Reviewer #2

This manuscript presents a thorough CCN closure study at the SMEAR II station in Hyytiälä, Finland, leveraging long-term observational data (2016–2020) of aerosol size distributions, chemical composition, and CCN concentrations. The authors compare three CCN prediction methods using κ-Köhler theory with different inversion schemes: i) constant kappa parameter, ii) based on bulk chemical-composition, and iii) inferring size-resolved (modal) composition consistent with total mass and CCN observations.

They demonstrate that allowing the Aitken and accumulation modes to have distinct chemical compositions (κ_{opt}) significantly improves the closure, especially at higher supersaturations (>0.5%), where Aitken mode particles contribute more to CCN. Seasonal trends show organic enrichment in the Aitken mode and a higher inorganic fraction in the accumulation mode, with implications for understanding biogenic contributions to CCN. This study addresses key limitations in CCN prediction models related to the lack of size-resolved chemical composition data and provides a novel methodology to infer this information from inverse modeling. The work is especially timely as climate models increasingly rely on more accurate aerosol-cloud interaction representations, particularly in biogenically influenced environments like boreal forests.

The manuscript is well-structured, the methodology is sound, and the conclusions are meaningful, therefore, the manuscript should be accepted in ACP. However, before publication some minor revisions are recommended to enhance clarity and strengthen the study.

We thank the reviewer for his/her positive view on the scope of this manuscript. Please note that κ_{opt} refers to the method where we use Nelder–Mead optimization, focusing only on the optimization of the modal chemical composition. In the revised manuscript, we have included additional analyses, the most significant of which involves DREAM-MCMC simulations. In this approach, referred to as κ_{MCMC}, we not only optimize the modal chemical composition but also account for the variability of the size-distribution lognormal parameters during the optimization process. See response to the specific comment #14 by Reviewer #1.

Minor comments:

- ***Lines 26–27:****"This optimization improved the CCN closure primarily at supersaturations above 0.5%..."*

  Please quantify the improvement in closure — e.g., percent error reduction or NRMSE change — so the reader can assess the magnitude of the model enhancement.

  Table 2 presents the NRMSE values for all the closure approaches (see Table S2 for the corresponding GMB values). We believe it is straightforward to calculate the requested differences from these tables.

  Lines 29–31: *"The mass fractions of inorganics in the two modes vary with season..."*

  Consider reporting the absolute inorganic mass fractions in addition to the percent difference. This would clarify the physical relevance of the enrichment, particularly for radiative implications.

  Thank you for this comment. We have included the following tables to the supplementary information accompanying the revised manuscript:

Table R1. Mean of optimized mass fractions of various chemical species in Aitken mode in different seasons

	Spring	Summer	Autumn	Winter
Organics	0.70	0.75	0.72	0.69
Inorganics	0.20	0.19	0.16	0.16
eBC	0.1	0.06	0.11	0.15

Table R2. Mean of optimized mass fractions of various chemical species in Accumulation mode in different seasons

	Spring	Summer	Autumn	Winter
Organics	0.54	0.65	0.55	0.44
Inorganics	0.37	0.28	0.33	0.41
eBC	0.09	0.06	0.11	0.15

- ***Line 182, Section 2.2***

  The method assumes the total submicron composition remains constant while redistributing it between modes. Please justify whether this assumption holds during periods of intense NPF or cloud processing, which may differentially affect modal composition.

  Thank you for this insightful comment. Indeed, the composition might vary during the CCN measurement cycle due to e.g. the processes mentioned in the comment. It is however beyond the scope of the study the estimate the magnitude of such variability due to the limited observational data in this regards.

- ***Line 213, Section 2.1.1:****"...more black carbon is also observed, which tends to decrease the overall hygroscopicity."*

  Since eBC is treated as size-invariant in the inverse approach, this assumption might bias winter κ estimates. It can be interesting evaluating the sensitivity of κ_{opt} to this fixed eBC partitioning.

  Thank you for this suggestion. We have now conducted an inverse closure study testing the sensitivity of the results to this assumption.

