Response to egusphere-2024-151 reviews for RC2

Referee comments are marked in black bold and are numbered as R1Cx with x the comment number. Author (AC) responses are marked in black directly below the comments. The original text from the manuscript is repeated in blue and corrected text in revised manuscript is typed in red. The former line numbers are given in "()" followed by the new line numbers.

In this study, Testa et al. investigate ice nucleation abilities of aerosols emitted by six different commercial aircraft engines fueled with Jet A-1 and running while on the ground. The authors further subject the aircraft-engine emitted soot aerosols to catalytic stripping and/or cloud chamber processing to simulate contrail clouds conditions and evaluate their impact on the aerosols' ice nucleation activity at temperatures relevant for cirrus formation. The authors investigate the effects of H2SO4 and volatile organic coating, the effect of morphology and compaction of soot aggregates on their ice nucleation ability. The authors conclude that H2SO4 and volatile organic coatings inhibit ice nucleation in preventing PCF to occur and that the compaction observed after "contrail-like processing" remained inefficient at promoting PCF, which makes aircraft-engine emitted unprocessed and processed soot unlikely INPs.

The manuscript is of good quality and the study relevant. However, the manuscript would benefit from a clear assessment of its potential limitations with respect to its representativity of real contrail processing conditions and thus cannot be generalized to the extent expressed in the title. I would therefore recommend this manuscript for publication after this major concern has been addressed, particularly in the experimental section.

We thank the reviewer and answer to the comments/questions individually below.

Some of the comments and questions below can help address this concern.

R2C1: I fell the title is misleading as the aerosols were flown through experimental chambers to simulate contrail processing but only to some extent since the experimental conditions were still far from what would happen in real conditions (e.g., high-altitude temperature, pressure, background gas or aerosols, versus ground). Maybe change to a humbler title?

AR1: We agree with the point raised in the comment. As proposed in the response AR15 to RC1, we propose to modify the title for "Simulated contrail processed aviation soot aerosol are poor ice nucleating particles at cirrus temperatures".

R2C2: Line 40: several engines' models from Pratt&Whitney and CFM international fueled with Jet A-1 were used to produce soot particles. How are these engines representative of the fleet? What about the fuel? Since their ice nucleation response can be different (as shown in this manuscript), it may be relevant to get an idea from the get go. Please specify.

AR2: The engine type and fuel used in this study are representative of the major part of commercial airliner. P&W and CFM International engines represented 68 % of the aircraft engine fleet in 2020 (52 % for CFM engines and 16 % for P&W engines; FlightGlobal.com, 2021). Jet A (largely used in North America) and jet A-1 (used in the rest of the world) fuel represent >60 % and 30 % of global fuel consumption, respectively (Jing et al., 2022; Pires et al., 2018), with Jet A and Jet A-1 having very close chemical composition (Pires et

al., 2018) and presumably results in aviation soot with similar properties. For the generalization of the results to the extent expressed in the paper and in the title, please see the response AR5 to R1C5 for a detailed argumentation.

Proposed text changes are presented below (line 284-293 in the revised manuscript): "Aviation soot samples that were catalytically stripped and contrail processed were able to nucleate ice around 145 % RH_i at 218 K (~7 % lower than RH_{hom}). The modest ice nucleation ability for the CS-CP-soot likely arises from increased cavity number and sizes within the soot aggregates, which would be absent in the unprocessed soot samples coated with organics and sulfate. [...] Thicker coatings for flight altitude aviation soot compared to our CP-soot would favor homogeneous nucleation and thinner coatings would be bound by the ice nucleation ability of our CS-CP-soot sample. Nevertheless, as long as aviation soot is co-emitted with H₂SO₄, it is likely to acquire a coating upon emission and further in the exhaust plume (Kärcher et al., 2007), thus we expect our unprocessed and CP-soot samples to be of higher atmospheric relevance for engines and fuel currently in use."

And lines 303-309 in the revised manuscript: "The number and size of cavities within the soot aggregates are the primary controlling factors of soot ice nucleation via PCF (Sect. 1). The cavity formation is controlled by the primary particle morphology (being determined in the engine combustor and therefore well simulated in our ground setup) and the aggregates size. High overlap of the primary particles has been observed on soot samples for all tested engines. Smaller aggregate size for aviation soot is expected for turbofan engines, hence we believe that the results from our study, that is, aviation soot particles are poor ice nucleating particle for cirrus formation can be generalized to soot emitted with the current aircraft fleet and fuel (Jet A/A-1; > 90 % of global usage; Jing et al., 2022; Pires, 2018)."

