

## Response to anonymous referee #1

Reviewer comments on acp-2020-145 revision

This manuscript, "Measurements of higher alkanes using  $\text{NO}^+$  chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China," is a revision of a manuscript I previously reviewed. In it the authors study the contribution of high-molecular-weight gasphase alkanes to SOA formation, specifically at two sites in China. The authors seem to have addressed most of my original concerns, though I note below a few things that are still of general concern and could be addressed better. I think the manuscript is generally suitable for publication, but would encourage the authors to consider some of these comments and suggests.

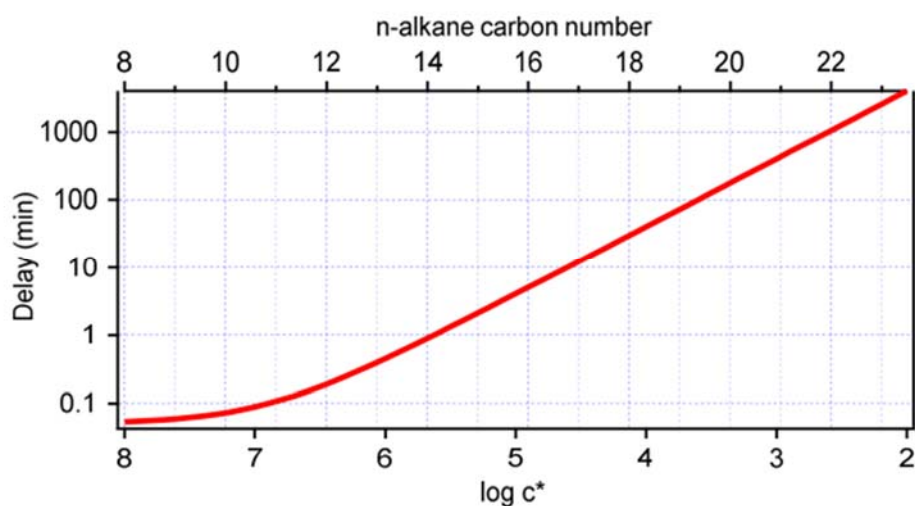
[Response: Thank you very much for your valuable comments and suggestions on our revised manuscript. These comments are all helpful for improving our article. All the authors have seriously discussed about all these comments. According to your comments, we have tried best to modify our manuscript to meet with the requirements for the publication in this journal. Point-by-point responses to the comments are listed below.](#)

General comments:

1) The authors provide much improved discussion of the sampling inlet design, and present data (Figure S11) demonstrating that the 8 meter length of tubing does not impact C8-C15 alkanes. I would note, however, that there are some limitations to their tests that leave me only partly convinced. For example, the C15 cal curve is not completely linear: 2 ppb gives a response below 200 ncps though 1 ppb gives a response of 100 ncps, but the same non-linearity is not observed for C10. There is also a clear time lag in the 8-meter tube that grows with carbon number, though it remains fast. Furthermore, the true sampling set up has many valves in line between the ambient sample and the instrument (6, by my count), which could substantially increase the surfaces and thus the time lag, and this effect is not considered in the tubing test.

Unfortunately, only up to C15 is tested, but these issues are likely to get much worse for up to C21. This effect can be modeled using the work of Pagonis et al. (Atmos. Meas. Tech., 10, 4687-4696, 2017). I have included a figure of this model below for the sampling system here (8 meter tube with 5 lpm flow), but roughly, C10 and smaller alkanes have essentially no lag, and up to C15 have lags on the order of a minute or so.

Notably, for larger alkanes, time delays increase, with C21 having a lag of hours; while this is likely a worst case, I would note that the estimates for C8-15 are more or less in agreement with Figure S11, so the model seems to be working to some degree. In addition to potential losses, this might have significant impacts on measured diurnals, etc.



Because much of the results of this work are not dependent on the diurnals or time-dependent measurements of higher-alkanes, I don't know that this issue is fatal. However, if the authors intend to continue these types of measurements, they will need to convince themselves (and reviewers) that their measurements of these lower-volatility gases are reliable. One option would be to show that diurnals for lower-volatility alkanes exhibit similar time dependence as higher-volatility alkanes, another would be to measure the time constant for step-function changes in concentrations of low-volatility alkanes even if quantitative concentrations can't be reliably generated.

Response: Thank you very much for your comment and nice suggestion. We recalculated the delay time of higher alkanes, which is determined as the time it takes for the signal to drop to 10% of its initial value caused by the step-function change in sample concentration (Pagonis et al., 2017). The results are from measurements during the field campaigns described in this study and also some other measurements that were conducted by our group, including measurements of emission sources and tubing losses test in laboratory. The delay times for higher alkanes are summarized Figure S10. It is found that delay times for various alkanes are in a range of few seconds to few minutes, among of which, higher-volatility alkanes (C8-C15) are better than 1 min and lower-volatility alkanes (C16-C21) are relatively long reaching several minutes. These results suggest that alkanes with higher carbon number, especially C20 and C21 might be

influenced by the tubing delay effect, as PTR-ToF-MS measured higher alkanes 10 minutes for ambient air and 3 minutes for background. We generally observe longer delay time with tubing (5 m or 8 m) than only instrument, consistent with the results in (Pagonis et al., 2017). However, the determined delay time for alkanes with carbon number larger than 18 is significantly lower than the modelled delay time by the reviewer using the model in (Pagonis et al., 2017).