  We tested the sensitivity of κ_{opt} to the assumed BC size distribution using the Nelder-Mead approach and (i) allowing the eBC fractions in both Aitken and accumulation modes to vary during the optimization and (ii) keeping eBC fixed in the accumulation mode only. In both cases, the optimized κ and resulting CCN spectra were very similar, suggesting that the BC size-distribution assumption has only minor impact on the CCN closure. However, when BC was optimized in both modes, the model produced an unrealistic composition with ~70% BC in the Aitken mode, while fixing BC in the accumulation mode yielded a more physically consistent result with Aitken mode dominated by organics (~99%). These findings indicate that varying eBC fractions does not significantly affect κ_{opt} but may distort the inferred chemical composition. We will include the results related to this case study in the supplementary as following:

  "Supplementary note R3
  Insights on effect of the assumption of fixed eBC mass in both modes: The CCN spectra obtained using bulk chemical composition generally depicts overprediction from the observations, with the largest bias at both lowest supersaturation (0.1%) and the highest supersaturation (1.0%). A way to reduce this overprediction is to have a size-segregated

composition that makes the Aitken mode as low in hygroscopicity as possible. As a conservative approach, we eBC is fixed only in accumulation mode leaving no eBC mass in Aitken mode, the 5 year averaged (median) NRMSE remains almost similar at 0.28 (a little on higher side), while Aitken kappa is a bit higher as an non-hygrosocopic element i.e. eBC is now completely is accumulation mode. In another approach, we allowed eBC to vary as an additional optimization parameter along with organics in the Aitken mode (see Sect. 2.2.3 for the inverse modeling setup), instead of keeping its mass fraction fixed in both modes. As expected, this adjustment lowers the NRMSE from 0.28 to 0.23, while the optimized κ remains nearly unchanged, but a little on lower side than the setup we use (see Table R6). Interesting to note that, this setup suggest that there should be 70% eBC in Aitken mode which seems unrealistic. Complementary results from DREAM-MCMC optimization (optimizing modal BC mass fraction while considering variability of lognormal parameters of size distribution during CCN cycle) of the same problem suggests similar results with around on an average 41% BC in Aitken mode – again a very high number considering the expected aerosol sources at the cite.

Table R3. Median of optimized mass fractions of various chemical species in Aitken and accumulation mode when all eBC are kept in accumulation mode

Organics (Aitken)	Inorganics (Aitken)	eBC (Aitken)	Organics (accumulation)	Inorganics (accumulation)	eBC (accumulation)
0.99	0.01	0.00	0.59	0.43	0.10

Table R4. Median of optimized κ in different seasons when all eBC are kept in accumulation mode using the Nelder-Mead .

	Spring	Summer	Autumn	Winter
κ_{Aitken}	0.12	0.12	0.12	0.12
$\kappa_{\text{accumulation}}$	0.27	0.21	0.24	0.29

Table R5. Median of optimized mass fractions of various chemical species in Aitken accumulation mode when eBC is also an optimized parameter

Organics (Aitken)	Inorganics (Aitken)	eBC (Aitken)	Organics (accumulation)	Inorganics (accumulation)	eBC (accumulation)
0.26	0.046	0.70	0.62	0.31	0.07

Table R6. Median of optimized κ in different seasons when eBC is also an optimized parameter

	Spring	Summer	Autumn	Winter
κ_{Aitken}	0.11	0.11	0.11	0.10
$\kappa_{\text{accumulation}}$	0.27	0.22	0.25	0.29

We will include a detailed explanation in the Supplementary note R3 in the revised manuscript.

- ***Table 1 and Eq. 4, κ values and densities:***

The use of fixed κ for organics (0.12) and organic nitrate might oversimplify temporal variability. Consider discussing the expected range of κ_{org} from literature (e.g., 0.05–0.2) and its potential influence on κ_{bulk} accuracy.

We agree, and have now conducted an inverse closure study testing the sensitivity of the results to this assumption. In our analysis, the κ parameter is used as an effective hygroscopicity parameter that implicitly accounts for various influences, including limited solubility and possible surface tension effects. However, we do not treat surface tension depression or solubility limitations explicitly. It is worth noting that incorporating surface tension depression into the κ-Köhler framework would typically reduce the activation diameter, leading to higher predicted CCN concentrations. Given that our closure results based on bulk chemical composition already tend to slightly overpredict CCN compared to observations, explicitly accounting for surface tension depression would likely worsen the agreement. To account for this comment (and similar comments from the other reviewers, we have now conducted an inverse closure study testing the sensitivity of the results to the assumptions of organic molecular properties. We performed two types of inverse-closure studies:

a) Using bulk-composition but optimizing only the organic density, ρ_{org} and organic hygroscopicity parameter, κ_{org}
b) Optimizing ρ_{org} and κ_{org} while also accounting for variability of size distribution lognormal parameters

