340   N., Avallone, L. M., Bauer, R., Bozóki, Z., Christensen, L. E., Davis, S. M., Durry, G., Dyroff, C., Herman, R. L., Hunsmann, S., Khaykin, S. M., Mackrodt, P., Meyer, J., Smith, J. B., Spelten, N., Troy, R. F., Vömel, H., Wagner, S., and Wienhold, F. G.: The AquaVIT-1 intercomparison of atmospheric water vapor measurement techniques, Atmos. Meas. Tech., 7, 3177-3213, 10.5194/amt-7-3177-2014, 2014.

345   Fraysse, F., Pokrovsky, O. S., and Meunier, J. D.: Experimental study of terrestrial plant litter interaction with aqueous solutions, Geochimica et Cosmochimica Acta, 74, 70-84, 10.1016/j.gca.2009.09.002, 2010.

Gillette, D. A., Clayton, R. N., Mayeda, T. K., Jackson, M. L., and Sridhar, K.: Tropospheric Aerosols from Some Major Dust Storms of the Southwestern United States, Journal of Applied Meteorology, 17, 832-845, 350   10.1175/1520-0450(1978)017<0832:tafsmd>2.0.co;2, 1978.

Ginoux, P., Chin, M., Tegen, I., Prospero, J. M., Holben, B., Dubovik, O., and Lin, S.-J.: Sources and distributions of dust aerosols simulated with the GOCART model, Journal of Geophysical Research: Atmospheres, 106, 20255-20273, 10.1029/2000jd000053, 2001.

355

Graça, M. A. S., Bärlocher, F., and Gessner, M. O.: Methods to study litter decomposition: a practical guide, Springer, Dordrecht, 2005.

Hande, L. B., and Hoose, C.: Partitioning the primary ice formation modes in large eddy simulations of mixed-360   phase clouds, Atmos. Chem. Phys., 17, 14105-14118, 10.5194/acp-17-14105-2017, 2017.

Hildemann, L. M., Rogge, W. F., Cass, G. R., Mazurek, M. A., and Simoneit, B. R. T.: Contribution of primary aerosol emissions from vegetation-derived sources to fine particle concentrations in Los Angeles, Journal of Geophysical Research: Atmospheres, 101, 19541-19549, doi:10.1029/95JD02136, 1996.

365

Hill, T. C. J., Moffett, B. F., DeMott, P. J., Georgakopoulos, D. G., Stump, W. L., and Franc, G. D.: Measurement of Ice Nucleation-Active Bacteria on Plants and in Precipitation by Quantitative PCR, Applied and Environmental Microbiology, 80, 1256-1267, 10.1128/aem.02967-13, 2014.

370 Hill, T. C. J., DeMott, P. J., Tobo, Y., Fröhlich-Nowoisky, J., Moffett, B. F., Franc, G. D., and Kreidenweis, S. M.: Sources of organic ice nucleating particles in soils, Atmos. Chem. Phys., 16, 7195-7211, 10.5194/acp-16-7195-2016, 2016.

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., Diehl, K.,
375 Dreischmeier, K., Ebert, M., Frank, F., Hoffmann, N., Kandler, K., Kiselev, A., Koop, T., Leisner, T., Möhler, O., Nillius, B., Peckhaus, A., Rose, D., Weinbruch, S., Wex, H., Boose, Y., DeMott, P. J., Hader, J. D., Hill, T. C. J., Kanji, Z. A., Kulkarni, G., Levin, E. J. T., McCluskey, C. S., Murakami, M., Murray, B. J., Niedermeier, D., Petters, M. D., O'Sullivan, D., Saito, A., Schill, G. P., Tajiri, T., Tolbert, M. A., Welti, A., Whale, T. F., Wright, T. P., and Yamashita, K.: A comprehensive laboratory study on the immersion freezing behavior of illite
380 NX particles: a comparison of 17 ice nucleation measurement techniques, Atmos. Chem. Phys., 15, 2489-2518, 10.5194/acp-15-2489-2015, 2015a.

