

We thank Referee #2 for his or her comments and constructive suggestions on how to improve the contents of the manuscript. The comments as posted are listed below on green font, our responses to them on red font and the specified modifications to the text on blue font.

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, presumably 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.

We have re-analyzed all SPIN data, and we have identified an ‘artifact’ in the data processing. Whenever the SPIN OPC counts per second exceed a certain threshold, then the SPIN data is stored in a slightly different manner, which is very simple to correct for. That correction was unfortunately not carried out for the ice-activated fractions (AFs) presented in figures 3 to 6 in the previous version of the manuscript. The correct AFs may be up to about 1 order of magnitude higher than what was previously presented for the very lowest temperatures around -41°C, while the differences in the AFs were relatively smaller or insignificant for temperatures above -39°C. Generally, these corrections do not affect the main findings of little to no indications of heterogeneous immersion freezing. Previously, we interpreted the pronounced low AF levels for several diesel samples near $T=-41$ °C relative to the homogeneous freezing reference to be due to small and/or very hydrophobic diesel particles not activating into cloud droplets with the potential for subsequent immersion freezing inside SPIN. For that reason, we found that there was a risk of misinterpreting low AFs as a result of low immersion freezing ice-nucleating ability – rather than an effect of very low CCN activity. That was the motivation for the AF scaling carried out in the previous version. With the

correctly analysed AFs, there are still indications of low CCN activity influencing the AFs but to a significantly less pronounced level. We still think that it is of relevance to consider how very high concentrations of nucleation mode particles and/or very hydrophobic seed particles may bias the immersion freezing AF low by contributing to the total particle concentration while not acting as CCN/INPs. However, we no longer consider it a risk that the 'raw' AFs can be misinterpreted in this context, so we have decided not to carry out the AF scaling and the figures 3.b to 6.b do not appear in the revised version of the manuscript. As a consequence of the revisions described above, the paragraphs in L215-225 and L273-282 have been deleted, and the merging of these two paragraphs is no longer of relevance.

For the comment concerning usage of INAS density normalization: we agree on this and have added the suggested calculation method (formulation and results) to Supplement S1. Moreover, the figures mentioned in the comments have been revised.

- Figs. 3-6: For consistency the y-axis labels should be " α " and "Normalized α " for panels a and b, respectively.

We have omitted the "Normalized α " from the revised manuscript, but we have kept 'Ice-activated fraction' as y-axis labels in the revised figures. Figures should appear as readable as possible, so in this case we do not see a need to introduce an abbreviation in labels.

Minor, specific and technical comments:

L27: change to "the energy budget of the"

Following the recommendations by all referees, the text has been changed from:

"Atmospheric aerosols affect the radiative forcing budget of the Earth and thus climate in multiple different ways, directly through absorption/scattering of radiation and indirectly through impacts on cloud properties."

to:

"Atmospheric aerosols affect the energy budget of the Earth and thus climate in different ways: directly through absorption and scattering of heat and light, respectively, and indirectly via affecting cloud formation and lifetime."

L30 add Kreidenweis et al. (2018)

Done.

L32: add „within them via immersion freezing (Murray et al., 2012)."

Done.

L33: replace reference by Korolev et al. (2017)

Done.

L33: "Furthermore...", this sentence seems a bit unconnected to the topic of immersion freezing and MPC, consider rephrasing.

We have deleted the statement and the reference from the revised text.

L36: add Lohmann et al. (2016)

Done.

L39: „ice nucleation“, here and elsewhere, e.g. L45.

Corrected throughout the text.

L39: add: “Particles that are ice-active at temperatures above...”

Done.

L41: change to: “fuels can act as..”

Done.

L42-44: Should also include Ikhenazene et al. (2020), Thomson et al. (2018)

References added.

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)

All the suggested studies were on deposition freezing. Similar studies associated with immersion freezing are scarce.