R2C3: Line 42: In which medium were the aerosols collected 1m downstream the exhaust nozzle, ambient air and room temperature? Do you expect this difference with real conditions to affect aerosols' properties, if yes how so?

AR3: The engines were fed with air at ambient temperature and humidity. The exhaust was sampled downstream of the engine without injection of air between the exhaust nozzle and the sampling probe, as such, the sample particles are representative of engine exit plane soot particles (response AR2 to R1C2 and AR3 to R1C3). Differences in particle properties could come from the low altitude of soot emission and measurement (ground compared to flight altitude) and are discussed in response AR4 to R1C4.

R2C4: Line 43: the exhaust is directed to an aerosol reservoir; do you expect any change in the aerosols' mixing state in the tank? Is this directly comparable to what happens in real conditions? What is the temperature in the tank? Are the air composition/energy carriers (e.g. UV photons) simulated the same way as in real conditions? This should be discussed so the reader can understand the potential limitations.

AR4: We agree with the comment, the exhaust temperature and the particle sampling in the mixing tank in our setup would influence the soot particles physicochemical properties. The limitation of our setup and expected difference in the sampled soot properties compared to what would be expected for in situ aviation soot particles are discussed in the response AR1.2 to R1C1.2.

Regarding the setup description, we propose the following edits. Lines (39-44) 40-51 now read: "The experimental setup was designed to simulate targeted atmospheric processes and to mimic the contrail processing of the sampled aviation soot particles (Fig. 1a). Limitations of the ground setup in representing

atmospheric processes (e.g., aircraft exhaust evolution, contrail formation) and soot ice nucleation ability are discussed in Sect. 5. Soot particles were sampled from in-use commercial aircraft engines (multiple models from Pratt & Whitney and CFM International) running in an indoor test cell, with air intake at ambient temperature and humidity. The engines were all fueled with Jet A-1 fuel and ran from low to high power (30-100 % sea level thrust). The detailed sampling system is described in Testa et al. (2024) which we briefly describe here. The engine exhaust gas and particles were sampled by a heat-resistant alloy probe ~1 m downstream of the engine exhaust nozzle and directed by a long trace-heated line (12 m at 433 K) to a stirred tank, that was in a room next to the engine test cell and acted as an aerosol reservoir where the soot particles accumulated and coagulated (Fig. 1b). The exhaust temperature drops in three steps, from the engine temperature (thousands of Kelvin) to the heated line temperature (433 K) and then to room temperature followed by a third drop from room temperature to the cloud chamber temperature (< 228 K, see below)".

Line (49-50) 57 now reads: "[...] set to contrail cloud thermodynamic conditions (*T* = 228 K and RH_w = 105 %, HINC1 in Fig. 1b) allowing [...]".

We also made the following changes to the text in response to the comment above. The title of Sect. 5 has been modified for: "5 Atmospheric implications and limitations"

