Comments to the Author:

Dear author, co-authors,

Having received a review of your revised version of your paper ACP-2020-233 it has become further clear that, in submitting your revision as well as your response to previous comments on the paper but also additional files such as the supplement, that you have not properly handled the shared feedback. Besides these observations also being explicitly mentioned in this new review, I also noticed that in your latest reply you didn't address my editors comments on a potential mix up of document versions. I have actually considered also for this reasons to reject the paper but having received now again this (constructive) review I give you once more again the opportunity to properly handle all those comments and then resubmit in due time a consistent selection of files including your replies (including an explanation what has been going wrong), a revision as well as a supplement that contain the changes as being addressed in your response letter. Hope that this then really allows to focus on the content features of your ms submitted for publication in ACP.

Laurens Ganzeveld

Dear editor,

Thank you for giving us the opportunity to revise the manuscript.

In the previous revised version, the reviewers' comments and suggestions were mainly focused on technical issues of the measurements and the comparisons between different instruments. However, the story of our manuscript was the chemistry of aerosol-boundary layer-solar radiation feedback. Considering the length of the manuscript, we responded the reviewers' comments only in response letter but we did not put the all changes into our revised manuscript. We really apologize for this.

In this revised version, we addressed all the comments and suggestion raised by the reviewer and the editor. Also, a revised version of manuscript and supplement information were uploaded. Please find the point to point response to the reviewer's comments below, and the revised manuscript according to the comments.

Best regards,

Yonghong Wang

A point to point response to the reviewer's report

Thank you for taking the time to provide a response and clarifications to the reviewer's comments. However, despite having provided a lot of information and figures, the authors failed to integrate these changes into the manuscript. The last version of the supplementary material dates to November 11, 2020, therefore unless it has been explicitly stated in the response to reviewer's questions it is unclear if more changes have been included.

My suggestions and comments of how this manuscript can be improved are detailed below.

We thank the referee for the fruitful comments, and we think these comments and suggestions improved our manuscript. We have made these changes into our manuscript. Here are points to points responses (in blue colored), accordingly, we also revised manuscript (in blue colored).

General introduction to the sampling period: It would be useful to provide an overview section of the measurements into the results section, prior to introducing the case study measurements. The authors can then provide information on why the chosen period is a representative case study. In this section, the long term temporal trend of the ACSM measurements, the OC from Sunset and the HOMS measurements, as well as the size distributions from both measurements (DMPS +PSM), could be included.

Response: Thank you for the comments and suggestions, and the overview section of the measurements was added in the manuscript (section 3.1). In that section, long term temporal trend of the ACSM measurements, the OC from Sunset and the HOMS measurements and the size distributions DMPS were plotted and introduced.

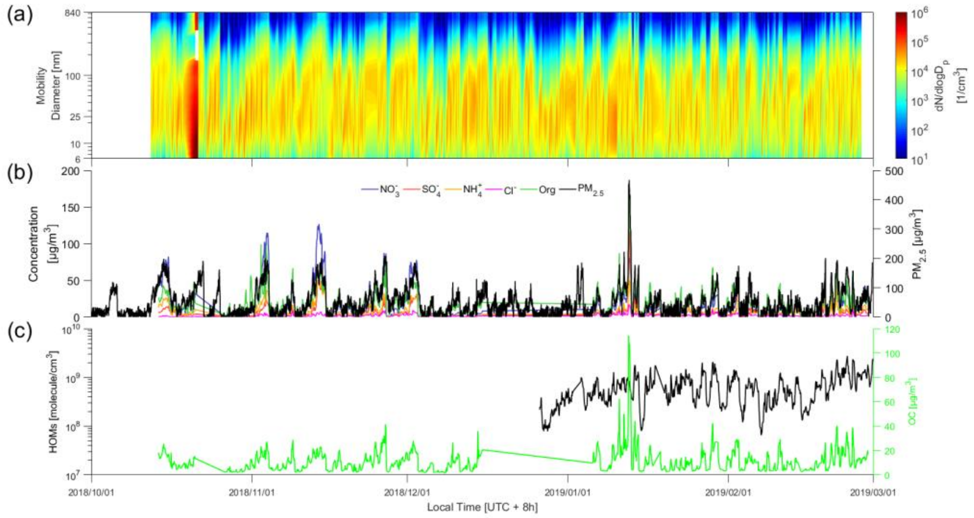

Figure R1. Time series of (a) particle number concentration distribution (PNSD) from 6 nm to 840 nm (b) chemical composition of NR_PM$_{2.5}$ and PM$_{2.5}$ mass concentrations (c) The concentrations of organic carbon (OC) and highly oxygenated organic molecules (HOMs).

