We want to thank the reviewers for their comments. Addressing those comments has improved the quality of the manuscript. Below, we list each reviewer's comment (regular font), followed by our response (indented, **bold** font), followed by corresponding changes in the revised manuscript (indented, blue font). RL and RSL represent the line number in the revised main manuscript and SI, respectively.

Anonymous Referee #1

This manuscript by Cheng et al. collected samples over three years at an interesting site (North Atlantic). They also used various measurement techniques (e.g., CCSEM-EDS and STXM-NEXAFS) for a significant number of samples as well as modeling and provided a unique conclusion regarding particle phases. Thus, I think this study will be an interesting contribution to our understanding of atmospheric aerosol particles.

We appreciate the positive feedback from the reviewer. Below are our responses to each comment:

Major comments.

1. I suggest including a discussion regarding the effect of relative humidity (RH) on the particle phase. Aerosol particle phases are sensitive to the RH when collected (e.g., Bateman et al. 2014 in the reference list). Inorganic aerosol particles can deliquesce, and organic particles can absorb water depending on RH, changing the shapes of sampled particles. The RH values should be obtained from an in-site measurement, if available, (not from a model result with a low spatial resolution) as the particle hygroscopicity is sensitive to the exact RH during the sampling. Although most particles should be in dry condition judging from Table S2, hysteresis phenomena may affect the particle hygroscopicity (e.g., Fig. S10). The current manuscript has a limited discussion regarding the ambient RH, and I suggest more discussion on RH effects for the particle phases. In addition, surface tension may also influence the height of the aspect ratio of sampled particles, and some discussion regarding surface tension may be useful.

> **We appreciate the reviewer for bringing up this point, which was not adequately discussed in the manuscript. We agree with the reviewer that particle phases are sensitive to relative humidity (RH) when collected. Based on the RH during sample collection, the shape of the particles will deform upon impaction, which we use to estimate their phase state (Cheng et al., 2021). We agree with the reviewer that the particles we investigated in this study might experience hysteresis phenomena that could affect the particle hygroscopicity and thus the phase state of particles during transport. RH-dependent phase state of ambient particles is an important topic and will be considered in future studies. However, as the reviewer suggested, we added the following sentences about RH-dependent phase states at the end of Line 375:**
>
>> RL406-411: "Besides these two potential explanations, many aspects can still affect the phase state of particles. Particles can transit from solid to semisolid to liquid state when RH and/or temperature increase (Koop et al., 2011). Thus, these particles might transit to different phase states if the ambient conditions change. For example, measured RH at OMP was highest during the S2 and S3 sample collection periods (61.3±2.4 % and 67.3±2.3 %, respectively) and lowest during the S4-2 and S4-3 collection periods (6.6±0.3 % and 9 %, respectively). The lower RH at OMP during S4-2 and S4-3 collection periods might help explain

> the observation of more abundant solid state particles in S4-2 and S4-3 rather than S2 and S3."

For the meteorological data, we added temperature and RH values measured at OMP during the specific sample collection periods (Table S2). However, meteorological data during transport were not experimentally accessible and were, therefore, extracted from the meteorology fields of the Global Forecast System (GFS) files (see Sect. 2.2) as the best option available to us. We agree that hysteresis phenomena can affect particle hygroscopicity, but these phenomena, at least during transport, cannot be investigated within the data availability of this study. As the reviewer suggested, we added the hourly variation of temperature and relative humidity as measured directly at OMP in the supplementary information (Fig. S2 in revision).

We also agree with the reviewer that surface tension plays an important role in the particle shape since different materials will have different surface tension, resulting in different contact angles at the substrate surface and liquid particle's surface. These are complex issues that depend on the properties of the particle material. However, we use Carbon Type-B TEM grids (Ted Pella Inc.) for our phase state assessment since our previous study (Cheng et al., 2021) was conducted with the same type of grids that have hydrophobic and oleophobic surfaces. Thus, the same aspect ratio threshold we found in our previous study should be appropriate. To make this point clear, we modified the sentence in Line 234:

> RL251-254: "These thresholds were determined based on known RH-dependent glass transition of organic materials (e.g., Suwannee River fulvic acid (SRFA)) on the same grids type (Carbon Type-B TEM grids, Ted Pella Inc) used in this study (Cheng et al., 2021). Using the same grid type should minimize the effect of changes in surface tension and wettability, which might potentially affect the contact angle and therefore the aspect ratios."

2. The authors discuss the CO source contributions using the FLEXPART model. Although the model is acceptable and useful for CO, I wonder if it can be used to interpret the source of aerosol particles, especially for those with aging more than ten days. CO is gas and will not be removed from the atmosphere. On the other hand, a fraction of aerosol particles will be removed by mainly wet depositions during the transport with more than ten days (Table 1). Thus, it is not sure if the estimates of "contribution of source" in the table are valid for aerosol particles. Some explanation will be needed here.

