

Interactive comment on “Measurement report: Effects of photochemical aging on the formation and evolution of summertime secondary aerosol in Beijing” by Tianzeng Chen et al.

Anonymous Referee #2

Received and published: 28 September 2020

Chen et al. presents observations collected for ~1 month in a suburb of Beijing to investigate the sources of secondary aerosols, including secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA). They suggest that higher SOA, total particulate matter (PM), and SIA increases with photochemical age, as determined by the ratio of toluene:benzene. The increase with photochemical age and correlation with ozone leads to a suggestion that SOA and SIA is controlled by photochemistry during this time period in the suburb.

Though of potential interest to the audience of ACP, similar to Reviewer #1, I have concerns about the methodology and interpretation of the data that needs to be addressed

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prior to being accepted and published into ACP. Also, many of the observations are not totally surprising due to studies from urban studies both in Beijing as well as around the world. Placing this study into the context of those studies, though, would add value, especially if a better contrast between suburban and urban chemistry can be drawn through those comparisons.

The concerns/comments are below.

Major comments

Section 2.1—In general, the authors are missing a lot of details here to fully evaluate the study as well as being able to reproduce and/or to put into context of other studies. This includes and is not limited to: -What material was used for the inlet lines? Different material has different impacts on losses of the particles and gases being sampled? - What was the length and residence time for the inlet lines? -Was the same inlet line used for gases and PM or different inlet lines? -Where was the inlet line located, e.g., was it sticking out a window, on the roof? How far was it located from the building? -Where was the sample line in regards of potential sources? This includes trees/parks, parking lots, roadways, any asphalt or paint material? -Was there an impactor used for PM sampling? Was the PM dried prior to being sampled by AMS to minimize the impact of aerosol liquid water on collection efficiency? -A figure that shows the inlet and a map of where the inlet was in location of the area would help with many of these questions.

Section 2.2—It's unclear if the W and V mode is used for all the analysis throughout the paper or if only one mode, please specify. -Further, to address reviewer #1 concerns and concerns I will bring up, was there a measurement of wind direction/speed?

Section 2.3.1—I appreciate the authors actually discuss the calibrations and how they determined CE. Thank you! -It is strongly recommended in the AMS community to not include charge with ammonium, sulfate, nitrate, and chloride, as some portion of the signal is from organic material (therefore it can not be stated directly that it is an

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inorganic compound with a charge).

Section 2.3.2—The PMF analysis currently as presented is not convincing, which impacts some of the conclusions of this paper. -First, it is generally recommended to use the "semi-volatile" when the factor coincides with a thermodenuder measurement, as "semi-volatile" is meaningless without measuring whether the components of OA actually volatilize at low vs high temperatures. -Second, looking at the SI material, there is not enough evidence/evaluation of the PMF solutions to be convinced the current solutions are actually separate factor or splits of a factor. The "LO-OOA" factor is missing a comparison. All factors should have the r or R^2 of the time series. LO-OOA and MO-OOA look similar and that LO-OOA may be a noisier version of MO-OOA. If the authors at least compare the spectra with published spectra, that provide more evidence of the solutions selected here.

Section 2.3.3—Reviewer #1 has mentioned many concerns about this that I agree need to be addressed. Other things to consider: -The authors are trying to differentiate urban and suburban chemistry and use an OH value for urban Beijing, where OH may be very different. Also, the use of this value can make it hard to compare against prior studies. Instead of making any assumptions, I would recommend using a value of 1.5×10^6 molec./cm³ OH, which allows for direct comparisons with prior studies. -I agree that the emission ratio of 3.3 is hard to discern from the SI figure. I recommend that authors to use the methods from de Gouw et al., JGR, 2017, where they looked at the ratios at nighttime, which removes the impact of photochemistry and boundary layer dilution on the emission ratio. -The time series in the SI strongly suggests different emission sources/airmasses being sampled during the period (e.g., Aug 4 where Benzene > Toluene). Use of wind speed/direction may give insight about the sources of the air being sampled and allow for better calculation of photochemical age. -The very old ages (>12 hrs) is very surprising as that has not been typically observed in most other urban SOA studies (including many urban studies that assume a much lower OH concentration). It could be due to (1) not including impact of dilution, (2) mixing

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different airmasses/sources, and/or (3) using toluene:benzene ratio. Toluene:benzene ratio is typically suggested for older air masses as trimethylbenzene is more sensitive to younger ages (Parrish et al., JGR, 2007). More investigation into the cause of these older ages would be of value. -Are the authors using all data (day & night) or only day time? Interpretation of night time data in regards to photochemical age can be challenging and misleading.