Lines (238) 242-283 in Sect. 5 now read: ""[...] leaving cirrus cloud properties essentially unperturbed. Due to constraints of the measurement facility in this work, the representation of aircraft exhaust processes in the ground set up and hence of the aviation soot properties might differ from those at flight altitude. For instance, differences in equilibrium temperatures and dilution would impact the partitioning of volatile unburned hydrocarbons and sulfur compounds and hence the soot ice nucleation ability. The higher temperatures in our setup (433 K, then room temperature, Sect. 2.1) compared to upper tropospheric temperature (< 228 K; Krämer et al., 2020), would not promote the condensation of volatiles onto soot as much as would occur at flight altitude temperatures. The interaction of nucleation mode particles with aviation soot in the young aircraft plume downstream of the engine is thought to increase the soot coating (Kärcher, 1998; Kärcher et al., 2007; Yu et al., 1999), but does not occur in our ground setup due to the absence of nucleation mode particles. Thus, soot particles in this study are expected to have a lower amount of coating from this effect. On the other hand, total particle surface area was less in our ground setup due to the absence of the nucleation mode particles, and the exhaust gases experience reduced dilution in the aerosol reservoir with synthetic air, compared to the strong dilution that would occur within the first seconds at flight altitudes (Karcher et al., 2007). This effect would enhance the condensation of volatiles onto the soot particles in our ground setup. However, even if lower amounts of organics and sulfate condense onto the soot particles in the atmosphere, these would first condense into the pores of the soot, due to the capillary effect, and thus inhibit ice nucleation of the soot particles. Thus, our conclusions of the poor ice nucleating ability of contrail processed soot would remain the same. Downstream of HINC1, the reemitted soot aggregates get compacted due to contrail processing and their sizes decrease. The formation of large soot aggregates (Petzold et al., 1998, 1999) due to the coagulation between ice crystals and scavenging of interstitial soot aggregates was not possible due to the low concentration of ice crystals and soot and non-turbulent flow in HINC1. Due to the absence of nucleation mode particles, coagulation of these with ice crystals, and coagulation with interstitial soot aggregates was not possible in HINC1. However, the absence of these processes does not change our conclusions as adding more organics onto the soot particles would only further result in poor ice nucleation activity (Gao & Kanji, 2022; Testa et al., 2024). Gas phase chemistry and particle oxidation are thought to considerably slow down while exiting the combustor chamber due to much lower temperatures in the exhaust nozzle and

downstream of the engine (Dakhel et al., 2007; Wong et al., 2008). Such a drop in temperature was also present in our sampling system (thousand degrees to 433 K and to room temperature), thus the primary particle overlap, size, crystallinity, and oxidation should be unaffected and comparable to in situ emitted aviation soot particles.

Summarizing, soot particles in our ground setup were larger and less dense than in situ soot due to coagulation in our aerosol reservoir. We believe the aggregate compaction in this work is atmospherically relevant as the parameters driving the soot compaction, i.e., RH_i experienced by the particles and bulk water condensation were represented in our ground setup. The primary particle properties and oxidation are fixed in the combustor and hence should be representative of their in-situ counterpart. Finally, we expect in situ particles to be coated with H₂SO₄ and organics but to which extent the coating of the aviation soot sample in our study is different from in situ aviation soot cannot be established from our study. For this reason, we quantified the ice nucleation ability of coating free (CS-CP-soot) and coated (unprocessed and CP-soot) soot in our study to constrain the possible effect of different soot mixing states on aviation soot ice nucleation."

R2C5: Line 49-51: how long do the aerosols remain in the first cloud chamber? In the subsaturated flow tube? Do these residence times have an influence?

AR5: The residence times in both cloud chambers and the sublimation flow tube are about 10s each (Testa et al., 2024; Mahrt et al., 2020). Once the soot particles nucleate ice in the first cloud chamber, we do not expect their properties to evolve with time (slow molecular diffusion within the ice phase). In the sublimation flow tube, we could envision that longer residence time could allow the volatile material coating the soot particles to further partition in the gas phase, changing the soot mixing state. The effect of aviation soot mixing state in the ability of aviation soot to reactivate as ice crystal in cirrus have been investigated in this study and in the companion study by catalytically stripping the particles.

R2C6: Line 64: what is the efficiency of the catalytic stripper, it is not specified?

AR6: The efficiency of removal of organic volatile compounds is about 99 % but can degrade over time due to sulfur depositing on the catalyst. In the companion paper (Testa et al., 2024), we quantified the soot particle mass loss upon catalytic stripping for different engine type and particle size (we measured up to 10 % mass loss) and we refer to those measurements in the present paper rather than on the catalytic stripper's efficiency specified by the constructor.

R2C7: Line 70: do you expect any sampling-induced change in morphology when collecting particles on TEM grids? This should be discussed as results interpretations are based on this morphology analysis.

AR7: We agree with the comment. Soot aggregates can (partially) break apart upon impaction (Gao & Kanji, 2022), especially if the bonds between soot monomers are fragile due to prior heating (as for our CS-soot samples). We however did not detect any soot aggregate fragments with sizes similar to individual primary particles on the TEM images that would indicate aggregate break-up. We also did not observe a morphology difference between the unprocessed and the CS-soot samples, ruling out fragmentation of the heated particles upon impaction. Other possible effects are flattening of the particles, possibly more pronounced for large aggregates or bouncing of the particle on the grid, causing structural change (Virtanen et al., 2010). Such effects are likely limited with the Partector TEM sampler using electrostatic softer (than aerodynamic) impaction.