We agree with the review's comment on FLEXPART CO and the differences in chemical nature between CO and aerosols. We did not make it clear enough in the context that FLEXPART CO results in Table 1 are used as "*indicators*" of relative contributions from anthropogenic or biomass burning emissions and aging time during the transport instead of *quantitative estimates* of aerosol lifetime or mass. However, these indicators can reflect the aerosol sources and aging time because primary aerosols and aerosol precursors (NO_x, NH_4, BC, etc.) are heavily co-emitted with CO in anthropogenic and biomass burning emission sources. Comparisons of such indicators across the aerosol samples (in Table 1) reveal very useful information about the air mass source and transport history, which helps interpret the observed aerosol properties we got in the lab. Another reason for the long aging time (>10 days) reported for FLEXPART CO is due to the long simulation time we configured on

purpose. We track air mass transport back to 20 days for all samples. Aerosol lifetime against wet removal can be as short as a couple of days in the lower troposphere, but it can be extended to weeks in the free troposphere for long-range transport.

To make this clear, we have added the following:

> RL263-265: "The plume ages and relative contributions from anthropogenic and biomass burning emissions can reveal air mass sources, types, and transport patterns. Although they do not directly reflect aerosol sources and ages, they are still good indicators to help interpret observed aerosol properties, especially in the comparisons across different samples."

3. Quality of Supporting information is a problem. The figures and captions include many errors, including the title (!), which is different from the manuscript. I wonder if the authors submitted the correct one or a draft version.

We do apologize for the quality of SI. We have revised the SI in the new submission.

Specific comments.

4. Line 158. "an environmental SEM (ESEM) equipped with a FEI Quanta digital field emission gun, operated at 20 kV" and line 213 " Environmental Scanning Electron Microscopy (ESEM, Quanta 3D, Thermo Fisher)"

Are they different ESEM or the same one? The ESEM in line 158 is used for the CCSEMEDS? It isn't very clear, and please specify them clearly.

We used the same ESEM for both CCSEM-EDX and tilted imaging experiments. We revised line 158 and line 213 as below:

> RL167-168: "We utilized an environmental SEM (ESEM, Quanta 3D, Thermo Fisher) equipped with a FEI Quanta digital field emission gun, operated at 20 kV and 480 pA."
>
> RL226-228: "We utilized tilted view imaging combined with the ESEM to estimate the phase state of particles based on their shapes. For each sample, we evaluated more than 150 randomly selected particles. Moreover, tilted view imaging and CCSEM-EDX experiments were performed independently."

5. Line 193 "inorganic components (In)"

In, IN, and "inorganics" are inconsistently used. For example, In is in line 207, "inorganics" is used in line 209, and IN is in line 324. In addition, "In" is confusing as it is like In (preposition).

We are sorry for the confusion. The revised manuscript uses IN for inorganic components retrieved from STXM-NEXAFS spectroscopy.

6. Line 296-297. "Our particles are internally mixed based on tilted transmission electron microscopy (TEM, the titled angle was 70°) (Fig. S8)."

Please explain how to see Fig. S8, i.e., how the TEM image indicates internally mixed particles. Same for the description in line 328

Thanks for bringing up this point. We have revised the manuscript:

RL316-319: "Tilted transmission electron microscopy (tilted angle 70°) images show that inorganic inclusions (e.g., sea salt, nitrate, sulfate, dust) are internally mixed and coated by organics (Fig. S9)."

And:

RL351-352: "This observation is consistent with our tilted TEM images showing that EC and IN inclusions were internally mixed with organics (Fig. S9)."

We also revised Fig. S8 (Fig. S9 in revision) and its caption:

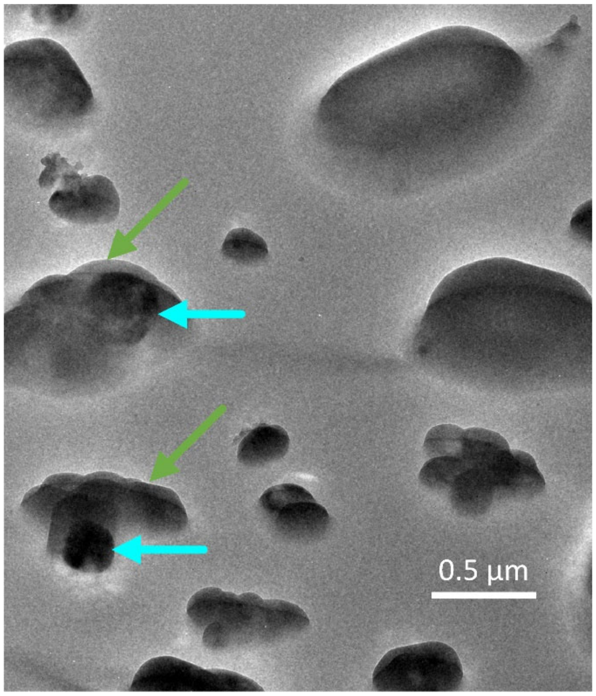


Figure S9. Representative tilted transmission electron microscopy (TEM) images (tilt angle 70°) for S3-2. Green arrows indicate examples of thin organic coatings, and cyan arrows indicate examples of internally mixed inorganic inclusions (e.g., sea salt, nitrate, sulfate, dust, cycled by solid red lines) coated by organics.