Section 3.1 The sentences leading up to the sentence in line 214/215 ("With further improvement in air quality, PM1 concentration would decrease in the future. Then, the contribution of OA in PM1 is likely to increase.") currently do not support this. The logic is hard to follow, especially as other factors could influence PM1, including meteorology (boundary layer height, RH, and temperature have confounding impacts as well as wind direction/speed = source) and specific emission controls as certain controls might have different overall impacts on the precursors, OH concentration, etc that leads to the observed PM1.

Section 3.2 By itself, the section is not fully convincing, in large part due to the concerns about photochemical ages discussed above and in Reviewer #1. Some other analysis that can be done to improve the section and to be able to compare to other studies is to look at the OOA vs Ox (e.g., Herndon et al., GRL, 2008; Wood et al., ACP, 2010; Hayes et al., JGR, 2013) and/or OA/CO vs photochemical age (e.g., de Gouw et al., JGR, 2005; Hayes et al., JGR, 2013). Both analysis would take dilution and other processes out of the impacts observed.

Fig. 2—The figure by itself is not convincing as there can be a lot of scatter within each value that is binned. The figures suggested above would help to understand the potential scatter or not. Also, the figure in of itself is not very convincing for the overarching story trying to be discussed here. Further, it's surprising that Ox is continuously going up with increasing PM1 as at a certain level, PM1 should be decreasing Ox due to less photochemistry. How much of the observations shown here are from day time vs night time?

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Fig. 3—The fitting for some of the PM1 components here is surprising, as they are not produced through photochemistry (e.g., NH₄ and Cl). Similar to Fig. 2, what does the scatter look like? Also, as NR-PM1 is being largely controlled by SO₄ & OA, not sure that it's needed to be shown here.

Line 295 - 298—It is erroneous to say that NH₄ mainly exists in the form of ammonium sulfate without calculating in a thermodynamic model (e.g., Pye et al., ACP, 2020). Though the measurement may show 2xNH₄ mol = SO₄ mol, it may actually be a combination of ammonium sulfate and ammonium bisulfate that depends on temperature, aerosol liquid water, and ammonia partitioning that is not directly related to the AMS measurement. I strongly suggest removing or softening this language (here and other parts of the manuscript).

Section 3.3 and Fig 5—N/C and S/C ratios are typically not reported for V mode and only reported for W mode due to signal-to-noise issues, especially for the fitting of organic compounds in the V mode that contain nitrogen and/or sulfur. Were only the W mode used here or both? If both, I would recommend W only analysis or to compare W only vs W + V to see if there is a systematic difference. This noise in the fitting could also explain line 362-365 where there was no discernable change in these ratios with age.

Fig 6—The oxidation state lines (-1, -0.5, 0, etc.) should be expanded to +/-2 for completeness.

Line 403-406 This conclusion is misleading with the recent studies that have come out discussing the importance of non-transportation emissions of VOCs and how they dominate the photochemistry of urban environments, including from heating, cooking, and volatile chemical products. Though transportation is an important source, the authors need to at minimum recognize and discuss these important sources (see first minor comment below).

Minor comments

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line 254-255: Though temperature has an impact on biogenics, it also impacts many anthropogenic emissions (e.g., Pusede et al., ACP, 2014), including paint (e.g., McDonald et al., Science, 2018) and asphalt (Khare et al., Science Advances, 2020). Both need to be stated and discussed.

Line 331-333—It has generally been found and considered lower NO₃ at higher photochemical age is due to dilution and evaporation of ammonium nitrate (e.g., DeCarlo et al., ACP, 2008; Nault et al., ACP, 2018).

Line 340 - 343—I am unsure where the numbers come from. If I try to relate the numbers listed here vs the numbers shown in Fig. 4, they do not match.

Line 346 - 347—There are too many confounding factors to discuss the relationship between HOA and photochemical age, including dilution and evaporation. Either these need to be included or the sentence needs to be changed.

Fig. 1 y-axis for SMPS. Are the units correct

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-792>, 2020.

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