Second, multiple soot particles might aggregate on the TEM grid if impacting at the same position. This is however limited for with electrostatic impaction with the Partector TEM sampler. Nonetheless, we avoided imaging particles that would be the result of aggregation on the grid upon compaction by carefully imaging clearly isolated soot aggregates.

We propose to add the following edits in lines (73) 83-85: "The Partector TEM sampler uses a soft particle impaction technique (electrostatic precipitation), limiting the effect of the sampling process on the particle morphology. Soot aggregate breaking upon impaction was not observed on the various soot samples. Only clearly isolated soot particles on the grid were imaged to avoid imaging aggregated particles on the grid. Individual soot aggregates were imaged with a JOEL-JEM [...]"

R2C8: Line 106: "trigger modest PCF at 5% RHi [...]": Why is this qualifier used? Modest compared to what? The nucleation onset is reached at RHi below RHhom, so it does trigger PCF, doesn't? If it is implicitly compared to other potential INPs, please make it explicit.

AR8: The qualifier "modest" refers to a comparison with aviation soot proxies (e.g., Marth et al., 2020). To remain clear, we have deleted the word "modest" and kept the explicit comparison with the onset RH values.

Line (106) 118 now reads: "trigger PCF at 5% RHi [...]"

R2C9: Line 112: Were all the engines used for each sample type to derive the results shown in Figure 2? It is not specified.

AR9: The ice nucleation ability of unprocessed and CP-soot were systematically measured for all engines tested (13). The ice nucleation ability of the CS-soot and CS-CP-soot were measured for only 5 out 13 engines because of time constraints and the fact that we were piggy backing on the engine testing experiments, i.e. the engines were not explicitly run for our measurements. This would be too costly. Figure 2 includes all ice nucleation measurements (the number of engines is indicated in the x-axis, as specified in the figure caption).

Line (66) 73-75 now reads: "[...] and catalytically stripped plus contrail processed soot ("CS-CP-soot"). The ice nucleation ability for the unprocessed and CP-soot samples were systematically measured for all engine tested (13 engines in total). The ice nucleation ability of the CS-soot and CS-CP-soot were measured for 5 engines."

R2C10: Line 125: "for all engines, the soot aggregate mass increases for given sizes". However, it seems that the error bars displayed in Figure 3b prevent any comparison between CP soot and unprocessed soot as the error bars fully overlap. Same goes for the distinction between 150 nm particles and smaller ones regarding their compaction upon "contrail processing". The interpretations should be moderated accordingly.

AR10: We agree with this remark and propose to change the text accordingly. Lines (124-125) 136-139 now read: "For the engines shown in Fig. 3a, the soot aggregate mass increases for given sizes, which we explain by particle densification through its compaction, resulting in a higher mass-mobility exponent. For the smaller PW4168A engine soot particles ($D_m = 150 \text{ nm}$; Fig. 3b), we also note a mass change upon contrail processing although within the measurement uncertainties."

R2C11: Line 139-141: here again comparisons are done between processed and unprocessed soot for different engines but the stated results (e.g., ΔDm is larger for CP soot compared to CS CP soot) rely on

differences that fall within measurement uncertainties (clearly said this time). More caution should be taken in such case and the interpretations should be moderated accordingly.

AR11: We agree that differences in size between CP-soot and CS-CP-soot fall within measurement uncertainties. However, the difference is consistent among the three engines (size change for CS-CP-soot always smaller than for CP-soot), and this will be confirmed with the TEM image analysis in Sect. 3.2.3.

We propose the following edits (lines 152-154 in the revised manuscript): "We note that although the difference remains within measurement uncertainties, ΔD_m is consistently larger for CP-soot compared to CS-CP-soot for all engines (as confirmed in Sect. 3.2.3). This would be expected as soot particles become more hydrophobic upon catalytic stripping, hence less sensitive to compaction upon contrail processing (discussed further in Sect. 4)".

R2C12: Line 148: "[...] for all investigated engine types, which is indicative of aggregate compaction". What about the previous limitation for particles below 150 nm that showed no compaction in mass measurements; TEM results do not show such limitation?