7. Line 317-319. "Sulfate (CNOS and sea salt with sulfate) particles are also very abundant in all samples (~18 to 34 %), suggesting that these particles were involved in cloud processing (Ervens et al., 2011; Kim et al., 2019; Lee et al., 2011, 2012; Zhou et al., 2019)."

   I am not sure why they were involved in cloud processing. Sulfate can originate from various processes. Does it mean organosulfates (CNOS)??

We appreciate the reviewer's valid comment, and we agree with the reviewer that sulfate can originate from various processes. With the CCSEM-EDX result, we cannot confirm if sulfates are organic. However, during the long-range transport of aerosol, the particles are expected to experience several cloud cycles. We modified the sentence as follows:

> RL338-340: "Sulfate (CNOS and sea salt with sulfate) particles are also abundant in all samples (~18 to 34 %), suggesting that these particles were possibly involved in cloud processing (Ervens et al., 2011; Kim et al., 2019; Lee et al., 2011, 2012; Zhou et al., 2019)."

8. Line 324-325. states of OC (green), IN (blue), and EC (red) found in S3-3 and S4-2, which are (a) organic particle (green), (b) EC core (red) and coated by OC (green), (c) internally mixed EC (red) and In (cyan) coated by OC (green), and (d) In (cyan) coated by OC (green).

   Both "cyan" and "blue" are used for In. I think it should be blue or IN and In are different??

   Sorry for the confusion. We have corrected our content and used cyan for IN in Fig. 4.

   > RL344-347: "Figure 4 shows STXM-NEXAFS Carbon K-edge chemical speciation maps and spectra for four typical particle mixing states of OC (green), IN (cyan), and EC (red) found in S3-3 and S4-2, which are (a) organic particle (green), (b) EC core (red) and coated by OC (green), (c) internally mixed EC (red) and IN (cyan) coated by OC (green), and (d) IN (cyan) coated by OC (green)."

9. Line 373-375. "These results suggest that apart from environmental factors, the inorganic components, the molecular weight of organic compounds, and the O/C ratio (or aging time) all affect the phase state of internally mixed particles."

   They are true at specific RH values. For example, < RH 80%, ammonium sulfate is solid (crystal), and > RH 80%, they become liquid (deliquesce). These factors change the specific RH % that changes the particle phase state. Although it says "apart from environmental factors", some words about RH will be useful. Please see my comment 1.

   Please see our response to comment 1. We added a discussion about the ambient RH on the phase state of the particles.

10. Line 409-410. "Typically, particles with the same area equivalent diameter but higher TCA are more viscous (more solid-like) since they are less flat in shape (Fraund et al., 2020; Tomlin et al., 2020)."

    The particle height may be also influenced by its surface tension if they are liquid. Please see my comment 1.

    Please see our response to comment 1.

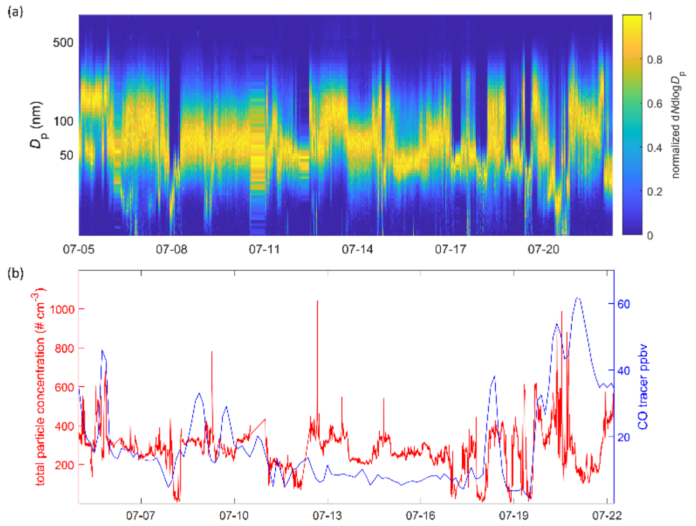
11. Figure 1. Please indicate what are the color indicate and what are the boxes and numbers.