Hiranuma, N., Möhler, O., Yamashita, K., Tajiri, T., Saito, A., Kiselev, A., Hoffmann, N., Hoose, C., Jantsch, E., Koop, T., and Murakami, M.: Ice nucleation by cellulose and its potential contribution to ice formation in
385 clouds, Nature Geosci, 8, 273-277, 10.1038/ngeo2374, 2015b.

Hiranuma, N., Adachi, K., Bell, D., Belosi, F., Beydoun, H., Bhaduri, B., Bingemer, H., Budke, C., Clemen, H. C., Conen, F., Cory, K., Curtius, J., DeMott, P., Eppers, O., Grawe, S., Hartmann, S., Hoffmann, N., Höhler, K., Jantsch, E., Kiselev, A., Koop, T., Kulkarni, G., Mayer, A., Murakami, M., Murray, B., Nicosia, A., Petters, M.,
390 Piazza, M., Polen, M., Reicher, N., Rudich, Y., Saito, A., Santachiara, G., Schiebel, T., Schill, G., Schneider, J., Segev, L., Stopelli, E., Sullivan, R., Suski, K., Szakáll, M., Tajiri, T., Taylor, H., Tobo, Y., Weber, D., Wex, H., Whale, T., Whiteside, C., Yamashita, K., Zelenyuk, A., and Möhler, O.: A comprehensive characterization of ice nucleation by three different types of cellulose particles immersed in water, Atmos. Chem. Phys., 19, 4823-4849, 10.5194/acp-19-4823-2019, 2019.

395

Hoffmann, C., Funk, R., Li, Y., and Sommer, M.: Effect of grazing on wind driven carbon and nitrogen ratios in the grasslands of Inner Mongolia, Catena, 75, 182-190, 10.1016/j.catena.2008.06.003, 2008.

Hoffmann, C., and Funk, R.: Diurnal changes of PM10-emission from arable soils in NE-Germany, Aeolian
400 Research, 17, 117-127, 10.1016/j.aeolia.2015.03.002, 2015.

Hoose, C., and Möhler, O.: Heterogeneous ice nucleation on atmospheric aerosols: a review of results from laboratory experiments, Atmos. Chem. Phys., 12, 9817-9854, 10.5194/acp-12-9817-2012, 2012.

405 Hummel, M., Hoose, C., Pummer, B., Schaupp, C., Fröhlich-Nowoisky, J., and Möhler, O.: Simulating the influence of primary biological aerosol particles on clouds by heterogeneous ice nucleation, Atmos. Chem. Phys., 18, 15437-15450, 10.5194/acp-18-15437-2018, 2018.

Iturri, L. A., Funk, R., Leue, M., Sommer, M., and Buschiazzo, D. E.: Wind sorting affects differently the
410 organo-mineral composition of saltating and particulate materials in contrasting texture agricultural soils, Aeolian Research, 28, 39-49, 10.1016/j.aeolia.2017.07.005, 2017.

Kanitz, T., Seifert, P., Ansmann, A., Engelmann, R., Althausen, D., Casiccia, C., and Rohwer, E. G.: Contrasting the impact of aerosols at northern and southern midlatitudes on heterogeneous ice formation, Geophysical
415 Research Letters, 38, L17802, 10.1029/2011gl048532, 2011.

Kanji, Z. A., Ladino, L. A., Wex, H., Boose, Y., Burkert-Kohn, M., Cziczo, D. J., and Krämer, M.: Overview of Ice Nucleating Particles, Meteorological Monographs, 58, 1.1-1.33, 10.1175/amsmonographs-d-16-0006.1, 2017.

420

Kögel-Knabner, I.: The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter, Soil Biology and Biochemistry, 34, 139-162, 10.1016/S0038-0717(01)00158-4, 2002.

Möhler, O., Field, P. R., Connolly, P., Benz, S., Saathoff, H., Schnaiter, M., Wagner, R., Cotton, R., Krämer, M.,
425 Mangold, A., and Heymsfield, A. J.: Efficiency of the deposition mode ice nucleation on mineral dust particles, Atmos. Chem. Phys., 6, 3007-3021, 10.5194/acp-6-3007-2006, 2006.

Möhler, O., DeMott, P. J., Vali, G., and Levin, Z.: Microbiology and atmospheric processes: the role of biological particles in cloud physics, Biogeosciences, 4, 1059-1071, 10.5194/bg-4-1059-2007, 2007.