The statement has been changed from:

“In most of those past ice-nucleation studies of soot particles, little if any information about the aerosol particle properties is provided.”

to:

“In most of those past immersion freezing ice nucleation studies of soot particles dating back to pre-2010s, little if any information about the aerosol particle properties is provided.”

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).

The statement has been changed from:

“In most of those past ice-nucleation studies of soot particles, little if any information about the aerosol particle properties is provided.”

to:

“In most of those past immersion freezing ice nucleation studies of soot particles dating back to pre-2010s, little if any information about the aerosol particle properties is provided.”

L50: Delete reference to Mahrt et al. (2018) and instead consider adding: Mahrt et al. (2020)

Done and reference added. Following the suggestion by Referee #2, also added another study by Mahrt et al. (2020).

L59: Add space after “m-2”

Done.

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.

We agree with the suggestion and have moved the information about fuels to Sect 2.1. In addition to that, we have made the paragraph more concise and put the focus on 1) the atmospheric relevance of diesel emissions and 2) the motivation for ice nucleation studies, such as this one.

L68: Please add a brief description here (or where appropriate) what the diesel oxidation catalyst (DOC) does to the exhaust particles in your setup.

We agree about this and have added the following statement in Sect. 2.1 where the aftertreatment system combinations are described:

“Using the DOC reduces engine emissions via completing the oxidation of particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) components from exhaust gas (Russell and Epling, 2011).”

L77: consider adding Bove et al. (2019)

Reference added.

L93: What do you mean by “was added in the aging phase”? Were the particles coated with SOA?

Yes. Please see our response to your comment on L269 where we discuss the OA formation due to photochemical aging of the particles.

L97: What do you mean by “where aging played an important role”? Was the ice nucleation activity enhanced or decreased?

The text has been changed from:

“Kulkarni et al. (2016) studied the deposition freezing ice nucleating potential at temperatures from -50 to -40 °C of fresh and aged diesel engine emissions and they reported heterogeneous freezing in many cases, where particle aging played an important role.”

to:

“Kulkarni et al. (2016) studied the deposition freezing ice nucleating potential at temperatures from -50 to -40 °C of fresh and aged diesel engine emissions and they reported heterogeneous freezing in many cases, and found that humidification of organic-coated (aged) soot particles increased their ice nucleating abilities.”

L107: Change to “ability down to temperatures where homogeneous freezing starts to dominate.”

Done.

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.

Please see our response to the comment below.

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.

The following details about the aging and simulated atmospheric dilution phase in this study have been added to the text:

“The aerosol was diluted ~100 times upstream the PAM and the TD. It should be pointed out that just as upon atmospheric dilution after the tailpipe, a fraction of the primary organic aerosol will evaporate as the aerosol is progressively diluted towards atmospherically relevant concentrations. Furthermore, the OA formed will partition depending on OA loadings: high concentration favors particle phase partitioning. The OA concentration in the PAM chamber ranged from 0.2-25 $\mu\text{g}/\text{m}^3$, atmospherically relevant concentrations. The PAM reactor used in this study consisted of a 13 L steel chamber containing two Hg lamps with peak intensities at 185 and 254 nm. The UV light generates ozone and hydroxyl radicals (OH) that oxidize the aerosol as it moves through the chamber. The flow rate through the PAM was controlled to 5–7 L min^{-1} . The same UV light intensity was used in all experiments. During the experiments involving the PAM, the OH concentrations varied between 3.2×10^{11} – 1.3×10^{12} molecules cm^{-3} s, resulting in corresponding atmospheric aging between 2.5-9.9 days, when an average OH concentration of 1.5×10^6 molecules cm^{-3} (Mao et al., 2009) was assumed. Extensive SOA formation occurred in the PAM in all engine-out experiments, while less SOA was formed in measurements after the DOC. The thermodenuder (Aerodyne Inc.,) was held at 250 °C in all experiments where it was used.”

A discussion about the coating of particles has been added in the manuscript. Please see our response to comment on L339 below.