We revised the caption of Fig. 1, Fig. S6, and Fig. S7 in revision:

> **"Figure 1. Column-integrated residence time over the 20-day transport time retrieved from FLEXPART retroplumes for 2017. (a) S3-1, (b) S3-2, (c) S3-3, (d) S3-4, (e) S4-1, (f) S4-2, (g) S4-3, (h) S4-4. The vertical distribution of the retroplumes residence time at given upwind times are shown in Fig. S6. The color bars indicate the ratio of column integrated residence time to the maximal residence time at each upwind time in the logarithmic scales, and the X-axis and y-axis represent latitude and longitude, respectively. The numbers indicate locations of the highest vertically integrated residence time on a given upwind day."**
>
> **"Figure S6. The vertical distribution of the retroplumes residence time at given upwind times retrieved from FLEXPART retroplumes for (a) S3-1, (b) S3-2, (c) S3-3, (d) S3-4, (e) S4-1, (f) S4-2, (g) S4-3, and (h) S4-4. The color bar represents the ratio of residence time to the highest residence time across the height scale at each upwind time. The black lines indicate the average height of the plumes during transport."**
>
> **"Figure S7. Column-integrated residence time over the 20-day transport time and the vertical distribution of the retroplumes residence time at given upwind times retrieved from FLEXPART retroplumes for Pico 2015. (a, b) S1, (c, d) S2, (e, f) S3, (g, h) S4, (i, j) S5, (k, l) S6. For panels a, c, e, g, and i, the color bars indicate the ratio of column integrated residence time to the maximal residence time at each upwind time in the logarithmic scale, and the X-axis and y-axis represent latitude and longitude, respectively. For panels b, d, f, h, j, and l, the color bars represent the ratio of residence time to the highest residence time across the height scale at each upwind time, and the black lines indicate the average height of the plumes during transport."**

12. Figure 2. These "solid black cycles" (circle?) are difficult to see with dark blue background.

Based on all comments regarding Fig.2, we have revised Fig. 2 and its caption as below:



“Figure 2. (a) Normalized particle size distribution from 10 to 800 nm measured from SMPS measurements, and (b) SMPS derived total particle concentrations (left y-axis, red line) and CO tracer retrieved from FLEXPART simulations (right y-axis, blue line) from 05 to 21 July 2017.”

13. Figure 3. Although I can imagine what the inserted normalized number fractions with size distributions in the upper right of each panel mean, it is better to have some explanation, especially the meanings of Y-axes.

Thanks for pointing that out. We have revised the caption:

“Figure 3. Chemically-resolved size distributions were inferred from the CCSEM-EDX data for 2017. (a) Fraction of different particle types for all samples. Normalized chemically-resolved size distributions of (b) S3-1, (c) S3-2, (d) S3-3, (e) S3-4, (f) S4-1, (g) S4-2, (h) S4-3, and (i) S4-4. Inserts represent the normalized number fraction of different particle types as a function of particle size.”

14. Figure 4. Please indicate which samples were used for each panel.

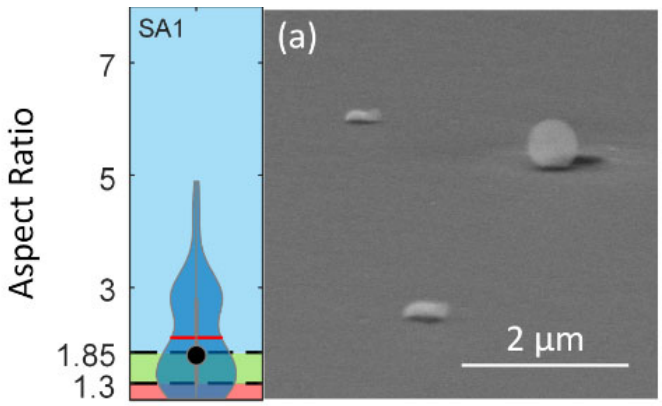
We revised the caption of Fig. 4:

“Figure 4. Representative STXM-NEXAFS spectra of (a) organic particle (green), (b) EC core (red) coated by OC (green), (c) internally mixed elemental carbon (red), and IN (cyan) core coated by OC (green), and (d) IN (cyan) core coated by OC (green) from Pico 2017 S3-3 and S4-2 samples. White scale bars represent 500 nm.”