In both tests, κ_{org} was varied between 0.05 and 0.15, while ρ_{org} was varied between 1000 and 3000 kg m^{-3}. Method (a) resulted in a lower NRMSE but suggested a median optimized organic density of 1000 kg m^{-3}, which seems unrealistic. Method (b) produced a slightly higher NRMSE (0.085 compared to 0.079 from κ_{MCMC}) but yielded a probably unrealistically high organic density of 2179 kg m^{-3}, with clear seasonal variability (minimum around 1750 kg m^{-3} in summer). This is notably higher than the 1500 kg m^{-3} assumed in the original inverse-closure approach. Both methods produced optimized κ_{org} values between 0.05 and 0.07 depending on the season.

We will add a detailed discussion in the supplementary to the revised manuscript.

- ***Figure 4, Forward and Inverse Closure:*** *The figure would benefit from adding shading or markers to show uncertainty (e.g., interquartile range) of observations. Right now, it's difficult to assess fit quality beyond the median.*

Thank you for the comment – we do not understand what is meant here however as the whiskers corresponding to the quartiles are already present in the figure. Perhaps there has been an issue with the reproduction of the figure?

- ***Lines 532–535, κ Discussion:*** *The increase in Aitken mode organic fraction during summer aligns with biogenic SOA production. This would be strengthened by directly comparing seasonal κ_{opt} to expected κ values from known BVOC oxidation products (e.g., monoterpenes, sesquiterpenes).*

Thank you for this useful comment. The optimal organic hygroscopicity of about 0.1 corresponds generally well for most organics, including known oxidation products from BVOCs (see e.g. Siegel et al., 2022 and references therein). We have added a sentence about this to the revised manuscript.

- ***Lines 536, CCN overestimation:*** *The consistent overestimation of CCN concentrations across all supersaturations may point to a limitation of the internal mixing assumption, especially during periods of aerosol complexity. Previous studies suggest that such overestimations are exacerbated during times of mixed aerosol sources (e.g., biogenic + anthropogenic + aged background), where internal mixing assumptions break down. I recommend the authors to explore whether episodes of high bias correlate with increased variability in PNSD, eBC, or*

chemical markers—and to discuss the implications of external or mixed-state aerosols on the robustness of κ-based predictions.

Thank you for raising this excellent point. See response to the specific comment #18 by Reviewer #1.

- ***Supplementary Table S2:***

Although GMB is a useful summary metric, standard deviation or interquartile ranges of GMB values could help assess variability and robustness across time.

Thank you for this useful suggestion. We will add the following information to the supplementary information accompanying the revised manuscript:

"Supplementary note R4
In figure S11 (see the preprint version), we looked at GMB but importantly, another quantity, the standard deviation (SD) of GMB provides insight into the robustness of each method: a lower SD indicates that the bias is consistent across cases, while a higher SD suggests larger variability in performance. This makes it a key metric to consider when evaluating the stability of CCN prediction methods.