The following text has been added:

“It should be pointed out that just as upon atmospheric dilution after the tailpipe, a fraction of the primary organic aerosol will evaporate as the aerosol is progressively diluted towards atmospherically relevant concentrations. Furthermore, the OA formed will partition depending on OA loadings: high concentration favors particle phase partitioning. The OA concentration in the PAM chamber ranged from 0.2-25 $\mu\text{g m}^{-3}$, which are atmospherically relevant mass concentrations”

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).

Done.

L138: What physical particle properties are derived from the AMS data?

The text has been changed from:

“A soot particle aerosol mass spectrometer (SP-AMS, Aerodyne inc.) was used for physicochemical analysis of the exhaust particles.”

to:

“A soot particle aerosol mass spectrometer (SP-AMS, Aerodyne Inc.) was used for chemical analysis of the exhaust particles.”

L157: change to: “at a flow”

Done.

L161: change to: “as the aerosol-lamina”

Done.

L163: “whose temperature corresponded to the average aerosol-lamina temperature”

Done.

L170: change to: “allowed lower detection limit...”

Done.

L171: “sample”. Do you mean aerosol number concentration here?

Yes, we do. We have changed the term to ‘sample aerosol number concentrations’ in the revised text.

L174: change to: “done using T-scans at constant...”

Done.

L181: Please quantify aerosol residence time in evaporation section.

Done. The text has been changed from:

“The co-existence of droplets and ice is due to the evaporation section of the SPIN, which is less efficient than for most other CFDCs (Garimella et al., 2017).”

to:

“The co-existence of droplets and ice is due to the evaporation section of the SPIN, which is less efficient than in most other CFDCs due to insufficient residence time of approximately 2 seconds (Garimella et al., 2017).”

L183: replace “in the IN chamber” by “CFDC”

Done.

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).

The previously applied ice size threshold of 6 μm would ensure that no droplets would contribute to the ice counts for the temperature range up to -32°C . The size of the droplet mode after the evaporation section decreases with decreasing sample temperature (Korhonen et al., 2020) in part because the evaporation section turns more efficient at lower temperatures. Since, we do not observe any indications of ice formation for temperatures above -36°C , it allows us to apply a lower ice size threshold of 4 μm without liquid droplets contributing to detection of ice crystals. This correction has been performed in the re-analysis of all ice activated fractions presented in the figures 3-6. For the homogeneous freezing reference, there is only a modest difference between applying a threshold of 4 μm versus 6 μm (a factor between 1.3 and 1.7). Differences in the ice-activated fractions from applying an ice size threshold of 4 μm versus 6 μm would typically correspond to factors of about 1.5 to about 5 in the inferred ice-activated fractions for the diesel exhaust samples. Hence, for some of the studied samples, a significant fraction of the ice crystals may appear in the size range from 4 μm to 6 μm . We cannot rule out that ice crystals potentially can be present at sizes below 4 μm . Unfortunately, we do not have a simple way to quantify that whenever ice crystal counts above the ice size threshold are low as typically observed for average lamina temperatures above -38.5°C to -38.0°C . For lower temperatures when ice crystal size modes can be identified in the OPC data, they are in many cases centered around sizes well above 4 μm . However, in some cases, significant and varying fractions of the ice crystal mode appears to be present at sizes below 4 μm overlapping with the size range where liquid droplets may be present. Hence, the maxima in ice-activated fractions observed for temperatures around -41°C may to some extent be biased low due to (i) ice crystals being present at sizes below 4 μm , and (ii) due to only a fraction of the sample being focused in the lamina. It is unclear to which extent those two effects may be coupled – in the sense that the very smallest ice crystals potentially may be associated with particles present outside the lamina. Further detailed studies are needed for such assessments.

L190: Delete “the IN chamber of the”

Done.

L192: Change to: “counts measured during... from the OPC signal. The background values between...”

Done.

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.