15. Figure 5. Is panel (b) SA1 or SA2?

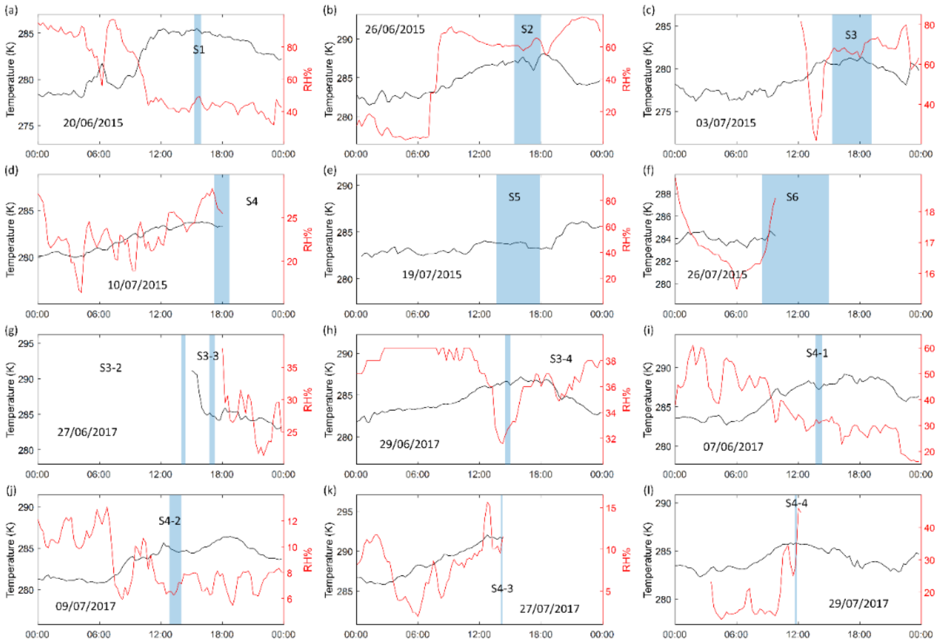
Table 1 indicates that 29.8% of SA1 particles are solid. Although I see SA1 includes relatively more semisolid particles, I cannot see solid particles. Could you indicate some examples of solid particles in the SEM images using ambient samples?

We appreciated the reviewer's comment. We revised Fig. 5 to show the presence of solid particles. The revised portion is shown below:



I also suggest adding RH values when collected for these samples.

Thanks for your comments. We have corrected panel (b) from SA1 to SA2. We have included available RH and temperature in Table S1 and S2. We also added a plot that shows the available hourly variation of temperature and RH during the sampling days:



"Figure S2. Hourly variation of temperature and relative humidity for available days. Shaded areas represent the sample collection periods."

16. Figure 6. In panel (a), there are 3 or 4 solid particles in SA2, but the solid particle % in SA2 is 0.0 in Table 1. Are they correct?

Sorry for the confusion. In Table 1, the percentage of particles in each stage is determined by the titled image, which might have different results than the TCA estimated phase state due to technique differences and the difference in the investigated area on the grid. To make that clear, we modified the caption of Table 1 as below:

> **"Table 1. Summary of Pico 2014, 2015, and 2017 samples. "S3-" and "S4-" for Pico 2017 samples were collected on stage 3 (50 % cut-off size: >0.15 µm) and stage 4 (50 % cut-off size: >0.05 µm) of a four-stage cascade impactor (MPS-4G1), respectively. Pico 2014 samples were collected on stage 3, and Pico 2015 samples were collected on stages 3 and 4 of the cascade impactor. Particle percentages of different phase state were retrieved based on tilted imaging. Additional information on sampling time and conditions and fractions of different species in each sample based on CCSEM-EDX and STXM-NEXAFS is listed in Tables S1 and S2."**

Supplementary information

I do not think I could indicate all errors. Please check the data carefully (or maybe it is a wrong file?).

17. The title is different from the main text.

    We updated the title and uploaded a new supplementary information file. We carefully reviewed the supplementary section and corrected all the mistakes we could find.

18. Line 21. "where Tg,w is equal to 136 K, is the Tg for pure water," Tgw is 136K, correct? " is the Tg for pure water " is correct?

    We have revised the sentence as below:

    > RSL51-52: "where $T_{g,w}$ is the T_g for pure water, k_{GT} is the Gordon-Taylor constant, κ_{org} is the CCN-derived hygroscopicity parameter of the organic fraction, ρ_{org} and ρ_w are the density of water and organic material, respectively."

19. Equation S3. C_real=(123.2±1.4)−(4.738±0.214)log(H)−(1.186±0.02)C_measured.

    This equation indicates that less measured C atomic percentages yield a high "real" C percentage. I.e., if a particle includes no measured carbon percent (0%), it will have ~100 % of real C percent (by assuming H = 1). Although I do not have a way to check the accuracy, it is difficult to believe the result without more explanation. The calculation may influence the results in Figure S2, in which a fraction of particles consists of only C (no O nor other elements).

    The equation S4 is also questionable. How can O=0%, which is seen in Fig. S2, be achieved?

    O_real=(13.68±0.18)−(0.3413±0.0636)log(H)+(0.2579 ± 0.0072)O_measured (S4)

    Thanks for pointing this issue out. Theoretically, we can get 100% of C even if we do not detect any C by assuming H = 1. However, if we do not detect C and O, or C and

O are equal to 100%, we do not do any correction. Moreover, if corrected C and O fractions are either smaller than 0 or larger than 100%, we will discard these data since they are not realistic. We admit this correction method has limitations, and it is based on statistical analysis with some assumptions that CNQX disodium salt particles are perfect spheric, and all particles have the same aspect ratio. However, this is still a reasonable method and provides a better estimate than the raw data. We agree with the reviewer that some explanations would help to clarify the limitations and assumptions. To this aim, we added the following sentence in SI:

> RSL36-44: "Moreover, we only perform this correction when $C_{measured}$, $O_{measured}$, and $N_{measured}$ are not equal to 0 or 100% since these cases are not realistic. Furthermore, if corrected C, N, and O values are less than 0 or greater than 100%, we discard these data since they are also not realistic. Therefore, we applied this correction to measured C, N, and O, and after correction, we re-normalized the fraction of all elements. It should be kept in mind that this correction method is based on empirical fittings with assumptions that CNQX disodium salt particles are perfect spheric, and all particles have the same aspect ratio. The first assumption might lead to overestimating the particle height of CNQX disodium salt particles, and the second one might misrepresent the particle shape. Moreover, using one standard might not fully represent the chemical complexity of ambient particles. Thus, more data from different standards are necessary for improving this method."

20. Line 49-51. "Since the particles are spheric, the measured area equivalent diameter (μm) is approximately equal to the height of particles. Therefore, when applying the correction function on our CCSEM-EDX data, we need to estimate the H by dividing the longest diameter retrieved from CCSEM-EDX measurement by the aspect ratio retrieved from tilted images (see Sect. 3.3.2). "

    Do you have all aspect ratio data for all EDS measured particles? I think the aspect ratio was measured using ESEM, and the EDS was by CCSEM-EDS.

    Thanks for your comment. We have all aspect ratio data from CCSEM-EDX measurements from the top-view measurement. We used the same instrument (ESEM) for tilted view imaging and CCSEM measurements. However, these measurements are performed separately. The current configuration of the instrument does not allow for simultaneous measurements. We added the following text to the revised manuscript.

    > RL227-228: "Moreover, tilted view imaging and CCSEM-EDX experiments were performed independently."

21. Table S1. Are there CCSEM data that can be listed for these samples?

    Thanks for your comment. CCSEM data are reported in table S2 for 2017 samples, and data for 2014 samples are already published (Lata et al., 2021). Data for 2015 samples will be published in a separate manuscript focusing on aerosol optical properties. All CCSEM-EDX raw data are available upon request.

22. Figure S2. These data, especially for C, look different between those from SA1 to S6 and those from S3-1 to S4-4 (different sampling periods). Are there any technical differences?

Potassium (K) may be used for a biomass-burning tracer. Have you checked it?

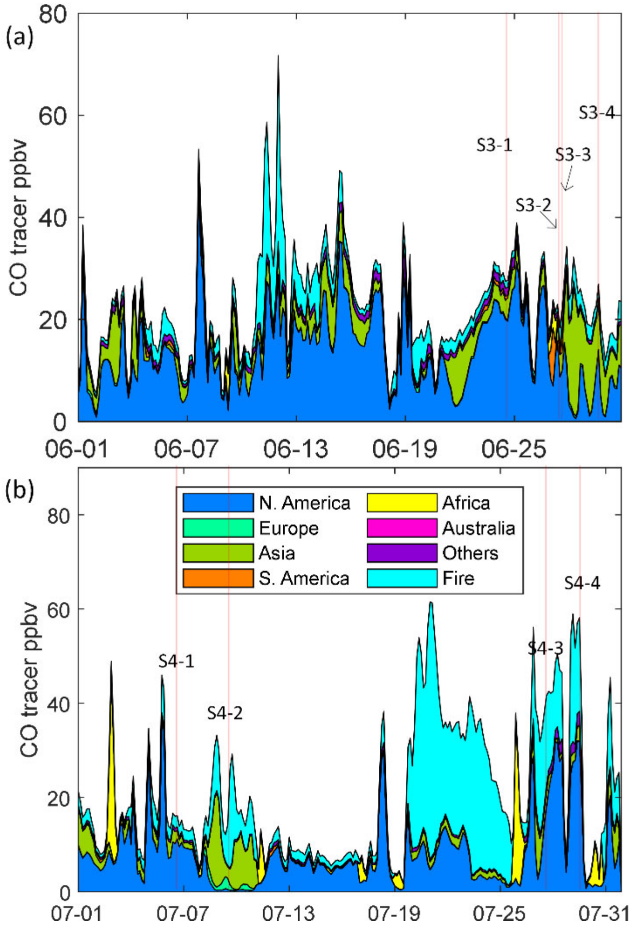
We appreciate that reviewer brought this question up. We agree with the reviewer that the C looks different for SA1 to S6 (collected in 2014 and 2015) than S3-1 to S4-4 (collected in 2017). Data were acquired with the same instrument and same configuration (e.g., same working distance, accelerating voltage, and beam current), so we think that there is no technical difference rather than the difference in the sample itself. We also agree with the reviewer that potassium is a good indicator of biomass burning emission. However, the elemental percentage of K is very low (less than 0.5%), below the sensitivity of the measurements. This is why we did not specifically use K as a tracer for this study.

