Response to acp-2021-645 reviews for RC1

Dear Bernd Kärcher,

Thank you very much for reviewing our manuscript acp-2021-645. We are grateful for your comments and constructive suggestions. Please find our itemized response in below and corrections in the revised version. Your comments are reproduced **in bold** and our responses are given directly afterward in normal font. *The original text in previous manuscript version is reproduced in red italic* and *revised text is added in blue italic*.

All the best,

Kunfeng and Zamin

- **Major:**

1 **L81-83: To me, it is unclear if contrail processing had actually happened in the measurements of Petzold et al. (1998) or whether the peculiar signature of the probed soot particles (bimodality) was a feature of the fresh emissions. Please check.**

R: Petzold et al. (1998) sampled contrail and cirrus crystals using a counter-flow virtual impactor (CVI) and characterized the chemical composition, morphology and size distribution of ice-residual particles. It is evident that cloud processing occurred in the study, because characterized ice-residual particles (majorly soot particles, ~87 %) are leftover substances from the ice crystal after sublimation or melting followed by evaporation. Petzold et al. (1998) only characterized the size distribution of ice-residual particles by statistically analyzing the size of sampled particles on filters and divided the residual particles into three size bins, including fine particles (0.1-0.5 μm), intermediate (0.5-1.5 μm) and coarse particles (1.5-5.0 μm). However, the authors did not measure the size distribution of interstitial aerosol particles or fresh soot particles. This description therefore suggests contrail processing.

We added two references (see L86-87 in revised manuscript) to support that cloud processing can modify the morphology of freshly emitted soot particles. The first literature is from Colbeck et al. (1990) who observed a fractal dimension value increase for fresh soot particle (~ 1.8) after exposing to cloud processing simulation conditions (> 2.0-2.5). The second literature is from Petzold and Schröder (1998) who suggested the fresh soot particle size distribution is dominated by fine particles (< 0.1 μm), which is different from cloud processed soot particles which have larger sizes. We present the corrected text in L85-87 in the revised manuscript:

'*In addition, soot with a more compacted morphology than the freshly emitted particles are detected in aviation contrail ice crystal residues (Colbeck et al., 1990; Petzold and Schröder, 1998; Petzold et al., 1998) suggesting a change in shape and size of the soot-aggregates due to contrail processing.*'

2 **L354: Please define what a mesopore is. This is especially relevant as pore properties feature prominently in the data discussion (mostly in section 3.1). In l402, the term 'micropore' is used and it is unclear what sets it apart from a mesopore.**

R: Thanks, we agree this is a valuable definition to include. We updated this in revised manuscript L362-364 as below:

'*...homogeneous freezing conditions in the cirrus cloud regime (Mahrt et al., 2018). Herein, mesopores are defined as pore structures with a width between 2 and 50 nm whereas pore structures with a width less than 2 nm refer to micropores (Thommes et al., 2015).*'

3 **L668ff: The authors may want to more clearly state in this paragraph that current data**

suggest that only soot particles with sizes 200 nm and 400 nm actually contribute to cirrus formation, hence are 'atmospherically relevant'. In the case of aviation soot (l683f), most particles emitted at altitude belong to the Aitken mode, i.e., they are much smaller.

R: Thank you for raising the concern on the size dependence of soot ice nucleation. In the referred paragraph we state that "*Field studies detected soot-aggregates with 0.1-1 μm sizes in ice crystal residuals sampled from cirrus clouds (Petzold et al., 1998; Twohy and Poellot, 2005; Cziczo and Froyd, 2014) and the presence of 100-800 nm BC particles in the interstitial aerosol samples increases with increasing altitude from 8 to 11 km in the cirrus cloud regime (Petzold et al., 1998).*", which implies soot particles in the size range of 200 and 400 nm are relevant to cirrus formation. We agree, that fine particles (< 100 nm) dominate the number concentration of aviation soot particle population, but soot particles larger than ~ 100 nm in the aviation emission take a large proportion of volume/mass concentration (Brito et al., 2014; Fushimi et al., 2019). In addition, Zhang et al. (2020) reported that fine particles coagulate into larger soot aggregates downstream of the emission, upon evolution of the aviation plume. Therefore, our study of 200 and 400 nm aviation soot proxies are relevant for the evaluation of aviation soot contribution on cirrus cloud formation, considering the size dependence of soot ice nucleation, i.e. larger soot particles are more active INPs. We updated the manuscript text at the end of the paragraph (L697-700 in revised manuscript) as following:

'*... Soot particles emitted from biomass burning and aviation activities are dominated by fine particles (< 100 nm) in number concentration, however, large particles (> 100 nm) dominate in volume concentration (Brito et al., 2014; Fushimi et al., 2019). In addition, Zhang et al. (2020) reported that fine particles coagulate into large soot aggregates downstream of the emission upon aviation plume evolution. Thus, we believe that the results presented in this study are of atmospherically relevant sizes (200 and 400 nm).*'

4 **Even poor INPs can be efficient in altering cirrus if present in sufficiently high concentrations. BC particles are often present in high number concentrations close to their sources. It may be good to add that besides size-dependent ice nucleation ability the soot particle number concentration must be known in order to judge their potential to affect cirrus formation notably.**

R: Thank you for this comment. We agreed and modified the statement in between the second paragraph in Sect. 4 as below (L707-710 in revised manuscript):

'*Despite the minor ice nucleation ability of mCASTblack soot via PCF even at 218 K as presented in this study, uncoated aviation soot analogous to fractal and hydrophobic mCASTblack may still influence cirrus cloud properties if soot particles are in present in sufficiently high number concentration near their sources because a non-negligible number will nucleate ice crystals (Kärcher et al., 2021).*'

5 **I was also wondering whether the authors like to add the importance of further measurements probing smaller soot particles (if feasible, down to 50 nm) to confirm the trend of ice nucleation ability diminishing with decreasing size. This would be especially important for the case of aviation soot, but possibly for other high-temperature combustion sources, too.**

R: Thank you for this suggestion. Yes, we agree that the investigation of size threshold for soot ice nucleation is important. In fact, we have just submitted a manuscript to ACP where we present ice nucleation onto soot particles down to 60 nm (Gao et al., 2021). A new statement was added at the end of the Sect. 5 as below (L767-770 in revised manuscript):

'*...Moreover, measuring the lower size limit to identify the threshold of soot ice formation will be*

important for future laboratory studies, given the strong particle size dependence of (soot) ice nucleation and that the Aitken mode dominates size distribution from aviation soot emissions and also other high temperature combustion sources.'

- **Minor:**

1 L11: I believe you mean 'net warming'. Same in L39.

R: Yes. Corrected (now L11 and L40 respectively in revised manuscript)

2 L38: The plural of aircraft is still aircraft.

R: Corrected (L40 in revised manuscript).

3 L39: As written, it is unclear whether the climate warming effect relates to cirrus or to aviation soot.

R: Thank you. The sentence was restructured as below (L39-41 in revised manuscript):

'*...Aviation soot particles, directly emitted by commercial aircraft in the upper troposphere, exert net-warming effects on climate (Liou, 1986) by acting as potential ice nucleating particles (INPs) at high altitudes where cirrus clouds usually form.*'

Original sentence: '*Aviation soot particles, directly emitted by commercial aircraft in the upper troposphere, are potential ice nucleating particles (INPs) at high altitudes where cirrus clouds usually form, and exert net-warming effects on climate (Liou, 1986).*'

4 L48: Please clarify that for T<235 K, homogeneous ice formation occurs in liquid aerosol droplets only, setting cirrus apart from mixed-phase clouds.

R: Thanks. The sentence (now L52-53 in revised manuscript) was modified as below:

'*...Homogeneous ice nucleation can only be triggered at T < 235 K (homogeneous nucleation temperature, HNT) and relative humidity with respect to ice (RH_i) higher than 140 % (Koop et al., 2000), where the nucleation rates of liquid aerosol particles are large enough to freeze spontaneously leading to cirrus cloud formation.*'

5 L63: Sentence ending with 'where aeroengines exhaust sulphur emissions' appears to be incomplete.

R: Thank you. Agreed and corrected as below (now L66 in revised manuscript):