The calculations of random errors follow standard approaches described in basic textbooks. Hence, we do not see a need to document all such very basic and simple steps in a scientific publication. We have included a reference to the textbook: ‘Taylor: An introduction to Error analysis’ in the lines 196 and 197. As we state in this context in L. 197-199, it is important to keep in mind that the random

error only relates to counting statistics and not any potential biases (systematic errors). The biases in CFDC measurements are known to be pronounced though not well-constrained (Garimella et al., 2017).

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?

The study by Levin et al. (2016) is, to our knowledge, the only one where the potential effect of water vapor depletion inside a CFDC is studied in detail. Their empirical results are not comparable to our experiments, and their modeling is carried out for other operation conditions (a lamina temperature of -30°C and a nominal supersaturation of 5% with respect to liquid water). Their modeling results indicate that minor water vapor depletion may occur when particle number concentrations in the lamina reach levels somewhere between 10³ and 10⁴ cm⁻³, or potentially for higher concentrations depending on the accommodation coefficient used in their model. Hence, it is not straightforward to report anything quantitatively on the potential effect of water vapor depletion in our study, based on the results reported by Levin et al. (2016). This is further complicated by the following fact: It is obvious that potential water vapor depletion inside a CFDC will not depend on the sample number concentration alone, it will depend on the fraction of the particle number concentration focused in the lamina, which serves as cloud condensation nuclei and/or INPs. In other words, very hydrophobic and/or particles too small to serve as neither CCN nor INPs will not play a role in this context. For clarification we have modified L 204-209 from:

“The sampled particle number concentration was diluted to 5000 to 20000 cm⁻³ before introduction to the SPIN (marked ‘dilution’ in Fig. 1), depending on sample treatment; higher number concentrations were used in experiments involving the PAM with extensive formation of new relatively small secondary aerosol particles. It is known that too high sample particle number concentrations may lead to depletion of water vapor inside a CFDC (Levin et al., 2016), while too low number concentrations reduce the measurement sensitivity.”

to:

“The sampled particle number concentration was diluted to 2000-20000 cm⁻³ before introduction to the SPIN (marked ‘dilution’ in Fig. 1), depending on sample treatment; higher number concentrations were used in experiments involving the PAM with extensive formation of new relatively small secondary aerosol particles. It is known that too high sample particle number concentrations may lead to depletion of water vapor inside a CFDC (Levin et al., 2016), while too low number concentrations reduce the measurement sensitivity. We cannot rule out that the

effective water saturation inside the lamina could have been biased slightly low when the highest particle number concentrations were studied (Levin et al., 2016). However, only a fraction of the studied particles was focused within the lamina, and only a fraction of the particles focused in the lamina was likely to activate into cloud droplets due to small sizes and/or hydrophobicity. Hence, it is unlikely that cloud droplet concentrations inside SPIN exceeded 10000 cm^{-3} , for which minor water vapor depletion may occur for slightly different CFDC operation conditions (Levin et al., 2016)."

The number concentrations detected with the SPIN OPC are substantially lower than the sample concentrations detected with the CPC. We have no reason to expect that the SPIN OPC got 'saturated' to a level where the results were significantly biased, at least not for average lamina temperatures above -38°C , where concentrations of super-micron particles were limited. Also, for lower temperatures, we do not observe substantial differences in the ice-activated fractions between samples with concentrations at the order of 200 cm^{-3} over 2000 cm^{-3} , to $20\,000 \text{ cm}^{-3}$.

Considering the very low number concentrations of INPs active at temperatures well above -38°C , we consider it unlikely that more than one INP was present inside ice crystals formed at those temperatures. Ice forming at lower temperatures may be due to homogeneous freezing.

We did not test varying particle number concentrations for the homogeneous freezing experiments. A larger sample number concentration should improve the signal to noise ratio allowing for reliable detection of smaller ice-activated fractions, ranging about an order of magnitude lower in the suggested case. Apart from that, we have no reason to expect any other substantial effects from applying a sample number concentration at the order of 2000 cm^{-3} instead of 150 cm^{-3} .

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?