23. Figure S3. If you go to "No" and "No," you will find a question "Al+Si+Fe+Fe>Na", where you have double Fe.

Thanks for pointing this out. We have corrected Fig. S3 (Fig. 4 in revision) to represent the right particle classification logic.

24. Figure S4. Panel (a). There is "S-2," but it should be "S3-2." Y-axis should have "100" instead of "00". The caption should be "June" instead of "Jun."

Thanks for your comment. We have revised Fig. S4 (Fig. S5 in revision) and its caption.



"Figure S5. FLEXPART CO tracer simulation for (a) June 2017 and (b) July 2017."

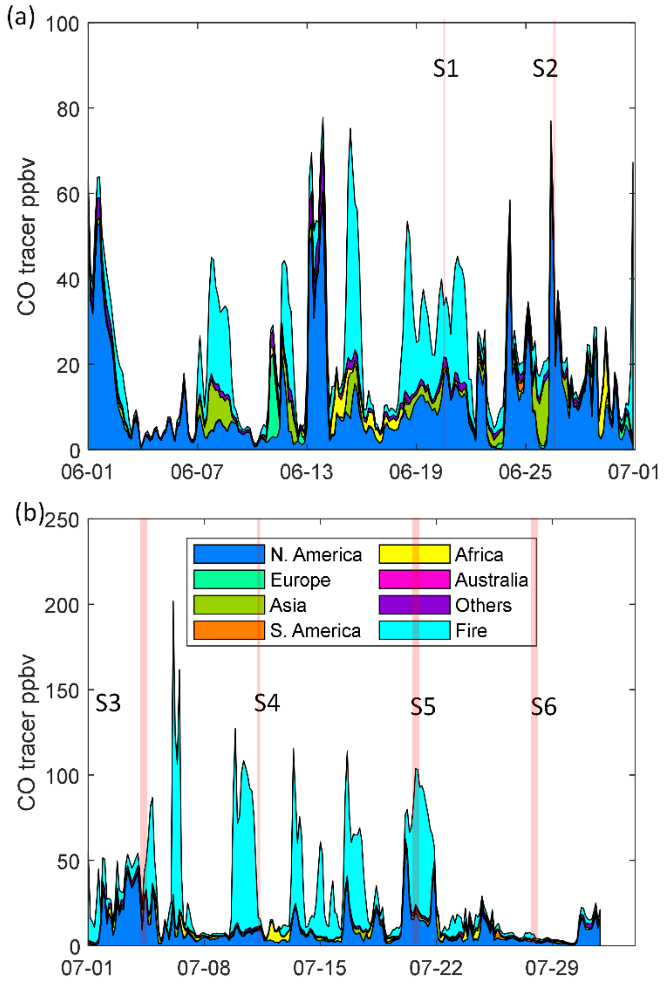
25. Figure S5. The caption indicates from (a) to (i), whereas the panels are from (a) to (h).

Thanks for your comment. We revised the caption as below (Fig. S6 in revision):

"Figure S6. The vertical distribution of the retroplumes residence time at given upwind times retrieved from FLEXPART retroplumes for (a) S3-1, (b) S3-2, (c) S3-3, (d) S3-4, (e) S4-1, (f) S4-2, (g) S4-3, and (h) S4-4 for Pico 2017. The color bar represents the ratio of residence time to the highest residence time across the height scale at each upwind time. The black lines indicate the average height of the plumes during transport."

26. Figure S7. "Jun" should be "June." Panel (a) and (b) is upside down. The legend in the panel (a, bottom) is overlapped with the plot.

Thanks for pointing this out. We have revised Fig. S7 (Fig. S8 in revision) and its caption as below:



“Figure S8. FLEXPART CO tracer simulation for (a) June 2015 and (b) July 2015.”