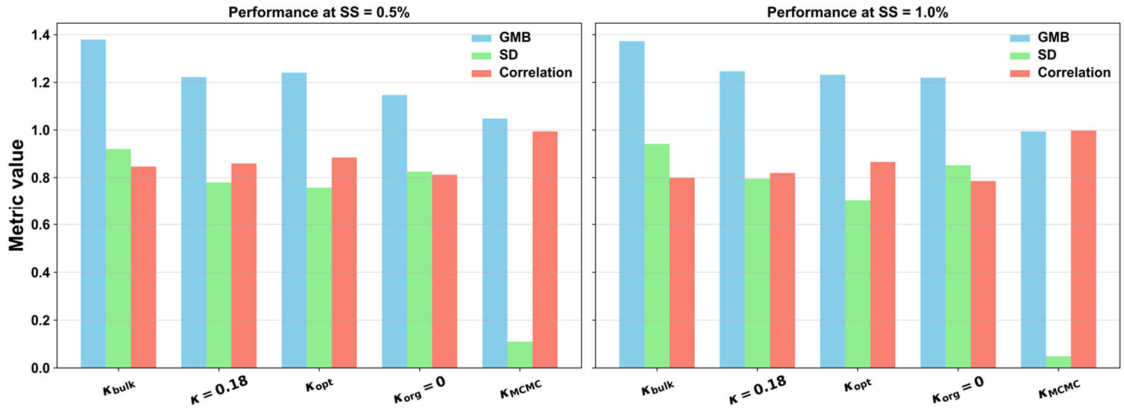

Figure R4 Comparison of CCN prediction performance at supersaturations of 0.5 % and 1.0 % using different methods. Metrics shown are geometric mean bias (GMB), its standard deviation (SD), and correlation between predicted and observed CCN.

The results show that DREAM-MCMC (κ_{MCMC}) performs best overall, with a geometric mean bias very close to unity, extremely high correlation with observations, and the lowest spread. This indicates that it provides the most accurate and stable CCN predictions. The κ_{opt} method, which optimizes only size-segregated composition, ranks second: it achieves high correlation and relatively low variability, though the bias remains slightly above one, suggesting moderate overprediction. $\kappa_{\mathrm{org}} = 0$ falls in the middle, with moderate bias, correlation, and variability, making it balanced but not particularly strong in any metric. The fixed $\kappa = 0.18$ approach performs similarly to $\kappa_{\mathrm{org}} = 0$ but is slightly weaker, with somewhat lower correlation. Finally, κ_{bulk} performs the worst, showing the highest bias and systematic overprediction of CCN, along with only moderate correlation and spread."

References

Clerx, M., Robinson, M., Lambert, B., Lei, C. L., Ghosh, S., Mirams, G. R., & Gavaghan, D. J. (2019). Probabilistic Inference on Noisy Time Series (PINTS). Journal of Open Research Software, 7(1), 23. https://doi.org/10.5334/jors.252

Ervens, B., Sorooshian, A., Aldhaif, A.M., Shingler, T., Crosbie, E., Ziemba, L., Campuzano-Jost, P., Jimenez, J.L., Wisthaler, A., 2018. Is there an aerosol signature of chemical cloud processing? Atmospheric Chemistry and Physics 18, 16099–16119. https://doi.org/10.5194/acp-18-16099-2018

Gelman, A., Shalizi, C.R., 2013. Philosophy and the practice of Bayesian statistics. British Journal of Mathematical and Statistical Psychology 66, 8–38. https://doi.org/10.1111/j.2044-8317.2011.02037.x

Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, Atmos. Chem. Phys., 7, 6131–6144, 2007

Gao, F., Han, L., 2012. Implementing the Nelder-Mead simplex algorithm with adaptive parameters. Comput Optim Appl 51, 259–277. https://doi.org/10.1007/s10589-010-9329-3

Hao, L., Romakkaniemi, S., Kortelainen, A., Jaatinen, A., Portin, H., Miettinen, P., Komppula, M., Leskinen, A., Virtanen, A., Smith, J.N., Sueper, D., Worsnop, D.R., Lehtinen, K.E.J., Laaksonen, A., 2013. Aerosol Chemical Composition in Cloud Events by High Resolution Time-of-Flight Aerosol Mass Spectrometry. Environ. Sci. Technol. 47, 2645–2653. https://doi.org/10.1021/es302889w

Heikkinen, L., Äijälä, M., Daellenbach, K.R., Chen, G., Garmash, O., Aliaga, D., Graeffe, F., Räty, M., Luoma, K., Aalto, P., Kulmala, M., Petäjä, T., Worsnop, D., Ehn, M., 2021. Eight years of sub-micrometre organic aerosol composition data from the boreal forest characterized using a machine-learning approach. Atmospheric Chemistry and Physics 21, 10081–10109. https://doi.org/10.5194/acp-21-10081-2021

Isokääntä, S., Kim, P., Mikkonen, S., Kühn, T., Kokkola, H., Yli-Juuti, T., Heikkinen, L., Luoma, K., Petäjä, T., Kipling, Z., Partridge, D., Virtanen, A., 2022. The effect of clouds and precipitation on the aerosol concentrations and composition in a boreal forest environment. Atmospheric Chemistry and Physics 22, 11823–11843. https://doi.org/10.5194/acp-22-11823-2022