Comparison with collocated measurements: The authors provided details of the comparison between the NR-PM$_{2.5}$ ACSM and the PM$_{2.5}$ from the TEOM. This comparison should at least be included in the supplementary section on the manuscript and this agreement should be referred to in the main text.

Response: We thank you for the suggestion. The comparison between the NR_PM2.5 ACSM and PM2.5 from TEOM has been added in the supplementary section and the agreement has been referred in the main text (Line: 130-131).

From the figure provided in R1, it appears that there are a small number of points (above the fit line) where the agreement between the ACSM and the TEOM are better. Do these data points correspond to any period in particular (Haze events/nonevent days)?

Response: These data points above the fit line are correspond to haze period in our research (October 1, 2018 ~ February 28, 2019). The points (above the fit line) indicate more higher ratio of NR-PM$_{2.5}$ to PM$_{2.5}$ and higher ratio of inorganic matter to NR-PM$_{2.5}$.

Is this level of agreement TEOM (or other external measurements) considered good for the PM$_{2.5}$ inlet of the ACSM, please provide references? Can the authors show this fit as a function of time.

Response: The two instruments' inlet separate $PM_{2.5}$ using the same method, which ensure constant air flow to get enough accuracy of separated particle size. The maintenance will be performed periodically. We think this the agreement is considered good for the $PM_{2.5}$ inlet of the ACSM[2-5]. Figure R2 shows the fit as a function of time.

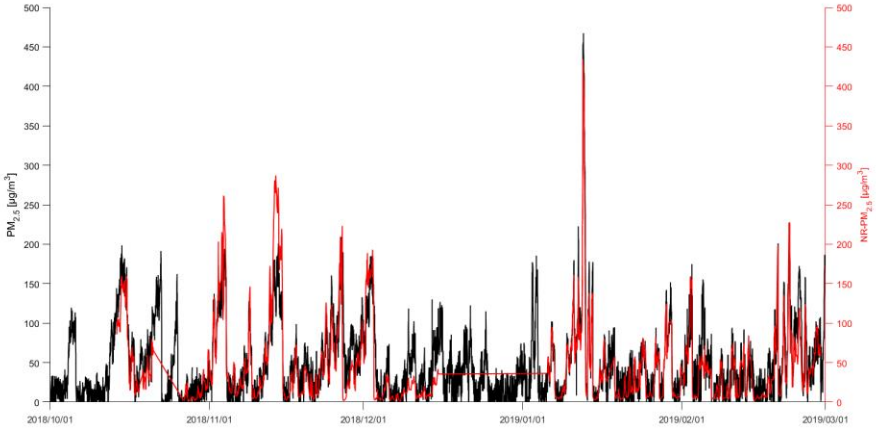

Figure R2. Time series of $PM_{2.5}$ mass concentrations and NR-$PM_{2.5}$ mass concentrations.

Regarding the CO_2 artefact. Thank you for the response to the reviewers queries, however it would be expected to include these details into the main part (or at least the supplementary part) of the manuscript, and to include information as to how this artefact varied throughout the sampling period.

Response: Thank you for the comment. These details have been added in the supplementary part.

CO_2^+/ NO_3 artefact correction of ACSM as follows:

Recently, it was discovered that NO_3 induces a positive bias on organic CO_2^+ concentrations in the AMS/ACSM systems, which can be described as a function of ambient NO_3 (μg/m^3) in combination with the CO_2^+/NO_3 ratio from pure NH_4NO_3 measurements $(CO_2^+/NO_3)_{AN}$:

For pure NH_4NO_3 aerosol from calibrations, we determined the magnitude of the CO_2^+/NO_3 artefact [6] and parametrized it as a function of the fragmentation pattern of $NO_3(NO^+/NO_2^+)$ to account for changes in the vaporizer in the ACSM:

$$(CO_2^+/NO_3)_{NH4NO3} = 0.025 \pm 0.002 \times (NO^+/NO_2^+)_{NH4NO3}$$

Then we determined the CO_2 concentration from OA using a two week moving average (NO^+/NO_2^+) from ambient observations:

$$(CO_2^+)_{OA,meas} = (CO_2^+)_{meas} - (CO_2^+/NO_3)_{NH4NO3} \times (NO_3)_{meas}$$

The correction described by the authors is a modification of that described in Pieber et al., so it is necessary to provide a reference for this modification or at least a more detailed description of this method as well as a justification of its use compared to the previous published correction.

Response: The Detailed information of the method can be found in Cai et al. (2020) [1].

The authors should show the impact of this correction on the total mass concentrations (as well as the F44 vs F43 plots) etc. What are the differences in the fit between the ACSM and TEOM with and without the mz44 artefact correction? Reword «In addition to the RIE correction, a correction for the mz44 artefact (Pieber et al., 2016) and a collection efficiency correction were applied".

