Review to "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. ACPD, 2021

Korhonen et al. present laboratory experiments of the ice nucleation ability of soot particles. Combustion particles are generated in a controlled laboratory setup using a diesel engine, operated with three different fuel types. The ice nucleation ability is tested on with a commercial continuous flow diffusion chamber (SPIN), operated at a fixed relative humidity (*RH*) of 110% and performing *T*-scans over a temperature range between -32 °C to -43 °C. These conditions are relevant for ice formation in tropospheric mixed-phase clouds. The ice nucleation activity is tested for fresh exhaust particles and compared to the ice nucleation activity of exhaust particles that underwent different types of exhaust aftertreatments. Also included are ice nucleation experiments where exhaust particles were first (photochemically) aged in an oxidation flow reactor (PAM chamber) prior to testing the ice nucleation in SPIN. All ice nucleation experiments are performed on polydisperse aerosol populations, with most particles having diameters well below 100 nm. The ice nucleation experiments are supported by a suite of auxiliary measurements to characterize the chemical and physical properties of the exhaust particles. Overall, the authors find the tested soot particles to be poor ice nucleation particles (INPs) in the immersion freezing mode. Photochemical aging in the PAM chamber slightly increased the ice nucleation activity for exhaust particles when burning fossil diesel, but no enhancement was found when burning HVO or RME fuel, although a direct comparison between these measurements is somewhat hampered by using different aging times (and/or combinations of aftertreatments) when operating the engine with these different fuel types.

Overall, I find these results very interesting and within the scope of Atmospheric Chemistry and Physics (ACP). Certainly, the conclusions of this study are largely in-line with previous work and further help to establish the notion that soot particles are inefficient INPs in immersion freezing mode and more generally at temperatures above -38 °C, i.e. above the homogeneous freezing temperature of water. The manuscript is clearly written in most parts (some structural improvements are suggested below), and conclusions drawn are mostly supported by the data shown in the figures. Nonetheless, some issues need further clarifications. Below I list my comments and suggestions that should be addressed upon revising the manuscript. My main concern is related to the "alternative method" that is presented and used to calculate the ice active fraction. In my eyes this point warrants major changes and additional explanations before this paper can be accepted for ACP. In addition, the analysis of measurement uncertainty reported for the AF curves warrants clarification.

Major comments:

The authors analyze their ice nucleation measurements in two different ways: In a first ("classical") approach the ice nucleation of the soot particles is presented in terms of the activated fraction (AF), given by the ratio of the ice counts detected by the optical particle counter of SPIN to the particle counts detected by a condensation particle counter operated in parallel to SPIN (see their Eq. 1). This way of data analysis corresponds to the "default" analysis of CFDC data in the ice nucleation community. In an "alternative method", each AF curve is normalized to the maximum ice-active fraction of an AF curve, as the authors note on L217-225. The goal of this alternative method is to estimate the immersion freezing ability of (the largest) particles in the polydisperse aerosol population, which acted as CCN inside SPIN (see L278-281). While the classical approach determines the immersion freezing ability of the entire polydisperse particle population, the alternative approach can be interpreted as a scaled/normalized AF resulting mainly from the larger particles.

For each fuel type tested, the authors report and compare the ice nucleation activity using the classical and the alternative approach (see Figs. 3-6). My interpretation is that this alternative approach, which overall shows a slightly enhanced ice formation signal compared to the homogeneous freezing (ammonium sulfate) reference, aims at teasing out the ice signal resulting from the larger aerosol particles. However, this alternative approach left me somewhat puzzled and the authors will need to significantly revise the text, in order to clarify the added value/benefit of interpreting their ice nucleation data using this alternative approach. Upon revision of the text, I suggest to also combine the paragraphs L215-225 and L273-282, which contain similar/identical information, into one paragraph that should be located within Sect. 2.2.

Related to this issue, questions that should be addressed include:

- The homogeneous reference curve was obtained by testing the ice nucleation activity 350 nm monodisperse ammonium sulfate particles (L212), whereas the combustion particles

are polydisperse aerosols with diameters mainly below 100 nm (Fig. 1). How do the authors justify using their alternative method to compare ice nucleation from such aerosol populations that significantly differ in size? Why not using e.g. the frequently applied ice nucleation active surface site density (INAS)?