AR12: As stated in AR10, we observe a mass change for the PW4168A CP-soot but that falls within the measurement uncertainty. Uncertainties on the mass measurements are larger for the soot particles emitted by the PW4168A engine due to their small particle size (absolute mass change is weaker for lighter particles). The TEM measurements confirm that even the 150 nm particles undergo a morphology change upon contrail processing.

R2C13: Line 162-163: "CS-CP soot undergo [...] than CP soot upon processing". Which processing? Both samples have already been processed. Please clarify/reword.

AR13: Here we mean "contrail processing". Line 162-163 (175-176) now read: "CS-CP soot undergo [...] than the CP-soot".

R2C14: Line 160-169: "CS-CP-soot show morphology changes similar to CP soot" [...] CS-CP-soot undergo smaller size reduction than CP-soot upon processing" [...] "CS-CP soot are on average more hydrophobic. This is due to the removal of H2SO4 upon catalytic stripping". I do not understand what parameter is preponderant here to explain why CS-CP-soot need the lowest %RHi to activate ice nucleation compared to CP-soot (Fig 2), is it because of the pore size, hydrophobic character and/or H2SO4 removal? Could you please clarify?

AR14: As stated in lines (186-188) 199-201 and (197-200) 211-213, the removal of material condensed in the soot pore (e.g., H_2SO_4) explain the ability for the CS-CP-soot samples to trigger ice nucleation at lower RH_i compared to the CP-soot sample. Empty pores for the CS-CP-soot become available for water condensation and ice nucleation, while pores partially filled with organics or H_2SO_4 for the CP-soot might either not fill with water due to the likely hydrophobic character of the organics or not freeze at the considered temperatures (-45 and -55°C) due to freezing point depression induced by the soluble material in the soot pores.

In addition, the pore size and hydrophobic character of the particles contribute to the ice nucleation ability of the CS-CP-soot and explain differences between the engines (lines (188-195) 201-208).

R2C15: Line 177: how is "the inability of CP-soot to promote ice nucleation [...] contrail processing does not generate pores relevant to PCF" similar to observing moderate enhancement for contrail-processed propane soot. Please remove "similarly" or reword.

AR15: Line (177) 190 now reads: "[...] mass measurements. Gao and Kanji (2022a) [...]"

R2C16: Line 182: "CFM56-7B", should it be "CFM56-7B26/3" instead?

AR16: This should be "CFM56-7B26" (same engine as in Testa et al., 2024; see their Table B1). The text has been changed accordingly (line 195 in revised manuscript).

R2C17: Line 203: possess

AR17: Text has been edited (see line 216 in revised manuscript).

R2C18: Line 223: again the very strong statement "aviation soot does not promote ice nucleation below [...] RHhom" tends to generalize this to all engines, while in the same paper (Testa et al. 2023) a subset of engines (2/10) were shown to activate ice via PCF when large soot aggregates were emitted. The statement needs to be moderated not to elude this result.

AR18: In Testa et al. (2024) the size of the ice-active aviation soot particles was large (400 nm monodisperse) and hence not atmospherically relevant. The size of in situ emitted aviation soot are much smaller, which strengthen the statement that aviation soot would not serve as INP for cirrus formation.

To be specific we changed the sentence to (see lines 236-239 in revised manuscript): "Recent measurements (Testa et al., 2023) showed that aviation soot does not promote ice nucleation below conditions required for homogeneous freezing of solution droplets (RHhom), particularly because the sizes of emitted soot particles are below 100 nm, which have been shown to be poor INPs for all conditions (variety of mixing states and particle morphologies)."

This investigation of the effect of the particle mixing state on the ice nucleation with the different soot samples investigated in this study further bound the possible in situ aviation soot ice nucleation ability, hence the generalization of the results. Please refer to AR5, AR6 and AR7.1 in the responses to R1C5, R1C6 and R1C7.1 for a detailed argumentation.

References:

Dakhel, P. M., Lukachko, S. P., Waitz, I. A., Miake-Lye, R. C., & Brown, R. C. (2007). Post-Combustion Evolution of Soot Properties in an Aircraft Engine. https://api.semanticscholar.org/CorpusID:136958147

FlightGlobal.com. (2021). Commercial engines.