Response: Response: The resulting CO_2^+ artefact bias derived from ACSM measurement should be trivial for Total mass concentration in our research (Figure 1). In the process of nitrate calibration, a signal of m44 was found, which we thought was a false signal from the instrument measurement. In the real measurement process, the effect of 44 should be deducted, in other words, the part of false signal should be subtracted from the organic matter (Cai et al., 2020;Pieber et al., 2016). Actually, we have already considered mz44 artefact correction in OA concentration calculation, where OA signs minus the mz44 signs as correction. The total mass concentrations after correction slightly below the total mass concentrations without correction.

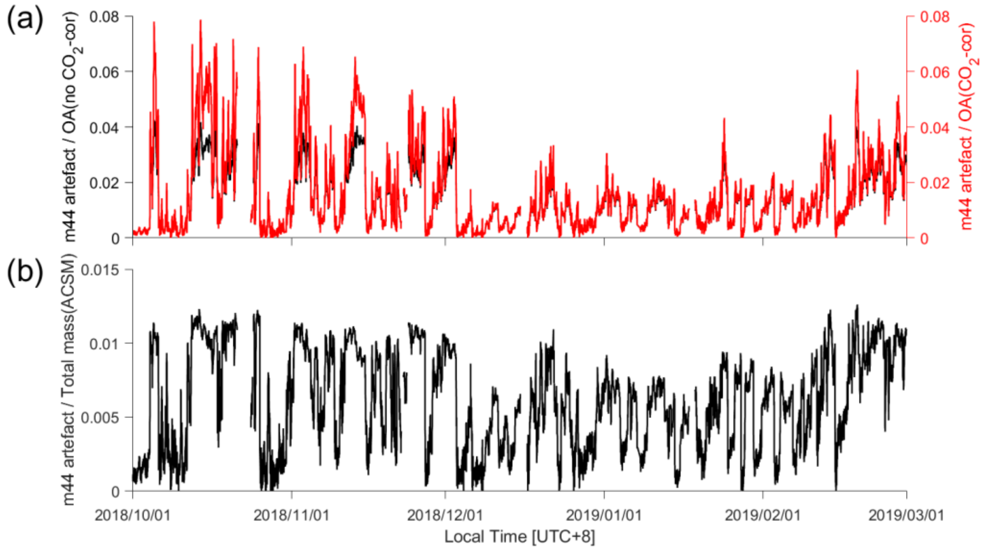

Figure R3. Time series of m44 artefact divided by OA without CO_2 correction and m44 artefact divided by OA with CO_2 correction (a), m44 artefact divided by total mass with CO_2 correction (b).

Comparison of ACSM Org and Sunset OC: In the response to the reviewers, the authors provided a comparison between Org measured by the ACSM and that from the Sunset, these comparisons could be included in an overview section or at least in the supplementary.

Response: Thank you for the suggestion. These comparisons have been added in the overview section.

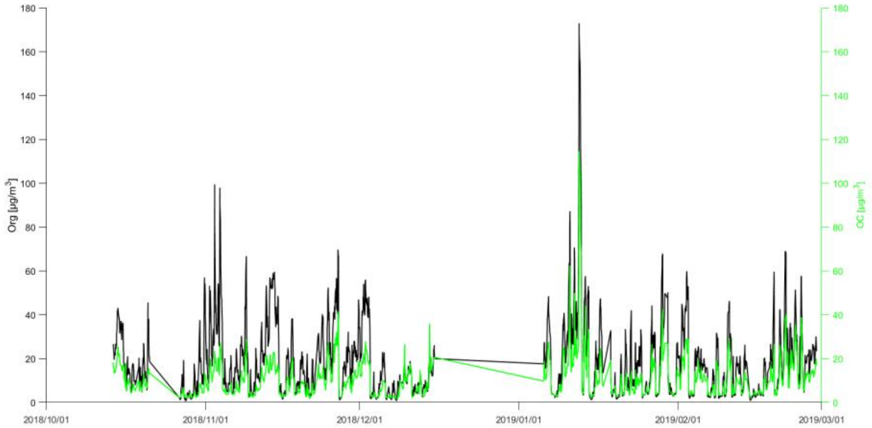

Figure R4. Time series of ACSM Org and Sunset OC.

Can the authors state if a denuder was used upstream of the sunset instrument and include a reference to what analysis protocol was used for the Sunset OC/EC measurements.

Response: We use a denuder upstream of the sunset instrument. And the analysis protocol called NIOSH-5040[7, 8] was used for the Sunset OC/EC measurements.

Figure R3/Table in supp: It appears that the OC from Sunset values are consistently lower than Org ACSM values? Please provide some explanation for this? What was the OM to OC ratio applied to the Sunset measurements?