As suggested by the reviewer, we also included the diurnal variations of all the measured alkanes (C8-C21) in this study in SI of the revised manuscript. As shown in the attached figure, the lower-volatility alkanes exhibit very similar time dependence as higher-volatility alkanes during both campaigns in PRD and NCP. These results also imply that the tubing effects should not significantly affect on the temporal variations of higher alkanes in this study.

As discussed above, the determination of tubing delay is really important for accurate measurements of higher alkanes and other intermediate volatile species. We agree with the reviewer and also strongly suggest to characterize the tubing used for this type of measurements. As suggested in (Pagonis et al., 2017) and other companion papers (Liu et al., 2019), shorter inlet and higher flow through the inlet are better practice for minimizing the tubing delay effect.

We extended the discussion of delay time on lines 186-198 of page 9-10 in the revised manuscript as follows:

**“Delay time is calculated as the time it takes for the signal to drop to 10% of its initial value caused by the step-function change in sample concentration (Pagonis et al., 2017). The delay times of higher alkanes for the field measurements in this study and some other measurements (e.g. emission source measurements and tubing losses test in the laboratory are summarized in Figure S10. It is found that delay times for various alkanes are in a range of few seconds to few minutes, among of which, higher-volatility alkanes (C8-C15) are better than 1 min and lower-volatility alkanes (C16-C21) are relatively long reaching several minutes. These results suggest that alkanes with higher carbon number, especially C20 and C21 might be influenced by the tubing delay effect during the measurements. However, as shown later in section 3.1, the lower-volatility alkanes exhibit very similar diurnal variations as higher-volatility alkanes during both campaigns in PRD and NCP, implying that the tubing effects should not**

significantly affect on temporal variations of higher alkanes reported in this study.”

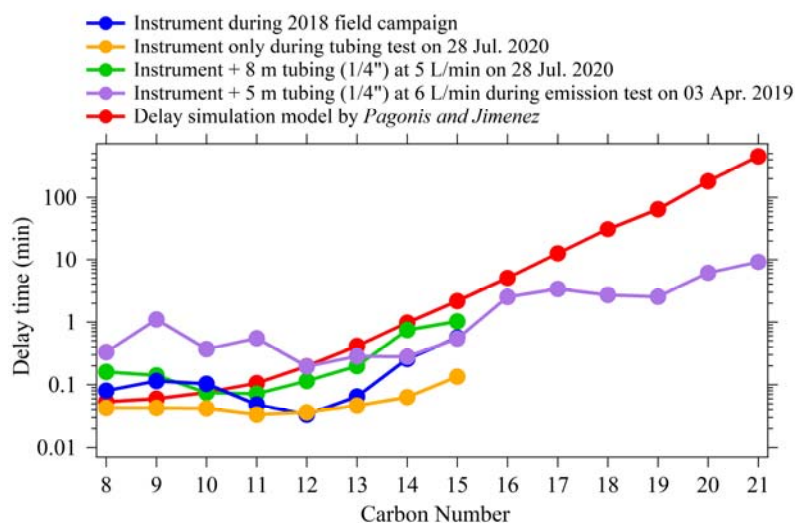


Figure S10. Delay times of higher alkanes for the field campaigns, emission source measurements and tubing losses test in the laboratory.