'*...It is conceivable that soot particles and H_2SO_4 can be internally mixed forming H_2SO_4 coated soot in the atmosphere, especially in high altitude aircraft corridors where aeroengines emit fossil fuel combustion aerosol.*'

6 L73: Sentence ends with 'but remaining unconstrained' sounds awkward.

R: Thanks. The sentence was revised as following (now L76-77 in revised manuscript):

'*...Thus, the internal mixing of soot particles with H_2SO_4 may regulate its ability to be a potential INP but the mixing state is unconstrained.*'

7 L118: What is a 'potential' pore?

R: In this context, 'a potential pore for PCF' means the pore structures in soot particles which have appropriate pore width and wettability, thus can induce capillary condensation under sub-saturation

conditions. But the activation of such a pore structure also depends on temperature condition, that is why we termed it as 'a potential pore'.

8 L292+293: Sentence sounds awkward.

R: We reorganized as below (now L296-297 in revised manuscript):

'*However, such a small size increase is absent for the case of coating 400 nm soot particles, and the size starts to decrease due to collapse when the coating mass percentage reaches ~ 20 %.*'

Original statement: '*Whereas 400 nm size selected soot particle does not show apparent size growth and starts to collapse when the coating mass percentage reaches ~ 20 %.*'

9 L331: Define AF.

R: The AF was already defined in L238 (in original manuscript, now L242 in revised manuscript).

10 L418: Please clarify that water uptake is reduced to the inverse Kelvin effect, which, what I believe, is what the authors mean to say.

R: Here, we intend to present that excess H_2SO_4 coating for pore filling will spread over soot surface and enhance soot surface hygroscopicity. To make a clear statement, we corrected the sentence as below (now L426-429 in revised manuscript):

'*With more coating (in medium and thick cases), hygroscopic H_2SO_4 adsorption on soot surfaces may occur simultaneously with H_2SO_4 pore filling and thus enhance soot surface hygroscopicity. Hence, soot particles with medium or thick coating will not only sustain pore filling but also form bulk water droplets more readily.*'

Original statement: '*With more coating (in medium and thick cases), hygroscopic H_2SO_4 adsorption on soot surfaces competes with H_2SO_4 pore filling and promotes the water uptake ability of soot particles to form a bulk water droplet more readily.*'

11 L686ff: A recent study* concluded that even a small number of ice-active aviation soot particles is capable of modifying the total number and mean size of cirrus ice crystals when nucleating ice alongside homogeneous freezing, albeit with a minor impact on cirrus optical depth. It was found that, based on soot-PCF, only uncoated (barely coated) soot particles with sizes >100 nm contributed to enhanced ice nucleation activity (after contrail-processing). This information may be used in this paragraph relating to mCASTblack soot to better explain what is meant by 'may not inhibit or compete with (aerosol) droplet homogeneous freezing' (l689f). In sum, while not making 'a significant contribution to cirrus cloud formation via PCF' (l693), soot particles may still perturb cirrus microphysical properties. This cautionary note also applies to the subsequent paragraph (l697ff) discussing FW200 soot samples.

***https://www.nature.com/articles/s43247-021-00175-x**

R: Thank you for this constructive comment. Following your suggestion, a short paragraph was added at the end of Sect. 3.4 as below (now L736-743 in revised manuscript):

'*In brief, H_2SO_4 coating modifies soot particle ice nucleation in the cirrus cloud regime by decreasing the pore availability for PCF activation thereby inhibiting ice formation below RH_{hom} conditions. This finding is consistent with a model simulation study based on soot-PCF framework (Marcolli et al., 2021) performed by Kärcher et al. (2021) who reported that only barely coated soot particles larger than ~ 100 nm with sufficient mesopore structures can contribute to cirrus clouds ice formation. Nonetheless, the*

authors also suggested that even a small number of active uncoated soot particles (~ 11 L^{-1}) can decrease the total number of cirrus ice crystals but increase the ice crystal mean size by forming ice via PCF processes while competing with the homogeneous freezing of aerosol droplets (Kärcher et al., 2021). Therefore, soot particles may still play an important role in regulating cirrus cloud properties, despite the suppressed ice nucleation ability caused by H_2SO_4 coating.'

12 L706: consider replacing 'nucleated' with 'water-activated' to avoid confusion with ice nucleation

R: Thanks. Agreed and corrected (now L723 in revised manuscript).