430

Murphy, D. M., and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Quarterly Journal of the Royal Meteorological Society, 131, 1539 - 1565, 10.1256/qj.04.94, 2005.

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

Niemand, M., Möhler, O., Vogel, B., Vogel, H., Hoose, C., Connolly, P., Klein, H., Bingemer, H., DeMott, P., Skrotzki, J., and Leisner, T.: A Particle-Surface-Area-Based Parameterization of Immersion Freezing on Desert Dust Particles, Journal of the Atmospheric Sciences, 69, 3077-3092, 10.1175/jas-d-11-0249.1, 2012.

440

O'Sullivan, D., Murray, B. J., Malkin, T. L., Whale, T. F., Umo, N. S., Atkinson, J. D., Price, H. C., Baustian, K. J., Browse, J., and Webb, M. E.: Ice nucleation by fertile soil dusts: relative importance of mineral and biogenic components, Atmos. Chem. Phys., 14, 1853-1867, 10.5194/acp-14-1853-2014, 2014.

445 O'Sullivan, D., Adams, M. P., Tarn, M. D., Harrison, A. D., Vergara-Temprado, J., Porter, G. C. E., Holden, M. A., Sanchez-Marroquin, A., Carotenuto, F., Whale, T. F., McQuaid, J. B., Walshaw, R., Hedges, D. H. P., Burke, I. T., Cui, Z., and Murray, B. J.: Contributions of biogenic material to the atmospheric ice-nucleating particle population in North Western Europe, Scientific Reports, 8, 13821, 10.1038/s41598-018-31981-7, 2018.

450 O'Sullivan, D., Murray, B. J., Ross, J. F., Whale, T. F., Price, H. C., Atkinson, J. D., Umo, N. S., and Webb, M. E.: The relevance of nanoscale biological fragments for ice nucleation in clouds, Scientific Reports, 5, 8082, 10.1038/srep08082, 2015.

Petters, M. D., and Wright, T. P.: Revisiting ice nucleation from precipitation samples, Geophysical Research
455 Letters, 42, 8758-8766, doi:10.1002/2015GL065733, 2015.

Pratt, K. A., DeMott, P. J., French, J. R., Wang, Z., Westphal, D. L., Heymsfield, A. J., Twohy, C. H., Prenni, A. J., and Prather, K. A.: In situ detection of biological particles in cloud ice-crystals, Nature Geoscience, 2, 398 - 401, 10.1038/ngeo521, 2009.

460

Pruppacher, H. R., and Klett, J. D.: Microphysics of clouds and precipitation, 2. ed., Atmospheric and Oceanographic Sciences Library, Springer, Dordrecht, 2010.

Pummer, B. G., Bauer, H., Bernardi, J., Bleicher, S., and Grothe, H.: Suspendable macromolecules are
465 responsible for ice nucleation activity of birch and conifer pollen, Atmos. Chem. Phys., 12, 2541-2550, 10.5194/acp-12-2541-2012, 2012.

Qiu, Y., Odendahl, N., Hudait, A., Mason, R., Bertram, A. K., Paesani, F., DeMott, P. J., and Molinero, V.: Ice Nucleation Efficiency of Hydroxylated Organic Surfaces Is Controlled by Their Structural Fluctuations and Mismatch to Ice, Journal of the American Chemical Society, 139, 3052-3064, 10.1021/jacs.6b12210, 2017.

470

Quiroz-Castañeda, R. E., and Folch-Mallol, J. L.: Hydrolysis of Biomass Mediated by Cellulases for the Production of Sugars, in: Sustainable Degradation of Lignocellulosic Biomass - Techniques, Applications and Commercialization, edited by: Chandel, A., and Silvério da Silva, S., InTechOpen, 2013.

475

Sánchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Gelencser, A., Legrand, M., and Pio, C.: Concentration of atmospheric cellulose: A proxy for plant debris across a west-east transect over Europe, Journal of Geophysical Research: Atmospheres, 112, D23S08, 10.1029/2006JD008180, 2007.

480

Schiebel, T.: Ice Nucleation Activity of Soil Dust Aerosols, PhD dissertation, Karlsruhe Institute of Technology, Karlsruhe, Germany, 2017.