- Gao, K., & Kanji, Z. A. (2022). Impacts of Cloud-Processing on Ice Nucleation of Soot Particles Internally Mixed With Sulfate and Organics. *Journal of Geophysical Research: Atmospheres, 127*(22), e2022JD037146. https://doi.org/https://doi.org/10.1029/2022JD037146
- Jing, L., El-Houjeiri, H. M., Monfort, J.-C., Littlefield, J., Al-Qahtani, A., Dixit, Y., Speth, R. L., Brandt, A. R., Masnadi, M. S., MacLean, H. L., Peltier, W., Gordon, D., & Bergerson, J. A. (2022). Understanding variability in petroleum jet fuel life cycle greenhouse gas emissions to inform aviation decarbonization. *Nature Communications*, 13(1), 7853. https://doi.org/10.1038/s41467-022-35392-1

- Kärcher, B. (1998). Physicochemistry of aircraft-generated liquid aerosols, soot, and ice particles: 1. Model description. *Journal of Geophysical Research: Atmospheres*, *103*(D14), 17111–17128. https://doi.org/https://doi.org/10.1029/98JD01044
- Kärcher, B., Möhler, O., DeMott, P. J., Pechtl, S., & Yu, F. (2007). Insights into the role of soot aerosols in cirrus cloud formation. *Atmospheric Chemistry and Physics*, 7(16), 4203–4227. https://doi.org/10.5194/acp-7-4203-2007
- Mahrt, F., Kilchhofer, K., Marcolli, C., Grönquist, P., David, R. O., Rösch, M., Lohmann, U., & Kanji, Z. A. (2020). The Impact of Cloud Processing on the Ice Nucleation Abilities of Soot Particles at Cirrus Temperatures. *Journal of Geophysical Research: Atmospheres, 125*(3), e2019JD030922. https://doi.org/https://doi.org/10.1029/2019JD030922
- Petzold, A., Döpelheuer, A., Brock, C. A., & Schröder F. (1999). In situ observations and model calculations of black carbon emission by aircraft at cruise altitude. *Journal of Geophysical Research: Atmospheres*, *104*(D18), 22171–22181. https://doi.org/https://doi.org/10.1029/1999JD900460
- Petzold, A., Ström, J., Ohlsson, S., & Schröder, F. P. (1998). Elemental composition and morphology of icecrystal residual particles in cirrus clouds and contrails. *Atmospheric Research*, *49*(1), 21–34. https://doi.org/https://doi.org/10.1016/S0169-8095(97)00083-5
- Pires, A. P. P., Han, Y., Kramlich, J., & Garcia-Perez, M. (2018). Chemical Composition and Fuel Properties of Alternative Jet Fuels. *Bioresources*, *13*(2), 2632–2657. https://doi.org/10.15376/biores.13.2.2632-2657
- Testa, B., Durdina, L., Alpert, P. A., Mahrt, F., Dreimol, C. H., Edebeli, J., Spirig, C., Decker, Z. C. J., Anet, J., & Kanji, Z. A. (2024). Soot aerosols from commercial aviation engines are poor ice-nucleating particles at cirrus cloud temperatures. *Atmospheric Chemistry and Physics*, 24(7), 4537–4567. https://doi.org/10.5194/acp-24-4537-2024
- Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., Mäkelä, J. M., Holopainen, J. K., Pöschl, U., Kulmala, M., Worsnop, D. R., & Laaksonen, A. (2010). An amorphous solid state of biogenic secondary organic aerosol particles. *Nature*, 467(7317), 824–827. https://doi.org/10.1038/nature09455
- Wong, H.-W., Yelvington, P. E., Timko, M. T., Onasch, T. B., Miake-Lye, R. C., Zhang, J., & Waitz, I. A. (2008). Microphysical Modeling of Ground-Level Aircraft-Emitted Aerosol Formation: Roles of Sulfur-Containing Species. *Journal of Propulsion and Power*, 24(3), 590–602. https://doi.org/10.2514/1.32293
- Yu, F., Turco, R. P., & Kärcher, B. (1999). The possible role of organics in the formation and evolution of ultrafine aircraft particles. *Journal of Geophysical Research: Atmospheres*, 104(D4), 4079–4087. https://doi.org/https://doi.org/10.1029/1998JD200062