- E.g. Fig. 3b: Why does the red line not go all the way up to unity? See also your statement on L223-226. Why is there no uncertainty for this red curve? In Fig. 3a, no data points are depicted for any of the AF curves at temperatures above -38 °C. However, for AF curves depicted in Fig. 3a calculated with the alternative method, data points show up at T > -38 °C. Is this an artefact resulting from extremely low AF (in Fig 3a, presumable below the detection limit of SPIN), showing up in Fig. 3b? Similar comments apply to Figs. 4-6 and to your statement on e.g. L315-317.
- Figs. 3-6: For consistency the y-axis labels should be “α” and “Normalized α” for panels a and b, respectively.

Minor, specific and technical comments:

L27: change to “the energy budget of the”
L30 add Kreidenweis et al. (2018)
L32: add „within them via immersion freezing (Murray et al., 2012).”
L33: replace reference by Korolev et al. (2017)
L33: “Furthermore…”, this sentence seems a bit unconnected to the topic of immersion freezing and MPC, consider rephrasing.
L36: add Lohmann et al. (2016)
L39: „ice nucleation“, here and elsewhere, e.g. L45.
L39: add: “Particles that are ice-active at temperatures above…”
L41: change to: “fuels can act as...:”
L42-44: Should also include Ikhenazene et al. (2020), Thomson et al. (2018)
L45: Remove reference to Hoose and Höhler (2012) and instead add: Schill et al. (2016, 2020), Vergara-Temprado et al. (2018), Adams et al. (2020)
L45: “In most of those…” I suggest to rephrase this sentence as there are a handful of ice nucleation papers on combustion aerosol, which carefully determine the properties of the particles (e.g. Mahrt et al., 2018; Nichman et al., 2019; Zhang et al., 2020).
L50 : Delete reference to Mahrt et al. (2018) and instead consider adding: Mahrt et al. (2020)
L59: Add space after “m^{-2}”
L61-8: These paragraphs discuss engine types and aftertreatment, whereas the paragraphs before and after this focus on ice nucleation on combustion aerosol. I suggest restructuring this part upon revision and keep the section relevant to ice nucleation together to improve readability. For instance, the references on L86 should be included/moved to the discussion of ice nucleation on soot (L36-60). As another suggestion, much of the description of the different fuel types (L76-85) could be taken out from the introduction and moved to a subsection of Sect. 2.1.
L68: Please add a brief description here (or where appropriate) what the diesel oxidation catalyst (DOC) does to the exhaust particles in your setup.
L77: consider adding Bove et al. (2019)
L93: What do you mean by “was added in the aging phase”? Were the particles coated with SOA?
L97: What do you mean by “where aging played an important role”? Was the ice nucleation activity enhanced or decreased?
L107: Change to “ability down to temperatures where homogeneous freezing starts to dominate.”
L119: Please specify the type of aging in the PAM chamber. On L339 you write that “SOA formation on diesel emission took place in the PAM chamber”, but I could not find any detailed information on what this means. Did you coat your exhaust particles? You might want to also refer to the work of Zhang et al. (2020) and relate your results to those presented in this study.
L122 and L126: Please comment on how the dilution steps in your set-up affect the gas-particle partitioning of semi-volatile material associated with the engine exhaust in the manuscript.
L130: Change to: “with sample and sheath flows of 0.3 L min^{-1} and 3 L min^{-1}, respectively” (or give as ratio without units).
L138: What physical particle properties are derived from the AMS data?
L157: change to: “at a flow”
L161: change to: “as the aerosol-lamina”
L163: “whose temperature corresponded to the average aerosol-lamina temperature”
L170: change to: “allowed lower detection limit…”
L171: “sample”. Do you mean aerosol number concentration here?
L174: change to: “done using T-scans at constant...”

