Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-792-RC1, 2020
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Atmospheric Chemistry and Physics Discussions

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 #1

Received and published: 13 September 2020

This manuscript reports the photochemical aging of PM1 components in a suburban site in Beijing. The discussions focus on the change of AMS-measured PM1 composition as a function of a photochemical clock calculated based on the toluene/benzene ratio. There is a major error is the analysis. The variation in the emission ratio of toluene/benzene is completely neglected when using the toluene/benzene ratio to calculate the photochemical clock. The air masses arriving at the measurement site likely originate from various sources (industrial plants vs vehicle emissions vs solvent use), which have different initial toluene/benzene ratio. The mixing of air masses with different origins will introduce significant uncertainties in the analysis. Further, the toluene/benzene ratio is influenced not only by photochemical aging but also by mix-

ing processes. This has been extensively discussed in the literature [McKeen and Liu, 1993; Parrish et al., 2007]. Lastly, it is not clear how the initial value of toluene/benzene ratio (i.e., 3.3) is determined in this study. To ensure the analysis is meaningful, the authors may consider to perform back-trajectory analysis and only analyze the measurements with similar origins. The authors may also estimate the photochemical age by using NOy/NOx ratio and compare it with toluene/benzene ratio. Besides the issues with toluene/benzene clock, many conclusions are drawn without solid evidence. Examples will be listed below. Overall, I cannot recommend publication in its current format.

Major comments 1. Below I list some examples of the bold conclusions drawn on weak evidence or missing links between evidence and conclusion. (1) Page 14 Line 256. Why would "NOx concentration decreased with increasing age" implied "the formation of O3 is in the VOC sensitive regime"? (2) Page 16 Line 298-300. "The boosted formation of Cl- with increasing age" is not sufficient to infer "the combination Cl- with NH4+ in the form of NH4Cl". (3) Page 12 Line 236. It is claimed that "longer aging time always corresponds to a higher concentration of O3 and [. . .]". This bold statement is not true, as the O3 concentration depends on a number of other factors. (4) Page 18 Line 331-333. The fraction of NO3- in PM1 shows a decreasing trend with increasing age, which is attributed to lower concentration of NOx at higher age. This reasoning is flawed. The lower NOx concentration at higher age is likely because NOx conversion to long-lived NOy species. The decreasing fraction of NO3- in PM1 could be due to enhanced production of other PM1 components, such as OA or SO4. 2. Another major issue is that only the binned data are show in the species concentration vs age plots. All raw data should be included. Also, I want to point out that the species concentration has a very large variation under the same age bin. I suspect there is any correlation between species concentration and age in the raw data. 3. Figure 2. When examining the photochemical evolution of a species, it is more intuitive to group species concentration measurements based on age, not the other way around as in Figure 2. 4. Many confounding factors are omitted in the analysis. For example, Figure S6 shows

that T has a positive relationship with age and RH has a negative relationship with age. Do the authors believe that these relationships are also due to photochemical aging? My point is that one cannot draw conclusion on the evolution of PM composition solely based on its relationship with photochemical clock.

Reference McKeen, S. A., and S. C. Liu (1993), Hydrocarbon ratios and photochemical history of air masses, Geophysical Research Letters, 20(21), 2363-2366, doi:10.1029/93gl02527. Parrish, D. D., A. Stohl, C. Forster, E. L. Atlas, D. R. Blake, P. D. Goldan, W. C. Kuster, and J. A. de Gouw (2007), Effects of mixing on evolution of hydrocarbon ratios in the troposphere, Journal of Geophysical Research: Atmospheres, 112(D10), doi:10.1029/2006jd007583.

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