Schnell, R. C., and Vali, G.: Atmospheric Ice Nuclei from Decomposing Vegetation, Nature, 236, 163-165, 10.1038/236163a0, 1972.

485

Schnell, R. C., and Vali, G.: World-wide Source of Leaf-derived Freezing Nuclei, Nature, 246, 212-213, 10.1038/246212a0, 1973.

Sharratt, B., Feng, G., and Wendling, L.: Loss of soil and PM10 from agricultural fields associated with high winds on the Columbia Plateau, Earth Surface Processes and Landforms, 32, 621-630, 10.1002/esp.1425, 2007.

490

Steinke, I., Funk, R., Busse, J., Iturri, A., Kirchen, S., Leue, M., Möhler, O., Schwartz, T., Schnaiter, M., Sierau, B., Toprak, E., Ullrich, R., Ulrich, A., Hoose, C., and Leisner, T.: Ice nucleation activity of agricultural soil dust aerosols from Mongolia, Argentina, and Germany, Journal of Geophysical Research: Atmospheres, 121, 13559-13576, 10.1002/2016jd025160, 2016.

495

Suski, K. J., Hill, T. C. J., Levin, E. J. T., Miller, A., DeMott, P. J., and Kreidenweis, S. M.: Agricultural harvesting emissions of ice-nucleating particles, Atmos. Chem. Phys., 18, 13755-13771, 10.5194/acp-18-13755-2018, 2018.

500

Tobo, Y., DeMott, P. J., Hill, T. C. J., Prenni, A. J., Swoboda-Colberg, N. G., Franc, G. D., and Kreidenweis, S. M.: Organic matter matters for ice nuclei of agricultural soil origin, Atmos. Chem. Phys., 14, 8521-8531, 10.5194/acp-14-8521-2014, 2014.

505

Ullrich, R., Hoose, C., Möhler, O., Niemand, M., Wagner, R., Höhler, K., Hiranuma, N., Saathoff, H., and Leisner, T.: A New Ice Nucleation Active Site Parameterization for Desert Dust and Soot, Journal of the Atmospheric Sciences, 74, 699-717, 10.1175/jas-d-16-0074.1, 2017.

Vali, G., DeMott, P. J., Möhler, O., and Whale, T. F.: Technical Note: A proposal for ice nucleation terminology, Atmos. Chem. Phys., 15, 10263-10270, 10.5194/acp-15-10263-2015, 2015.

510

Vandenburg, L. E., and Wilder, E. A.: The structural constituents of carnauba wax, Journal of the American Oil Chemists Society, 47, 514-518, 10.1007/bf02639240, 1970.

515

Vlachou, A., Daellenbach, K. R., Bozzetti, C., Chazeau, B., Salazar, G. A., Szidat, S., Jaffrezo, J. L., Hueglin, C., Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: Advanced source apportionment of carbonaceous aerosols by coupling offline AMS and radiocarbon size-segregated measurements over a nearly 2-year period, Atmos. Chem. Phys., 18, 6187-6206, 10.5194/acp-18-6187-2018, 2018.

520   Wagner, R., and Möhler, O.: Heterogeneous ice nucleation ability of crystalline sodium chloride dihydrate
       particles, Journal of Geophysical Research: Atmospheres, 118, 4610-4622, doi:1002/jgrd.50325, 2013.

       Williams, S. T., and Gray, T. R. G.: Decomposition of litter on the soil surface, in: Biology of Plant Litter
       Decomposition, edited by: Dickinson, C. H., and Pugh, G. J. F., Academic Press, London, 611-632, 1974.