L181: Please quantify aerosol residence time in evaporation section.
L183: replace “in the IN chamber” by “CFDC”
L184: The size threshold to discriminate ice crystals and droplets depends on the RH and T within the CFDC, i.e. the growth conditions of the hydrometeors. Is the indicated threshold valid for all the experimental conditions within your paper? How does this threshold compare to theoretical hydrometeor sizes assuming pure condensational/diffusional growth? See e.g. Rogers and Yau (1989).
L190: Delete “the IN chamber of the”
L192: Change to: “counts measured during… from the OPC signal. The background values between…”
L194-200: This part of the description of the uncertainties and error analysis should be expanded and written more clearly (e.g. by using equations), see also my main comment above. E.g. you might want to at least briefly comment how the “statistical error” (L198) compares to the other uncertainties associated with CFDC measurements.
L203-213: The discussion of the particle number concentrations used within SPIN should be expanded. Please be more quantitative when discussing the results of Levin et al. (2016) and how these values compare to the number concentrations used in your experiments. For instance, what does “high sample particle number concentration” (L207) mean? Considering the upper limit of your combustion aerosol number concentrations (20000 cm^{-3}; L205) and those used for ammonium sulfate (150 cm^{-3}; L213) and applying a dilution factor of ~10 due to the aerosol-to-sheath flow ratio within SPIN, one still obtains very high number concentrations of around 2000 cm^{-3} for the combustion aerosols and low concentrations for the homogeneous freezing tests. Can such high number concentrations be reliably detected in SPIN? Can you still ensure that there is one INP per ice crystal at these high concentrations? What would happen if you were to use number concentrations of 2000 cm^{-3} for your homogeneous freezing tests?
L230: Please indicate approximate number concentrations for these size-selected CCN measurements. Related to the comment above; can competition of water vapor from high aerosol number concentrations lead to a weak CCN signal? How were multiple-charged particles handled?
L241: Change to: “at seven different wavelengths between 370 nm to 950 nm…”
L243: add space after “<”
L252: do you mean ion number concentrations or ionization rates?
L260: Please specify the type of aging in the OFR. See also my comment above.
L265: Please define “GMD” on L259 and also give GMD for fossil diesel exhaust. In addition, please specify the standard deviations associated with each of the GMD listed.
L268: add space after “250 °C”
L269: How do you know that it is SOA? Combustion exhaust is often also associated with large fractions of hydrocarbon-like organic aerosol (HOA), which can be volatilized. For instance, HOA in engine exhaust is often associated with lubricating oil particles (Canagaratna et al., 2004; Worton et al., 2014); and you note on L149 that your engines was lubricated. Do you have AMS measurement to support your statement?
L272: change to : “SPIN, particles larger than 100 nm represented…”
L272: How does this number relate to the number concentrations listed on L205? See my comment above. I would have expected 10% of 2000 cm^{-3}, so the number you state here seems high.
L273: change to: “from the total sample number concentration.”
L287: Here and elsewhere (e.g. L291), be consistent on referring to your figures, e.g. use “Fig. 3a”.
L289: add space “-41 °C”
L295: “it can be expected that particles with little surface area have passed through the SPIN without any detectable effect.” I interpret your statement that you assume the surface area of the exhaust particles to correlate to their ice nucleation activity. Would it then not be more meaningful to use INAS densities, i.e. normalize to surface area instead of maximum AF? Please also see my main comment above. At the same time, I would like to point out that the recent studies by Nichman et al. (2019) and Mahrt et al. (2018) have identified the ice nucleation mechanism on soot particles as pore condensation and freezing (PCF). More recently the studies by Jantsch and Koop (2021) and Marcolli et al. (2020) have developed detailed frameworks how ice nucleation in complex pores of combustion particles can be modelled/predicted. Can such frameworks also be applied to your particles?
L296: Please see my comment to L195: The description of the error analysis should be expanded.
L301: I suggest to state this a bit more careful here. Homogeneous freezing of what? E.g. water freezes homogeneously below -38 °C, where you start seeing a signal. Could this be an indication that you are actually freezing pore water on your exhaust particles homogeneously, i.e. that ice nucleation takes place via PCF, even though homogeneous freezing rates at these temperatures are low? (see my comment to L295). Maybe a better formulation would be: “higher temperatures compared to the ice nucleation curve of ammonium sulfate.”

L300-305: Where to the authors expect aging mechanisms for combustion exhaust particles as sampled here and how to these aging times compare to typical tropospheric lifetimes of particles emitted by diesel engines?
L309: change to: “within 0.5 °C of the homogeneous freezing reference”
L339: What SOA formation took place in the PAM? Please see my previous comments.
L343: Write as “C_3O_2/C_3”
L339-346: For the discussion of the impact of aging and SOA coating on the ice nucleation activity of combustion aerosol, the authors might want to relate their results to previous work, e.g. Zhang et al. (2020).
L344: To support your statement on the oxidation state here and also your statement on the “extreme hydrophobicity” of the exhaust particles (L337), would it be possible to provide e.g. elemental oxygen-to-carbon and hydrogen-to-carbon ratios of these particles in addition to the fraction of surface oxides listed in Table 2?
L344-346: Is this statement based on the OA/eBC ratios listed in Table 2? If I understand your L253 correctly, the OA values in Table 2 were determine from the AMS measurements. These mass loadings seem extremely high, e.g. 2339 µg m^{-3} for fossil diesel engine-out +PAM. Please comment on the atmospheric relevance of such high mass loadings.
L346-247: The “HVO + engine out” has an OA/eBC ratio of 0.189 according to your Table 2. Do you mean the “RME + engine-out + PAM” instead?
L351: I suggest to explicitly repeat your T and RH conditions here again.
L353: “and we conclude…” this statement should be phrased more carefully and constrained to the experimental conditions studied here, as other studies have demonstrated that combustion particles can form ice at e.g. cirrus temperatures.
L354: delete “complete”
L356: should be phrased more carefully, e.g. “increase the IN activity of particles emitted from fossil diesel combustion…”
L359-360: “With these…”; see my comment to L353.
L361: I suggest to quantify “ultrafine” here in the conclusions again, i.e. give the values in parenthesis.
L362: What do you mean with “to an extent”? Please be more specific in your conclusion section.
L363: replace “production” by “signal”
L365: “slight potential as active INPs”; I suggest to tune this statement down. In the end your observed heterogeneous ice nucleation activity is extremely weak and in the atmosphere such combustion particles will not be able to compete with more efficient INPs such as e.g. mineral dust.