13 L727: 'require RH > RHhom conditions' — for what?

R: To make a clear statement, we revised the statement as below (now L753-754 in revised manuscript): '*High wt/wt% H_2SO_4 coated 200 and 400 nm mCASTblack soot particles form ice crystals via homogeneous freezing and low wt/wt% H_2SO_4 coating even depresses their ice nucleation to RH > RH_{hom} conditions at T < HNT.*'

Original statement: '*H_2SO_4 coating makes 200 and 400 nm mCASTblack soot particles form ice crystals via homogeneous freezing and low mass H_2SO_4 coating even depresses their ice nucleation activity at T < HNT to require RH > RH_{hom} conditions.*'

14 L738: 'systemically' -> systematically

R: Thanks. Agreed and corrected (now L766 in revised manuscript).

15 L739: 'soot role' -> role of soot

R: Agreed and corrected (now L767 in revised manuscript).

Reference:

Brito, J., Rizzo, L. V., Morgan, W. T., Coe, H., Johnson, B., Haywood, J., Longo, K., Freitas, S., Andreae, M. O., and Artaxo, P.: Ground-based aerosol characterization during the South American Biomass Burning Analysis (SAMBBA) field experiment, Atmos. Chem. Phys., 14, 12069-12083, https://10.5194/acp-14-12069-2014, 2014.

Colbeck, I., Appleby, L., Hardman, E. J., and Harrison, R. M.: The optical properties and morphology of cloud-processed carbonaceous smoke., J. Aerosol Sci., 21, 527–538, https://doi.org/10.1016/0021-8502(90)90129-L, 1990.

Cziczo, D. J. and Froyd, K. D.: Sampling the composition of cirrus ice residuals, Atmos. Res., 142, 15-31, https://doi.org/10.1016/j.atmosres.2013.06.012, 2014.

Fushimi, A., Saitoh, K., Fujitani, Y., and Takegawa, N.: Identification of jet lubrication oil as a major component of aircraft exhaust nanoparticles, Atmos. Chem. Phys., 19, 6389-6399, https://10.5194/acp-19-6389-2019, 2019.

Gao, K., Friebel, F., Zhou, C.-W., and Kanji, Z. A.: Enhanced soot particle ice nucleation ability induced by aggregate compaction and densification, Atmos. Chem. Phys. Discuss., http://10.5194/acp-2021-883, 2021.

Kärcher, B., Mahrt, F., and Marcolli, C.: Process-oriented analysis of aircraft soot-cirrus interactions constrains the climate impact of aviation, Commun. Earth Environ., 2, https://10.1038/s43247-021-00175-x, 2021.

Koop, T., Luo, B., Tsias, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 4, https://doi.org/10.1038/35020537, 2000.

Liou, K.-N.: Influence of cirrus clouds on weather and climate processes: A global perspective, Mon. Weather Rev., 114, 1167–1199, 1986.

Marcolli, C., Mahrt, F., and Kärcher, B.: Soot-PCF: Pore condensation and freezing framework for soot aggregates, Atmos. Chem. Phys., https://doi.org/10.5194/acp-21-7791-2021, 2021.

Petzold, A. and Schröder, F. P.: Jet engine exhaust aerosol characterization, Aerosol Sci. Tech., 28, 62-76, https://doi.org/10.1080/02786829808965512, 1998.

Petzold, A., Strom, J., Ohlsson, S., and Schröder, F. P.: Elemental composition and morphology of ice-crystal residual particles in cirrus clouds and contrails, Atmos. Res., 49, 21-34, http://doi.org/10.1016/S0169-8095(97)00083-5, 1998.

Twohy, C. H. and Poellot, M. R.: Chemical characteristics of ice residual nuclei in anvil cirrus clouds: evidence for homogeneous and heterogeneous ice formation, Atmos. Chem. Phys., 5, 2289–2297, 2005.

Zhang, X., Karl, M., Zhang, L., and Wang, J.: Influence of Aviation Emission on the Particle Number Concentration near Zurich Airport, Environ. Sci. Technol., 54, 14161-14171, https://10.1021/acs.est.0c02249, 2020.