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Comment on acp-2021-111

Anonymous Referee #3

Referee comment on "Particle emissions from a modern heavy-duty diesel engine as ice nuclei in immersion freezing mode: a laboratory study on fossil and renewable fuels" by Kimmo Korhonen et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-111-RC2>, 2021

Review of Manuscript acp-2021-111:

Particle emissions from a modern heavy-duty diesel engine as ice-nuclei in immersion freezing mode: an experimental study on fossil and renewable fuels, by Korhonen et al.

General comments:

Korhonen et al. perform systematic experiments about the ice nucleation ability of diesel engine particulate emissions at high relative humidity and mixed phase cloud relevant conditions, with auxiliary measurements about particle size distribution, hygroscopicity and chemical composition. The ice nucleation activity data and conclusion presented, demonstrating the poor ice formation ability of diesel engine particles and limited effects from photochemical ageing processes on the particle ice nucleation activity, are of interests to the ice nucleation community. However, some part of discussion and data interpretation are not thoroughly or comprehensively presented. I would like to suggest further revisions before recommending acceptance.

The ice nucleation experiments performed cover a variety of diesel engine emissions generated by three kinds of fuels. Different engine exhaust treatment techniques are used to mimic diesel engine particulate emission atmospheric relevant ageing processes. The research interests are of significance of the atmospheric ice nucleating particles and thus climate. An interesting ice nucleation story is clear. Nevertheless, some improvements need to be made, regarding to data interpretation and results discussion. In general, I have five major comments on this manuscript.

The authors should clarify their samples and research focus clearly and construct an unambiguous approach about the research story, illustrating the relations among all the measurements. For instance, the manuscript title and abstract tell me the particulate emission from a diesel engine will be the object for this experimental study, but the authors directly introduce soot particles in the introduction and the following parts. Note, the particulate emissions from diesel engines are not only comprised of soot particles. Differentiating the concept of soot particles from diesel engine particulate emissions is necessary. The authors also need to explain why soot particles emitted by land transportation diesel engines are atmospherically relevant.

Second, I highly recommend to harmonise the ice nucleation terminology through the manuscript, see Vali et al. (2015) as a reference. The aim is to make dissemination more uniform and consistent within the community.

Third, the ice nucleation pathway, immersion mode freezing, is not well introduced. Only referring to a reference (Korhonen et al. 2020) without a brief introduction about how this can be achieved is not enough, in my opinion. Both the concept and the approach to achieve it should be explained even as a summary and then referring to the previous literature can be of more clarity and convincingness.

Forth, a new approach to present normalized ice activation fraction results should be explained more clearly in Sect. 2 and 3. Also, it should be applied carefully. Note that, the particle samples are polydisperse with different particle size distributions (see Fig. 2) and the proportion of large particles (e.g. $> 100 \text{ nm} \sim 10 \%$) is still comparable or even higher than the highest ice activation fraction measured. For instance, the highest ice activation fraction for unaged RME fuel engine particles is less than 0.35 % even at the lowest temperature addressed, as shown in Fig. 6. To figure out the contribution of large particles (e.g. 100, 200 or 300 nm) to the ice activation fraction, ice nucleation experiments for size selected (e.g. 100, 200 or 300 nm) large particles are expected to be performed. In addition, the data processing or the calculation method needs to be formulated and then the specific equation can help the understanding.

Finally and most importantly, the results discussion is performed not thoroughly and reasonably. For example, comparing the ice nucleation results of polydisperse aerosol dominated by fine particles ($< 100 \text{ nm}$) with the homogeneous freezing of larger (350 nm) ammonium sulfate (AS) particles is inappropriate. Instead of 350 nm AS particles, the comparison with the homogeneous freezing results of small (≤ 100 or 150 nm) AS particles would be of more relevance to the results of diesel soot particles which has a small size distribution. Especially, the diesel engine particles already exhibit a homogeneous freezing depression event at temperatures lower than the homogeneous freezing temperature at such a high relative humidity ($\text{RH}_w = 110 \%$). In addition, the ice nucleation data is not well linked to the auxiliary measurement results. Similar findings in the literature are also helpful to support the conclusion (see detailed comments in next part).

Specific comments:

Line 17: change 'continuous-flow diffusion chamber' to the same as it is in Line 87

Line 19: change to '-43 and -32°C'. The same for Line 43, 92, 96, 175, 234 and 268. Please check through the mathematical notation and make it satisfy ACP terminology.

Line 23: change 'present' to 'presented'

Line 24: make 'different emission after-treatment systems' specified

Line 27: change to 'the radiative forcing of the Earth and thus climate in different ways'

Line 39: change to 'homogeneous ice nucleation'

Line 41: change to 'ice nucleating particles' and specify its abbreviation 'INPs'

Line 39 to 41: Please provide evidence or reference to show combustion emissions are relevant to the lower troposphere ice nucleation activities.

Line 44 and 45: If you write that soot particles are not active INPs, the relative humidity and temperature condition also need to be reported.

Line 50: the reference 'Mahrt et al. 2018' should be irrelevant to the atmospheric aging processes for INPs but Mahrt et al. (2020a) and (2020b) can be references.

Line 58 and 59: change to 'the climate forcing due to anthropogenic soot particles immersion freezing'

Line 60: change to 'ice nucleation abilities'

Line 72 to 74: The environmental pollution caused by diesel engine without DPF or DOC

technique is not relevant to this research topic.