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Tables

550   **Table 1:** Overview of samples used for ice nucleation experiments

Sample name	Acronym	Sample preparation/manufacturer
Ambient samples dominated by decaying plant material		
Leaf litter	LEAF	Dry leaf debris from either spruce or maple trees in Southwestern Germany, dried at 313 K, milled and sieved for particles smaller than 150 µm (collected in spring and autumn in the years 2014, 2015, and 2016)
Agricultural dust	AGDUST_HARV	Dry plant material collected from filters of harvesting machines after rye and wheat harvests in Northwestern Germany, sieved for particles smaller than 63 µm (collected in summer 2016)
Agricultural soil dust	AGDUST_WYO	Top soil samples collected in Wyoming on sugar beet fields (collected in spring 2011)
Alginate	ALG	C.E. Roeper GmbH (article no. NA 4012)
Lignin	LIG	Sigma-Aldrich (article no. 370959 and 471003)
Lipids (Carnaubawax)	LIP	Sigma-Aldrich (article no. 243213)
Plant-related organic compounds		
Pectin	PEC	Herbstreith & Fox KG (article no. AU 015 H I)
Protein (Rice, soy)	PROT_R, PROT_S	Erdschwalbe (article no. 30676 and 30744, food grade quality)
Starch (Potato)	STAR_P	Mueller's Muehle GmbH (food grade quality)
Starch (Corn)	STAR_C	Unilever (food grade quality)

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Figures
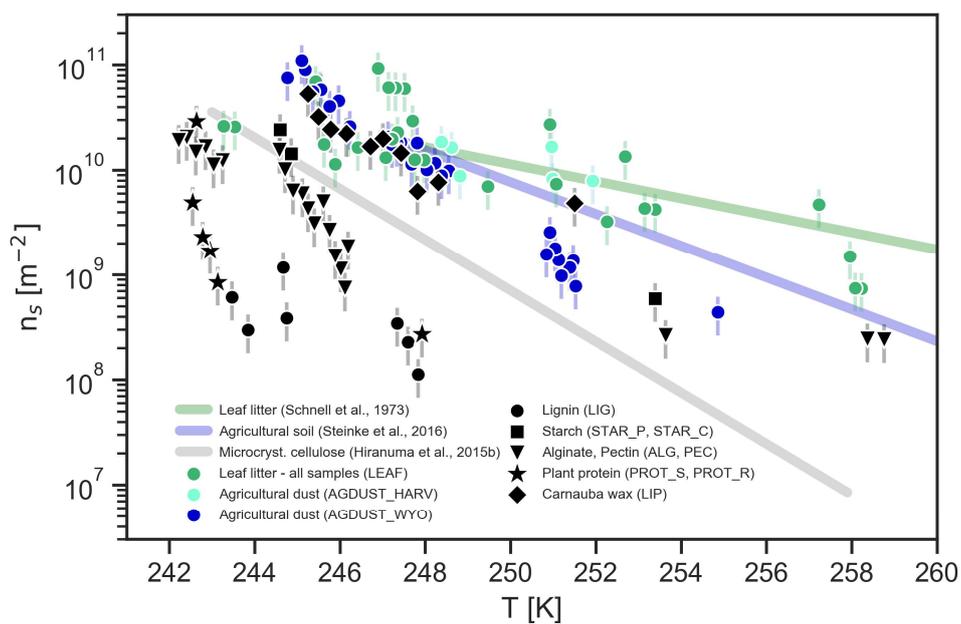
Figure 1: Immersion freezing results for plant-related organic compounds compared to ambient samples – ice nucleation
efficiency expressed as INAS density values based on AIDA cloud chamber experiments