The CCN concentrations varied substantially between experiments and selected mobility diameter. When CCN concentrations inside the CCN counter approach 5000 cm^{-3} , then a minor bias ($\sim 10\%$) is likely to occur due to depletion of water vapour (Latham and Nenes, 2011). The CCN number concentrations never exceeded 1000 cm^{-3} in our experiments, so there is no reason to assume that depletion of water vapor influenced our CCN results.

The following statement has been added to L230:

"The CCN number concentrations never exceeded 1000 cm^{-3} in these experiments."

The influence from the multiply charged CCN population was identified from the level of the lower plateau in the CCN spectra (Rose et al., 2008). We applied a standard procedure.

L241: Change to: "at seven different wavelengths between 370 nm to 950 nm..."

Done.

L243: add space after "<"

Done.

L252: do you mean ion number concentrations or ionization rates?

We mean ionization rates, expression corrected.

L260: Please specify the type of aging in the OFR. See also my comment above.

Please see our response to your comment on L269 below.

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.

We have added definitions for both GMD and GSD, and added the GMD and GSD for all fuels.

L268: add space after "250 °C"

Done.

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?

We know that it is secondary PM as it forms upon processing of exhaust in the PAM reactor. That is to say, engaging the reactor increases the mass concentration several-fold (referred to as "OA enhancement" in the revised manuscript (please see lines 355-370 in the revised version), consistent with oxidation of gas phase precursors that form lower vapor pressure products which condense. The mass spectra show this material is organic, hence we conclude that it is SOA. Indeed the mass spectra of the unprocessed exhaust particles do resemble "hydrocarbon-like organic aerosol" (HOA) while the processed OA resembles "Oxidized Organic Aerosol" (OOA) as observed in numerous field and laboratory AMS experiments. Please see figure 1 below.

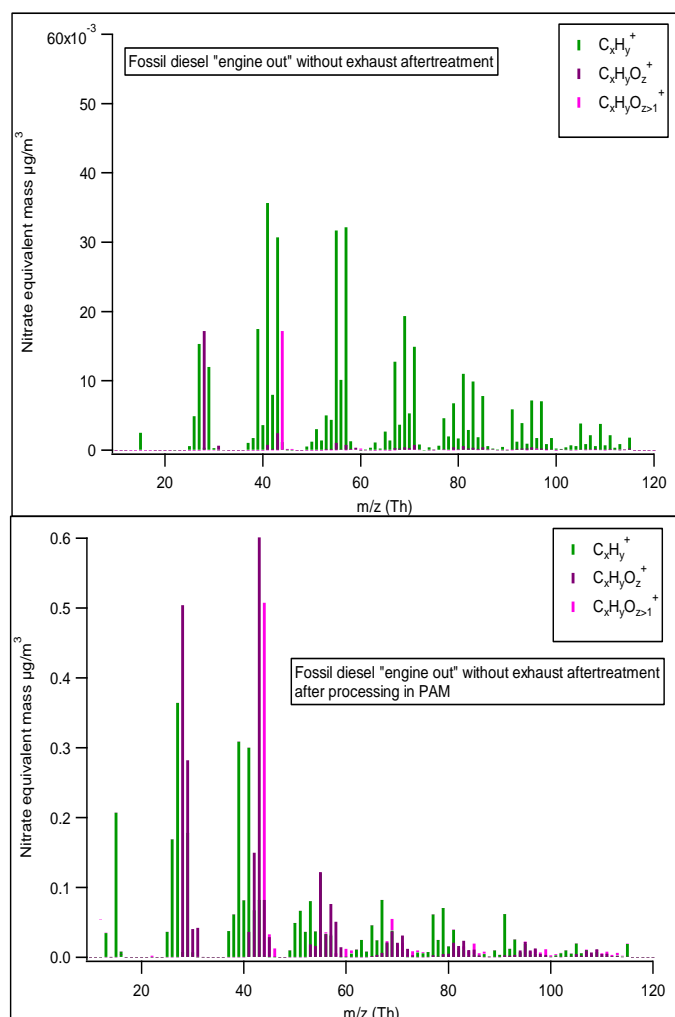


Figure 1: The effect of PAM treatment on exhaust organic aerosol mass spectra. N.B. the change in y-axis (OA is more abundant after PAM) and the transition from hydrocarbon to oxygen containing peaks.