Kreidenweis, S.M., Walcek, C.J., Feingold, G., Gong, W., Jacobson, M.Z., Kim, C.-H., Liu, X., Penner, J.E., Nenes, A., Seinfeld, J.H., 2003. Modification of aerosol mass and size distribution due to aqueous-phase SO2 oxidation in clouds: Comparisons of several models. Journal of Geophysical Research: Atmospheres 108. https://doi.org/10.1029/2002JD002697

Lance, S., Raatikainen, T., Onasch, T. B., Worsnop, D. R., Yu, X.-Y., Alexander, M. L., Stolzenburg, M. R., McMurry, P. H., Smith, J. N., Nenes, A. Aerosol Mixing State, Hygroscopic Growth and Cloud Activation Efficiency during MIRAGE 2006. Atmospheric Chemistry and Physics 2013, 13 (9), 5049–5062. https://doi.org/10.5194/acp-13-5049-2013.

Leaitch, W.R., 1996. Observations Pertaining to the Effect of Chemical Transformation in Cloud on the Anthropogenic Aerosol Size Distribution. Aerosol Science and Technology 25, 157–173. https://doi.org/10.1080/02786829608965388

Levin, E.J.T., Prenni, A.J., Palm, B.B., Day, D.A., Campuzano-Jost, P., Winkler, P.M., Kreidenweis, S.M., DeMott, P.J., Jimenez, J.L., Smith, J.N., 2014. Size-resolved aerosol composition and its link to hygroscopicity at a forested site in Colorado. Atmospheric Chemistry and Physics 14, 2657–2667. https://doi.org/10.5194/acp-14-2657-2014

Liwendahl, M., 2023. The seasonality and inter-annual variation of aerosol particle size distributions in boreal forest. BSc thesis, Department of Environmental Science, Stockholm University.

Massling, A., Lange, R., Pernov, J.B., Gosewinkel, U., Sørensen, L.-L., Skov, H., 2023. Measurement report: High Arctic aerosol hygroscopicity at sub- and supersaturated conditions during spring and summer. Atmospheric Chemistry and Physics 23, 4931–4953. https://doi.org/10.5194/acp-23-4931-2023

Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E., 1953. Equation of state calculations by fast computing machines. Journal of Chemical Physics 21, 1087-1092.

Paramonov, M., Aalto, P.P., Asmi, A., Prisle, N., Kerminen, V.-M., Kulmala, M., Petäjä, T., 2013. The analysis of size-segregated cloud condensation nuclei counter (CCNC) data and its implications for cloud droplet activation. Atmospheric Chemistry and Physics 13, 10285–10301. https://doi.org/10.5194/acp-13-10285-2013

Paramonov, M., Kerminen, V.-M., Gysel, M., Aalto, P.P., Andreae, M.O., Asmi, E., Baltensperger, U., Bougiatioti, A., Brus, D., Frank, G.P., Good, N., Gunthe, S.S., Hao, L., Irwin, M., Jaatinen, A., Jurányi, Z., King, S.M., Kortelainen, A., Kristensson, A., Lihavainen, H., Kulmala, M., Lohmann, U., Martin, S.T., McFiggans, G., Mihalopoulos, N., Nenes, A., O'Dowd, C.D., Ovadnevaite, J., Petäjä, T., Pöschl, U., Roberts, G.C., Rose, D., Svenningsson, B., Swietlicki, E., Weingartner, E., Whitehead, J., Wiedensohler, A., Wittbom, C., Sierau, B., 2015. A synthesis of cloud condensation nuclei counter (CCNC) measurements within the EUCAARI network. Atmospheric Chemistry and Physics 15, 12211–12229. https://doi.org/10.5194/acp-15-12211-2015

Partridge, D.G., Vrugt, J.A., Tunved, P., Ekman, A.M.L., Struthers, H., Sorooshian, A., 2012. Inverse modelling of cloud-aerosol interactions – Part 2: Sensitivity tests on liquid phase clouds using a Markov chain Monte Carlo based simulation approach. Atmospheric Chemistry and Physics 12, 2823–2847. https://doi.org/10.5194/acp-12-2823-2012

Ray, A., Pandithurai, G., Mukherjee, S., Kumar, V.A., Hazra, A., Patil, R.D., Waghmare, V., 2023. Seasonal variability in size-resolved hygroscopicity of sub-micron aerosols over the Western Ghats, India: Closure and parameterization. Science of The Total Environment 869, 161753. https://doi.org/10.1016/j.scitotenv.2023.161753