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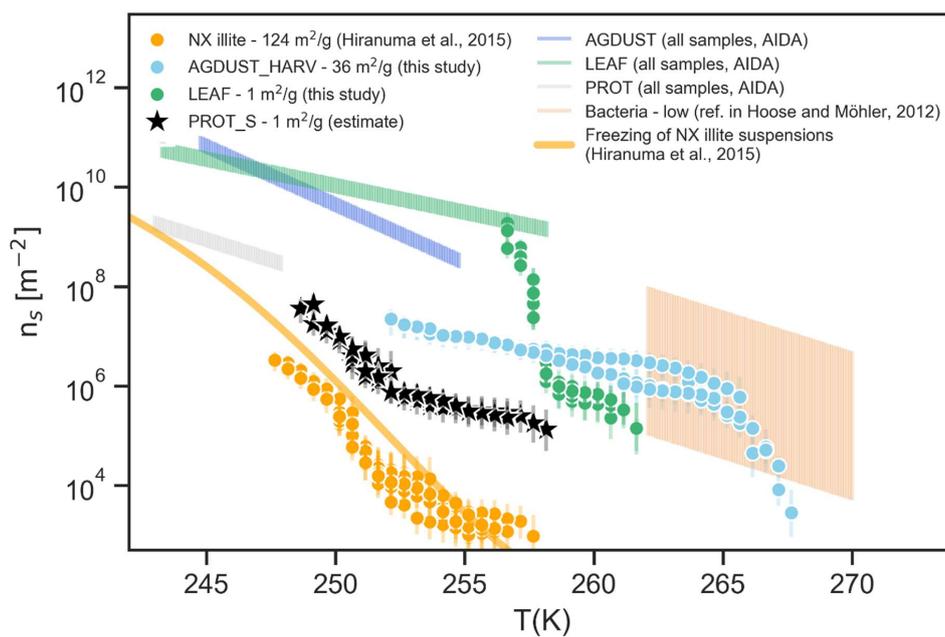
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Figure 2: Immersion freezing results for selected plant-related samples and illite, comparing INSEKT-derived INAS density values to results from AIDA experiments (Fig.1) – ice nucleation efficiency expressed as INAS density values based on INSEKT droplet freezing experiments and specific surface areas indicated in the legend

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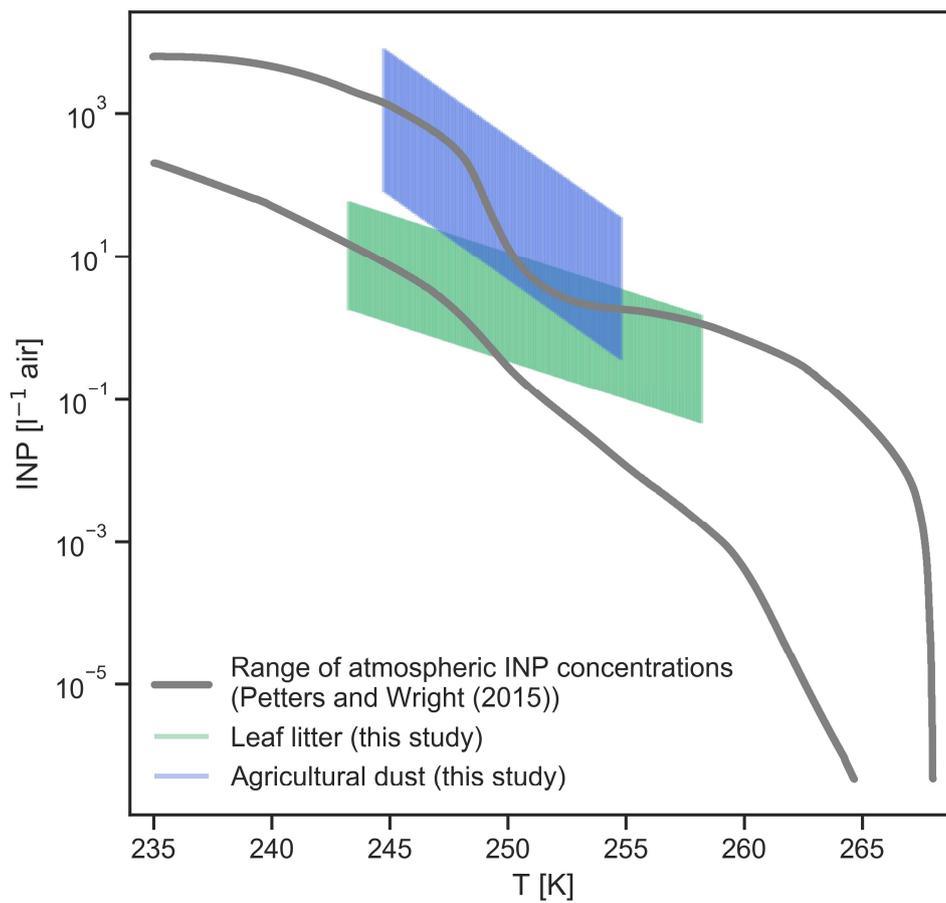
Figure 3: Comparison between atmospheric INP concentrations (Petters and Wright (2015)) and estimates for INPs from leaf litter and agricultural dust based on AIDA cloud chamber experiments

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