Fig. 2:

Panel 2a:

- Comparing the “engine-out + PAM” with the “engine-out + PAM + TD” it appears that your exhaust particles are associated with a large fraction of semi-volatile material. How do you ensure that this material is not list in the additional dilution stage upstream of SPIN (see your Fig. 1)?
- Comparing the “engine-out” and the “DOC” curves, does the difference in the signal mean that all particles smaller than approximately 40 nm are not soot but volatile material?

Panel 2b:

- Please add “engine-out curve”

Panel 2c:

- Why is there an increase at d < 20 nm for the black line, as the red curves in panels a and b suggest that DOC removes most of the particles in this size range?

Fig. 4:

- Error bars for red and blue curves in panel b are missing; please add.

Fig. 5:

- Why are only error bars for the green curve shown in panel b?

Table 1

- Change “Fraction” to “Percentage”.

Adams, M. P., Tarn, M. D., Sanchez-Marroquin, A., Porter, G. C. E., O'Sullivan, D., Harrison, A. D., Cui, Z., Vergara-Temprado, J., Carotenuto, F., Holden, M. A., Daily, M. I., Whale, T. F., Sikora, S. N. F., Burke, I. T., Shim, J.-U., McQuaid, J. B., and Murray, B. J.: A Major Combustion Aerosol Event Had a Negligible Impact on the Atmospheric Ice-Nucleating Particle Population, 125, e2020JD032938, https://doi.org/10.1029/2020JD032938, 2020.

Bové, H., Bongaerts, E., Slenders, E., Bijnens, E. M., Saenen, N. D., Gyselaers, W., Eyken, P. V., Plusquin, M., Roeffaers, M. B. J., Ameloot, M., and Nawrot, T. S.: Ambient black carbon particles reach the fetal side of human placenta, Nat Commun, 10, 1–7, https://doi.org/10.1038/s41467-019-11654-3, 2019.

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R.: Chase Studies of Particulate Emissions from in-use New York City Vehicles, 38, 555–573, https://doi.org/10.1080/02786820490465504, 2004.

Ikhenazene, R., Pirim, C., Noble, J. A., Irimiea, C., Carpentier, Y., Ortega, I. K., Ouf, F.-X., Focsa, C., and Chazallon, B.: Ice Nucleation Activities of Carbon-Bearing Materials in Deposition Mode: From Graphite to Airplane Soot Surrogates, J. Phys. Chem. C, 124, 489–503, https://doi.org/10.1021/acs.jpcc.9b08715, 2020.

Jantsch, E. and Koop, T.: Cloud Activation via Formation of Water and Ice on Various Types of Porous Aerosol Particles, ACS Earth Space Chem., https://doi.org/10.1021/acsearthspacechem.0c00330, 2021.

Korolev, A., McFarquhar, G., Field, P. R., Franklin, C., Lawson, P., Wang, Z., Williams, E., Abel, S. J., Axisa, D., Borrmann, S., Crosier, J., Fugal, J., Krämer, M., Lohmann, U., Schlenczek, O., Schnaiter, M., and Wendisch, M.: Mixed-Phase Clouds: Progress and Challenges, 58, 5.1-5.50, https://doi.org/10.1175/amsmonographs-d-17-0001.1, 2017.

Kreidenweis, S. M., Petters, M., and Lohmann, U.: 100 Years of Progress in Cloud Physics, Aerosols, and Aerosol Chemistry Research, 59, 11.1-11.72, https://doi.org/10.1175/amsmonographs-d-18-0024.1, 2018.