The text on L273 has been changed from:

“Thermodenuder treatment (250°C) removed a significant fraction of the SOA emissions.”

to:

“Thermodenuder treatment (250°C) removed a significant fraction of the OA emissions for both fresh and aged aerosol.”

Lube oil and HOA are discussed below on the comment at L344.

L272: change to: “SPIN, particles larger than 100 nm represented...”

Done.

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.

We agree that the highest estimate (in one case) is not the most representative indicator of the number concentrations of large particles. The text has been changed from:

“Regarding the high sample concentrations introduced to the SPIN, the particles larger than 100 nm represented number concentrations up to approximately 1200 cm^{-3} , implying a reasonable detection sensitivity.”

to:

“Regarding the high sample concentrations introduced to the SPIN, the particles larger than 100 nm represented number concentrations above 50 cm^{-3} , thus implying a reasonable detection sensitivity.”

L273: change to: “from the total sample number concentration.”

Done.

L287: Here and elsewhere (e.g. L291), be consistent on referring to your figures, e.g. use “Fig. 3a”.

Done. The references to all figures with two or more panels are now of form e.g. “Fig. 3a”.

L289: add space “-41 °C”

Done.

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?

Mahrt et al. (2018) and Nichman et al. (2019) studied deposition freezing. In our study, we operate the CFDC with conditions of relevance to condensation or immersion freezing. Hence, do not expect the reported mechanisms to be of direct relevance to our study. That said, it would of course be possible to investigate the studied soot particles with respect to properties potentially of relevance to deposition freezing.

When it comes to reporting our ice nucleation results, we agree with the reviewer that normalization to particle surface area would be the ideal approach. However, there are a few challenges associated with such an approach. Firstly, we did not measure the particle surface area, and secondly, several not well-constrained systematic errors will have to be corrected for in the calculation. Both issues add to rather substantial errors associated with the INAS density. However, we provide the best possible INAS density results in the supplementary based on the assumption of spherical particles.

L296: Please see my comment to L195: The description of the error analysis should be expanded.

Please see our response above.

L301: I suggest to state this a bit more careful here. Homogeneous freezing of what? E.g. water freezes homogeneously below $-38\text{ }^{\circ}\text{C}$, 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.”

As described in detail before, the reference based on ammonium sulfate seeds represents the homogeneous freezing of super-micron sized dilute aqueous droplets, for which the freezing temperature may be biased slightly low by less than 0.1 K relative to that for pure water droplets. The homogeneous freezing temperature of aqueous solution droplets increases with increasing droplet size, so we find no reason to expect that significantly smaller volumes of liquid water associated with the combustion particles could freeze homogeneously at temperatures higher than what we observe for our homogeneous freezing reference. Hence, if pores in the soot particles somehow facilitate freezing at temperatures well above the homogeneous freezing reference, then we would consider that heterogeneous freezing.

L300-305: Where do the authors expect aging mechanisms for combustion exhaust particles as sampled here and how do these aging times compare to typical tropospheric lifetimes of particles emitted by diesel engines?

Aging processes are likely to influence soot particle properties in most environments at most times. The respective impacts of various aging processes are likely to depend on parameters such as the actinic flux, available oxidants, condensable vapors, and the relative humidity. Those parameters are to some extent co-varying, but they vary substantially spatially and temporally worldwide. It is outside the scope of this study to go into detail with such complex atmospheric variability. However, it is evident that significant atmospheric aging of soot particles occurs over time scales of a couple to a few hours under various atmospheric conditions (e.g. Riemer et al., 2004; Moffet and Prather, 2009; Eriksson et al., 2017). Hence, it is highly likely that atmospheric aging would influence properties of most soot particles emitted near ground level before they potentially would be transported to mixed-phase cloud levels. Hence, it is clearly of relevance to study whether aging processes influence the ice nucleating ability of soot particles. We studied the effect of simulated intense photochemical aging in a diesel exhaust ‘atmosphere’, and we only observed modest changes in the ice nucleating ability. However, that does not rule out that other atmospheric aging processes could be of importance in this context.