Riuttanen, L., Hulkkonen, M., Dal Maso, M., Junninen, H., Kulmala, M., 2013. Trajectory analysis of atmospheric transport of fine particles, SO_2, NO_x and O_3 to the SMEAR II station in Finland in 1996–2008. Atmospheric Chemistry and Physics 13, 2153–2164. https://doi.org/10.5194/acp-13-2153-2013

Roelofs, G.-J. a N., Lelieveld, J., Ganzeveld, L., 1998. Simulation of global sulfate distribution and the influence on effective cloud drop radii with a coupled photochemistry sulfur cycle model. Tellus B 50, 224–242. https://doi.org/10.1034/j.1600-0889.1998.t01-2-00002.x

Siegel, K., Neuberger, A., Karlsson, L., Zieger, P., Mattsson, F., Duplessis, P., Dada, L., Daellenbach, K., Schmale, J., Baccarini, A., Krejci, R., Svenningsson, B., Chang, R.; Ekman, A. M. L., Riipinen, I., Mohr, C. Using Novel Molecular-Level Chemical Composition Observations of High Arctic Organic Aerosol for Predictions of Cloud Condensation Nuclei. Environ. Sci. Technol. 2022, 56 (19), 13888–13899. https://doi.org/10.1021/acs.est.2c02162.

Spitieri, C., Gini, M., Gysel-Beer, M., and Eleftheriadis, K.: Annual cycle of hygroscopic properties and mixing state of the suburban aerosol in Athens, Greece, Atmos. Chem. Phys., 23, 235–249, https://doi.org/10.5194/acp-23-235-2023, 2023.

Timonen, H., Saarikoski, S., Tolonen-Kivimäki, O., Aurela, M., Saarnio, K., Petäjä, T., Aalto, P.P., Kulmala, M., Pakkanen, T., Hillamo, R., 2008. Size distributions, sources and source areas of

water-soluble organic carbon in urban background air. Atmospheric Chemistry and Physics 8, 5635–5647. https://doi.org/10.5194/acp-8-5635-2008

Vrugt, J. A., ter Braak, C.J.F., Diks, C.G.H., Robinson, B. A., Hyman, J. M., Higdon, D., 2009. Accelerating Markov Chain Monte Carlo Simulation by Differential Evolution with Self-Adaptive Randomized Subspace Sampling. International Journal of Nonlinear Sciences and Numerical Simulation, 10(3), 273-290. https://doi.org/10.1515/IJNSNS.2009.10.3.273

Wang, J., Cubison, M. J., Aiken, A. C., Jimenez, J. L., Collins, D. R. The Importance of Aerosol Mixing State and Size-Resolved Composition on CCN Concentration and the Variation of the Importance with Atmospheric Aging of Aerosols. Atmospheric Chemistry and Physics 2010, 10 (15), 7267–7283. https://doi.org/10.5194/acp-10-7267-2010.

Wonaschuetz, A., Sorooshian, A., Ervens, B., Chuang, P.Y., Feingold, G., Murphy, S.M., de Gouw, J., Warneke, C., Jonsson, H.H., 2012. Aerosol and gas re-distribution by shallow cumulus clouds: An investigation using airborne measurements. Journal of Geophysical Research: Atmospheres 117. https://doi.org/10.1029/2012JD018089

Wu, Z.J., Zheng, J., Shang, D.J., Du, Z.F., Wu, Y.S., Zeng, L.M., Wiedensohler, A., Hu, M., 2016. Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China, during summertime. Atmospheric Chemistry and Physics 16, 1123–1138. https://doi.org/10.5194/acp-16-1123-2016

Yli-Juuti, T., Mielonen, T., Heikkinen, L., Arola, A., Ehn, M., Isokääntä, S., Keskinen, H.-M., Kulmala, M., Laakso, A., Lipponen, A., Luoma, K., Mikkonen, S., Nieminen, T., Paasonen, P., Petäjä, T., Romakkaniemi, S., Tonttila, J., Kokkola, H., Virtanen, A., 2021. Significance of the organic aerosol driven climate feedback in the boreal area. Nat Commun 12, 5637. https://doi.org/10.1038/s41467-021-25850-7