Lohmann, U., Lüönd, F., and Mahrt, F.: An Introduction to Clouds: From the Microscale to Climate, 1st edition., Cambridge University Press, Cambridge, https://doi.org/10.1017/CBO9781139087513, 2016.

Mahrt, F., Marcolli, C., David, R. O., Grönquist, P., Barthazy Meier, E. J., Lohmann, U., and Kanji, Z. A.: Ice nucleation abilities of soot particles determined with the Horizontal Ice Nucleation Chamber, Atmos. Chem. Phys., 18, 13363–13392, https://doi.org/10.5194/acp-18-13363-2018, 2018.

Mahrt, F., Alpert, P. A., Dou, J., Grönquist, P., Arroyo, P. C., Ammann, M., Lohmann, U., and Kanji, Z. A.: Aging induced changes in ice nucleation activity of combustion aerosol as determined by near edge X-ray absorption fine structure (NEXAFS) spectroscopy, Environ. Sci.: Processes Impacts, https://doi.org/10.1039/C9EM00525K, 2020.

Marcolli, C., Mahrt, F., and Kärcher, B.: Soot-PCF: Pore condensation and freezing framework for soot aggregates, 1–68, https://doi.org/10.5194/acp-2020-1134, 2020.

Murray, B. J., O'Sullivan, D., Atkinson, J. D., and Webb, M. E.: Ice nucleation by particles immersed in supercooled cloud droplets, 41, 6519–6554, https://doi.org/10.1039/C2CS35200A, 2012.

Nichman, L., Wolf, M., Davidovits, P., Onasch, T. B., Zhang, Y., Worsnop, D. R., Bhandari, J., Mazzoleni, C., and Cziczo, D. J.: Laboratory study of the heterogeneous ice nucleation on black-carbon-containing aerosol, 19, 12175–12194, https://doi.org/10.5194/acp-19-12175-2019, 2019.

Rogers, R. R. and Yau, M. K.: A short course in cloud physics, Pergamon Press, Oxford; New York, 1989.

Schill, G. P., Jathar, S. H., Kodros, J. K., Levin, E. J. T., Galang, A. M., Friedman, B., Link, M. F., Farmer, D. K., Pierce, J. R., Kreidenweis, S. M., and DeMott, P. J.: Ice-nucleating particle emissions from photochemically aged diesel and biodiesel exhaust, Geophys Res Lett, 43, 5524–5531, https://doi.org/10.1002/2016gl069529, 2016.

Schill, G. P., DeMott, P. J., Emerson, E. W., Rauker, A. M. C., Kodros, J. K., Suski, K. J., Hill, T. C. J., Levin, E. J. T., Pierce, J. R., Farmer, D. K., and Kreidenweis, S. M.: The contribution of black carbon to global ice nucleating particle concentrations relevant to mixed-phase clouds, PNAS, https://doi.org/10.1073/pnas.2001674117, 2020.

Thomson, E. S., Weber, D., Bingemer, H. G., Tuomi, J., Ebert, M., and Pettersson, J. B. C.: Intensification of ice nucleation observed in ocean ship emissions, 8, 1111, https://doi.org/10.1038/s41598-018-19297-y, 2018.

Vergara-Temprado, J., Holden, M. A., Orton, T. R., O'Sullivan, D., Umo, N. S., Browse, J., Reddington, C., Baeza-Romero, M. T., Jones, J. M., Lea-Langton, A., Williams, A., Carslaw, K. S., and Murray, B. J.: Is Black Carbon an Unimportant Ice-Nucleating Particle in Mixed-Phase Clouds?, 123, 4273–4283, https://doi.org/10.1002/2017JD027831, 2018.

Worton, D. R., Isaacman, G., Gentner, D. R., Dallmann, T. R., Chan, A. W. H., Ruehl, C., Kirchstetter, T. W., Wilson, K. R., Harley, R. A., and Goldstein, A. H.: Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles, Environ. Sci. Technol., 48, 3698–3706, https://doi.org/10.1021/es405375j, 2014.

Zhang, C., Zhang, Y., Wolf, M. J., Nichman, L., Shen, C., Onasch, T. B., Chen, L., and Cziczo, D. J.: The effects of morphology, mobility size, and secondary organic aerosol (SOA) material coating on the ice nucleation activity of black carbon in the cirrus regime, 20, 13957–13984, https://doi.org/10.5194/acp-20-13957-2020, 2020.