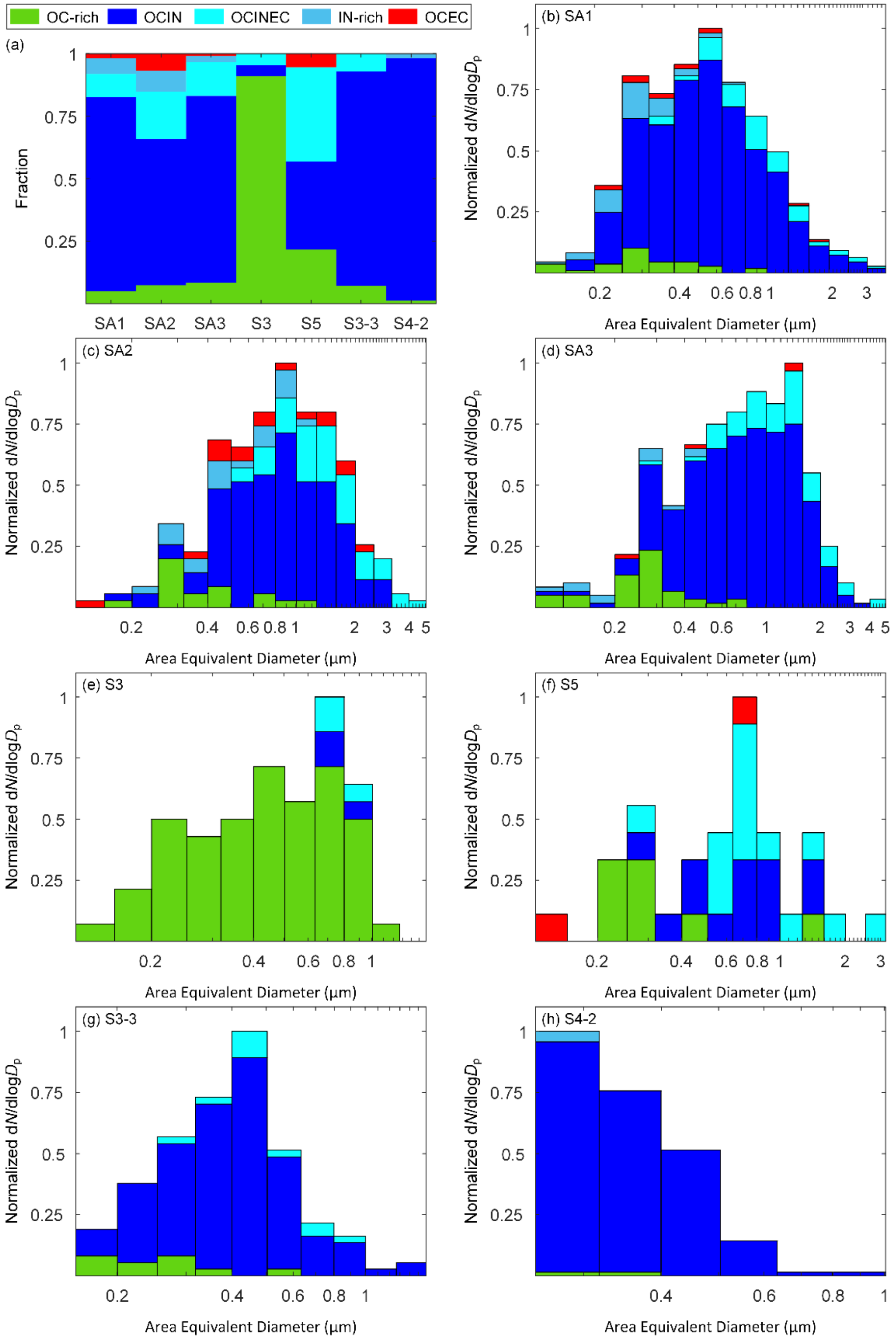
27. Figure S8. Please indicate where we should see. Please see my comment 6.

Thanks for your valid comment. We added cyan arrows in Fig. S9 to indicate inorganic inclusions and green arrows to indicate organic coatings. We have revised the caption of Fig S8 (Fig. S9 in revision).

> **“Figure S9. Representative tilted transmission electron microscopy (TEM) images (tilt angle 70°) for S3-2. Green arrows indicate examples of thin organic coatings, and cyan arrows indicate examples of internally mixed inorganic inclusions (e.g., sea salt, nitrate, sulfate, dust, cycled by solid red lines) coated by organics.”**

28. Figure S9. The colors in OCInEC and In are nearly the same and cannot be distinguished. For example, in panel (f), it is difficult to identify if the light blue is OCInEC or In.

Thanks for your comment. We have revised Fig. S9 (Fig. S10 in revision) as below:



29. Figure S10. "Mean ambient temperature (blue)"

    In the caption, the temperature is "blue," but in the legend, it is green. Same for Tg,org.

    "(g) S3-2, (g) S4-3, (h) S4-4, and (i) S4-54. " There are two (g) in the caption. (i) should be S4-5 but no (i) in the panel (!!). "uncertainties in RH (See SI). " Which SI should we see. we are now in SI.

    Thanks for your comment. We have revised the caption of Figure S10 (Fig. 11 in revision):

    > **"Figure S11. Mean ambient temperature (green) and relative humidity (RH) (red) extracted from the GFS analysis along the FLEXPART modeled path weighted by the residence time and the predicted RH-dependent $T_{g,org}$ values (blue) for (a) S3-1, (b) S3-2, (c) S3-3, (d) S3-4, (e) S4-1, (f) S3-2, (g) S4-3, and (h) S4-4. The blue and red shaded areas represent one standard deviation of ambient temperature and RH from the GFS analysis. The green shaded areas represent uncertainties of predicted $T_{g,org}$ estimated from the range of $T_{g,org}$(RH = 0%) and uncertainties in RH."**

30. References. The reference style is different from that of ACP.

    Thanks for pointing out this. We have corrected the reference style.

31. Line 134 "Zieger, P. and Va, O" Please check the authors' name.

    Thanks for mentioning this, and we have removed this reference since we do not cite it in the text.