Line 129 to 131: was the Aerosol Instrument Manager (AIM) software used to log the SMPS data? If so, the SMPS scan size upper limit should be much larger than 500 nm with such a high sheath to aerosol sample flow ratio (10 : 1) and a 180 s scanning time. And if the size scan did not cover the whole range of the aerosol particle size distribution, the multiple charge correction is not finished and then the results are biased by the uncomplete correction calculation.

Line 130 to 142: Better to introduce the measurements work flow following the sample flow sequence depicted in Fig. 1.

Line 179 to 181: The authors need to make a more conceivable and clear statement for distinguishing water droplets from ice crystals. I understand that the basic idea is to let the OPC running in different size channels and then to differentiate the particle phase according to their survival abilities through the evaporation section, i.e. water droplet can be evaporated because of the relative humidity condition. The statement about CCN ability and immersion mode freezing make readers confused. In addition, referring to the study performed by Korhonen et al. (2020) as an example does not make sense for me. This is because the samples are different between the current study (i.e. diesel engine particulate emissions) and the previous study (i.e. particulate emissions from solid-biomass-fired cookstoves). The OPC channel size used to discriminate water droplets from ice crystals should be stated from the current study.

Line 190: change to 'exiting the IN chamber' or 'exiting the SPIN'. Or, the authors can decide to use 'SPIN' or 'the SPIN' through the whole manuscript.

Line 215 to 225: In this paragraph is not well organised. In my point of view, the authors may need to explain how the freezing of a particle immersed in a water droplet could happen when the temperature decreases lower than the homogeneous freezing temperature (HNT), to illustrate the results presentation. A suggestion could be that sample particles might be activated as cloud droplets at $RH_w = 110\%$ for temperature conditions higher than the HNT, thus makes it possible to investigate the particles immersion mode freezing ability at $T < HNT$ in the flowing temperature scan because a droplet would freeze homogeneously when T is lower than HNT. Here again, the ice crystal formation of droplet activated particles at $T < HNT$ should be homogeneous freezing. If the authors claim this is immersion freezing, evidence of this should be presented. But if the freezing occurs at RH conditions above homogeneous RH condition at the same T , then it is unclear how the authors can conclude immersion freezing to be the relevant mechanism.

Line 223 to 225: A clear definition for the normalization of the ice activation fraction curves for each sample should be made. A formulation for this approach or an example may help.

Line 232 and 233: change 'L/min' to 'L min⁻¹'. Please check the unit through the manuscript.

Line 235: The CCNC calibration curves should be provided in the following section or in an Appendix part.

Line 251: The calibration results should be provided in the following section or in an Appendix part.

Line 265: What is the 'GMDs'?

Line 285: change to 'Ice activation fraction curves for fossil diesel emissions are presented in Figs. 3 and 4'

Line 287: change to 'Fig. 3a'. And the similar suggestion to that of Line 298, 310, 314, 324, 326 and 327. Please check the abbreviation for 'Figure' through the manuscript.

Line 291: change to 'Fig. 3b'; Specify which two samples

Line 294: Here, what is the size range for the so-called ultrafine particles? It should be 100 nm if the number 90 % refers to the size distribution results mentioned in Sect. 3.1. Please make the ultrafine particle with a quantitative value for clear discussion.

Line 300 to 307: The discussion in this paragraph can be better. First, the ice formation enhancement by lowering the ice onset temperature values should be clearly connected to the sample to make it easier for readability. Second, some evidence from auxiliary measurements should be provided to interpret the results. Also, relevant studies in the literature can be referred to for comparison, e.g. Zhang et al. (2020) also investigated the photochemical aging effects on soot particles ice nucleation activities at $T < HNT$.

Line 313: change to 'the lowest temperature'

Line 316 and 317: Arguing that the -36.1 °C is outside of the instrument uncertainty should refer to the homogeneous freezing temperature detection ability of SPIN.

Line 327 and 328: Why use the size distribution results about fossil fuel in Fig. 2a ('left-hand panel of Fig. 2' in text) to interpret the ice activation results of RME emissions?

Line 335 to 347: The discussion in this paragraph is too general and not specific enough. For example, the auxiliary measurement results for each sample should be connected to the sample directly, instead of making a general statement or a conclusion (e.g. Line 336 to 338 about CCNC results) for the overall study. The statements also should be clearly related to the quantitative values obtained from the supportive measurements. In addition, explanation or definition about each measurement result, e.g. OA, C_{11}/C_3 , should be made in the main text. Necessary references in the literature also need to be referred.

Line 348: change to 'Summary and conclusion'. Because the discussion is largely presented in previous sections and this part is more about conclusions.

Line 349 to 368: I disagree with the logicity in this part. On the one hand, the authors conclude that small diesel engine particles have no contribution to ice nucleation activities (Line 361). On the other hand, they are comparing the ice nucleation ability of the particles produced by different fuels. The authors need to firstly demonstrate ice nucleation activity via the immersion mode really occurs then they can make statement about the efficiency of the soot particles as potential ice nucleating particles (INPs). The reference about the study presented by Kanji et al. (2020) in Line 354 is inappropriate, which states that their findings are in complete agreement with Kanji et al. (2020).

Figures and Tables:

Figure 1: I cannot find where the 'FPA-fast particle analyser' is in the figure. It is not mentioned in the main text, either.

Figures 2: The size distribution measurement for 'engine-out + BP' sample presented in Fig. 5 is missed in Fig. 2b and should be provided. And there is no SPIN experiment corresponding to the sample 'DOC + PAM' in Fig. 2b. In addition, it would be helpful if the figure grids are on to guide reader's eyes.

Figure 3: Is the ice activation curve for 'Engine-out + BP' sample normalized by the sample approach as those of other samples? The highest ice activation fraction should be the unity. It looks in corrected.

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