Response: OC comes from the carbon part of Org, so OC concentration should be less than Org. In the early 1990s, Sunset Laboratory began to make commercially available thermal-optical OC-EC lab instruments, the Lab OCEC Aerosol Analyzer. In 2000, Model-4 Semi-Continuous OC/EC Field Analyzer, a semi-continuous OC-EC analyzer was developed for near real-time, in-situ measurement of carbon aerosol. However, the instruments from Sunset can't output OM, so that we can get the OM to OC ratio. The average OM/OC ratio is estimated to 1.54 (±0.20 standard deviation) [9] in urban area.

Significance of increases in concentrations during haze events: Thank you for providing the information on the significance of the aerosol mass concentration increases during the haze events. However, these additions do not appear to be included in the manuscript. A short sentence in the main part of the manuscript and some information in the supplementary would be informative for the reader.

Response: Thank you for the suggestion. We added a sentence in the revised manuscript. Line: 325.

Measurements from PSM and LTOFCIMS: Regarding the PSM measurements, they are only mentioned in the methods section and do not appear to be included anywhere else in the manuscript, (neither in the figures or supplementary figures), or used in the discussion. I would suggest either including more discussion of these measurements, or removing the instrument description.

Similarly, the majority of the discussion and the main conclusion of this manuscript is focused on ACSM (and DMPS) measurements, with little focus on the LTOFCIMS measurements (except in relation to Fig. 5), making their added value to this manuscript unclear. In the response to the reviewers comments the authors provided some interesting comments and figures comparing the temporal evolution of the OC (Sunset), Org (ACSM) and HOMS (LTOFCIMS), but did not include this discussion in the manuscript. These plots together with some discussion could also be included in the overview section of the manuscript.

Response: Thank you for the suggestion. The PSM introduction in the instrument part has been removed in the revised manuscript. The discussion about measurements of LTOFCIMS have been added in the overview section (3.1 overview of the measurement).

Minor remarks*

Line 317 75 μg /m correct to m3

Response: corrected.

Figure S1: Please provide a legend in the figure or in the figure caption for the gray shaded area.

Response: The gray shaded area corresponded to period with haze pollution. The figure caption has been refined.

Figure S2: It is still not clear what each of these groups of four figures refers to. Please provide the dates (and times) on the figures to distinguish them from each other; also a label on the color scale is needed. Also check the caption, there are only figures labeled (a) through (d).

Response: Thank you for the suggestion. The figure has been revised according to your suggestion. The dates and the label on the color scale have been added.

Figure S3: The axis labels could be improved here, they are very small.

Response: The axis labels have been improved in the revised version.

Figure S4: Neither a or b is included.

Response: corrected.

[1] CAI J, CHU B, YAO L, et al. Size-segregated particle number and mass concentrations from different emission sources in urban Beijing [J]. Atmospheric Chemistry and Physics, 2020, 20(21):

12721-40.

[2] CRENN V, SCIARE J, CROTEAU P L, et al. ACTRIS ACSM intercomparison – Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments [J]. Atmospheric Measurement Techniques, 2015, 8(12): 5063-87.

[3] POULAIN L, SPINDLER G, GRüNER A, et al. Multi-year ACSM measurements at the central European research station Melpitz (Germany) – Part 1: Instrument robustness, quality assurance, and impact of upper size cutoff diameter [J]. Atmospheric Measurement Techniques, 2020, 13(9): 4973-94.

[4] FRENEY E, ZHANG Y, CROTEAU P, et al. The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations [J]. Aerosol Science and Technology, 2019, 53(7): 830-42.

[5] PETIT J E, FAVEZ O, SCIARE J, et al. Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer [J]. Atmospheric Chemistry and Physics, 2015, 15(6): 2985-3005.

[6] PIEBER S M, EL HADDAD I, SLOWIK J G, et al. Inorganic Salt Interference on CO2(+) in Aerodyne AMS and ACSM Organic Aerosol Composition Studies [J]. Environ Sci Technol, 2016, 50(19): 10494-503.

[7] KEVIN ASHLEY P D A P F O C, NIOSH. NIOSH Manual of Analytical Methods (NMAM), 5th Edition [M]. DEPARTMENT OF HEALTH AND HUMAN SERVICES Centers for Disease Control and Prevention National Institute for Occupational Safety and Health, 2016.

[8] BAUER J J, YU X Y, CARY R, et al. Characterization of the sunset semi-continuous carbon aerosol analyzer [J]. J Air Waste Manag Assoc, 2009, 59(7): 826-33.

[9] BROWN S G, LEE T, ROBERTS P T, et al. Variations in the OM/OC ratio of urban organic aerosol next to a major roadway [J]. J Air Waste Manag Assoc, 2013, 63(12): 1422-33.