In the experiments, we applied relatively high levels of photochemical exposure to age the particles in order to observe potential effects on the ice nucleating ability. In other words, we intended to study how significantly different particle properties potentially could be of relevance to ice nucleation properties. Directly linking the applied particle processing to atmospheric processing is not something we can justify doing. Nevertheless, since atmospheric aging of soot particles potentially occurs within a couple of hours, it is most likely so, that if diesel particles emitted near the ground level act as INPs in the atmosphere – then they have in many cases likely underwent atmospheric aging before reaching the cloud base.

L309: change to: “within $0.5\text{ }^{\circ}\text{C}$ of the homogeneous freezing reference”

Done.

L339: What SOA formation took place in the PAM? Please see my previous comments.

Please see our response to your comment on L269.

L343: Write as “C3O2/C3”

Done.

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).

We acknowledge that this was too briefly described. The following text has been added:

“In the engine-out experiments, very strong SOA formation was obtained upon aging in the PAM. The OA enhancement (Processed OA/Fresh OA) was of a factor of ~ 20 for diesel and ~ 7 for RME. After the DOC the OA enhancement was substantially lower (~ 2 for both HVO and fossil diesel). The exhaust from fossil diesel combustion after simulated atmospheric aging and without emission aftertreatment was dominated by secondary organic mass (OA/eBC = 3.4). All experiments except aged fossil diesel and aged HVO at engine-out conditions provided eBC-dominated emissions. Substantial SOA production that led to increased OA/eBC ratios also occurred for RME at engine out and to a lesser extent HVO after the DOC. As shown by Gren et al. (2021), a majority of the formed SOA condensed on the nucleation mode particles and only a minor fraction ended up in the soot mode. This can be related to the engine type and operating conditions that led to relatively low soot emissions, typical for modern engines. The measurements of particle mass of mobility classified particles with the DMA-APM demonstrated a small but significant increase in effective density of soot particles at both 200 nm and 300 nm upon aging (sizes where the soot mode was completely dominating the size distribution without contribution from the nucleation mode). This is consistent with minor SOA uptake on the aged soot particles. However, it cannot be concluded if the SOA was evenly distributed as a thin coating on the primary particles in the soot aggregates or if it is unevenly distributed for example in the pores between the primary particles.”

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?

We acknowledge that the statement on the oxidation state was too brief. We have clarified that this refers to refractory surface oxides in the soot cores measured in the SP-AMS (laser on) mode. At present these measurements are not quantitative. We add a sentence and a reference discussing how these surface oxides may form during combustion. We also suspect that the reviewer refers to O:C and H:C ratios of the OA (coating) that can readily be quantified in the regular AMS mode. We have added example values for these and discuss the contribution OA may give to the surface properties of soot. We consider that adding the elemental oxygen-to-carbon and hydrogen-to-carbon ratios to Table 2 would include large uncertainties in many of the cases, due to the low mass loadings sampled (and short time).

The following text has been added:

“This is expected as modern diesel engines achieve low BC emissions by highly efficient late cycle soot removal by oxidation by OH radicals (Malmberg et al. 2017). However, the true surface of the mixed particles may also be affected by the organic aerosol. The mass spectra of OA in fresh emissions showed similarities with past experiments where it has been linked to lube oil (Worton et al. 2014). The O:C ratio and H:C ratios of OA measured in the conventional laser off AMS mode was X and Y for typical cases of fresh and aged aerosol respectively.”

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 determined from the AMS measurements. These mass loadings seem extremely high, e.g. 2339 $\mu\text{g m}^{-3}$ for fossil diesel engine-out +PAM. Please comment on the atmospheric relevance of such high mass loadings.

The reported concentrations are dilution adjusted (500-900 times dilution) to allow direct comparison between experiments as dilution ratios varied slightly between each experiment. A note about this has been added in the table heading. The concentrations measured with the AMS were thus low and corresponding to typical atmospheric conditions.

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?

We have revised the discussion on emission particle properties, and this statement has been removed from the revised text. A more detailed analysis on the results is provided instead.

L351: I suggest to explicitly repeat your T and RH conditions here again.

We agree and have added the scanned T-RH range to the statement. The text has been changed from:

“at temperatures relevant to MPC conditions”

to:

“at temperatures relevant to MPC conditions ($RH_{\text{water}} = 110\%$, $-32\text{ }^{\circ}\text{C} > T > -43\text{ }^{\circ}\text{C}$).”

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.

We agree that the formulation may mislead the reader and have corrected it as follows. The text has been changed from:

“and we conclude that the studied diesel emission particles are poor INPs in general.”

to:

“and we conclude that the diesel emission particles studied using our setup were poor INPs in MPC-relevant temperature range.”

L354: delete “complete”

Done.

L356: should be phrased more carefully, e.g. “increase the IN activity of particles emitted from fossil diesel combustion...”

Corrected as suggested.

L359-360: “With these...”; see my comment to L353.

The statement has been changed from:

“With these observations altogether, it can be implied that the emissions from the studied diesel fuels produce no significant number concentrations of INPs to the atmosphere.”

to:

“With these observations altogether, it can be implied that the emission particles from the studied diesel fuels produce no significant number concentrations of active INPs at temperatures above homogeneous freezing. However, the particles can still act as IN in cirrus regime.”

L361: I suggest to quantify “ultrafine” here in the conclusions again, i.e. give the values in parenthesis.

Done. Size range (<100 nm in electrical mobility) is now given in parentheses.

L362: What do you mean with “to an extent”? Please be more specific in your conclusion section.

We agree that the statement was ambiguous and therefore, we have omitted it from the revised text.

L363: replace “production” by “signal”

Done.

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.

Statement tuned down as suggested. The text has been changed from:

“The only exception to this was for the HVO fuel whose emissions may have a slight potential as active INPs.”

to:

“The only exception to this was for the HVO fuel whose particle emissions showed slightly elevated, yet still weak INP activity.”

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 lost in the additional dilution stage upstream of SPIN (see your Fig. 1)?

We assume that the referee means lost, instead of “lost” as written in the comment. The additional dilution stage, just upstream of the SPIN, was a simple dilutor loop where a part of the sample flow was diverted through a HEPA filter to reduce the sample number concentration. In other words, no external air supply was used in this stage, and no pressure changes took place. This type of dilution should not affect the size distribution.

- 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?

The function of the DOC is to enhance the oxidation of unburnt fuel, hydrocarbons, and carbon monoxide (please see our response to comment on L68). The two latter components are gaseous after exiting the engine, so the particles mentioned in the comment must consist of unburnt fuel. In that sense yes, they are volatile material.

Panel 2b:

- Please add “engine-out curve”

Done.

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?

Regarding that the black curve appears to be unimodal in a similar way than the red curve in panel b, this suggests that there is also a nucleation mode, but it is beyond the size range of the SMPS system. In most other experiments, the nucleation mode occurred at 15 nm which is also close to the low end of this size range.

Fig. 4:

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

Upon revision of the calculation method, the panel b of Figs. 3-6 has been omitted from the revised manuscript. Therefore, this comment is no longer of relevance.

Fig. 5:

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

Upon revision of the calculation method, the panel b of Figs. 3-6 has been omitted from the revised manuscript. Therefore, this comment is no longer of relevance.

Table 1

- Change “Fraction” to “Percentage”.

Done.

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