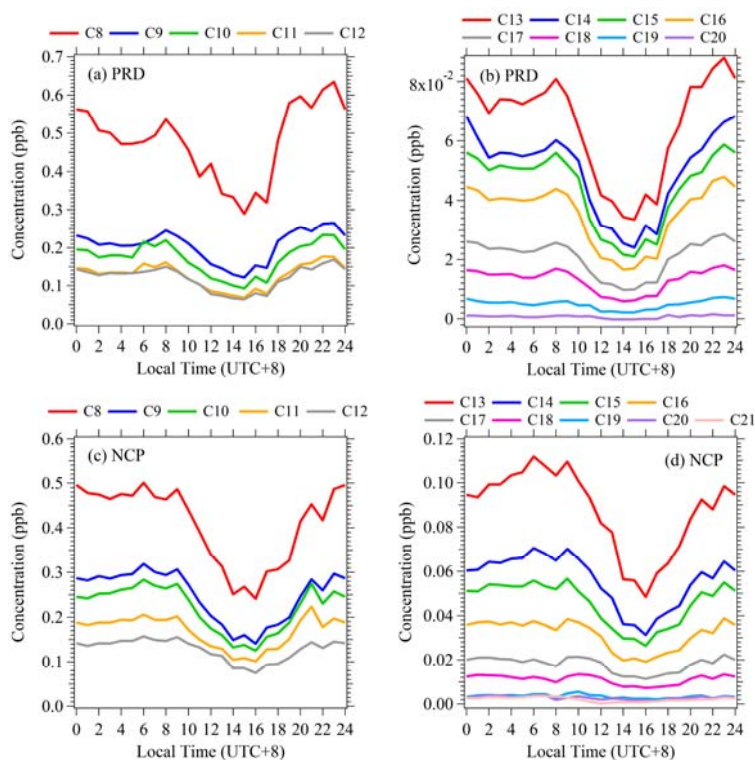


Figure S17. Similar diurnal profiles of C8-C21 alkanes during campaigns in PRD (a, b) and NCP (c, d).

Reference:

Pagonis, D., J. E. Krechmer, J. de Gouw, J. L. Jimenez and P. J. Ziemann: Effects of gas-wall partitioning in Teflon tubing and instrumentation on time-resolved measurements of gas-phase organic compounds. *Atmos. Meas. Tech.* 10(12): 4687-4696, 10.5194/amt-10-4687-2017, 2017.

Liu, X., Deming, B., Pagonis, D., Day, D. A., Palm, B. B., Talukdar, R., Roberts, J. M., Veres, P. R., Krechmer, J. E., Thornton, J. A., de Gouw, J. A., Ziemann, P. J., and Jimenez, J. L.: Effects of gas-wall interactions on measurements of semivolatile compounds and small polar molecules, *Atmospheric Measurement Techniques*, 12, 3137-3149, 10.5194/amt-12-3137-2019, 2019.

2) The new detail and discussion around OH exposure calculations are much improved. One suggestion I would make, though, is to change the language a little around this topic. I think many of us think of "OH exposure" as a feature of an air mass, so it is a bit confusing to talk about different OH exposure for different components, e.g., aromatics vs biogenics. The authors discussion in their response to reviewers of the reasons for this (differences in timing of the different emission sources) is helpful in understanding this. I think it might help to think of these calculations as "photochemical age", which could be described as the time between emission and detection - it might be more intuitive that this is different between components, and some inclusion of this discussion might help with interpretation of Figure S16.

Response: Thank you very much for your nice suggestion. In the main body of this study, we use the following formula to calculate the SOA formation for a given compound:

$$[SOA_i]_t = [VOC_i]_t \times (e^{k_{VOC_i} \times ([OH] \times \Delta t)} - 1) \times Yield_i$$

In the above formula,  $\Delta t$  represents the photochemical age,  $[OH]$  represents the OH concentration. In this study, we calculate the  $[OH] \times \Delta t$ , which was considered as OH exposure in some studies (Jimenez et al., 2009).

We added sentences on lines 297-299 of page 13 in the revised manuscript to mention the "OH exposure" and "photochemical age" clearly as follows:

**“[OH] is the OH concentration (molecules cm<sup>-3</sup>), Δt is the photochemical age. In this study, we calculate the [OH] × Δt (molecules cm<sup>-3</sup> s), which was considered as OH exposure in some studies (Jimenez et al., 2009).”**

Reference:

Jimenez, J. L., et al. (2009), Evolution of Organic Aerosols in the Atmosphere, *Science*, 326(5959), 1525-1529.

Specific comments:

Line 315. It is not really true that branched alkanes react faster than normal alkanes with OH in the gas phase. Though Isaacman et al. showed this was true in the particle phase (*Environ. Sci. Technol.* 2012, 46, 10632-10640), structure activity relationships do not predict the same effect in the gas-phase. Roughly speaking, branching increases the number of tertiary carbons, but concomitantly increases the number of primary carbons - these effects balance out at the estimated OH rate constant is mostly unchanged. For example, Kwok and Atkinson methods estimate  $k_{OH}=2.44e11$  for 2,6,10,14-tetramethylpentadecane ("pristane") and  $k_{OH}=2.38e11$  for n-nonadecane, a difference of less than 3%, well within uncertainty. The lower estimated yields for branched alkanes are consequently expected to "win out" in these calculations, since the effect of branching on yields is likely more substantial (Gentner et al. estimated branched yields were roughly half that of normal alkanes).

Response: Thank you very much for your correction. We modified the sentences on lines 329-332 of page 14 in the revised manuscript as follows:

**“Considering the SOA yields of branched alkanes are lower than *n*-alkanes, which is depending on chemical structures of the carbon backbone (Lim and Ziemann, 2009;Tkacik et al., 2012;Loza et al., 2014), the estimation of SOA from alkanes in this study might be a little overestimated.”**

Reference:

Lim, Y. B., and Ziemann, P. J.: Effects of Molecular Structure on Aerosol Yields from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO<sub>x</sub>, *Environmental Science & Technology*, 43, 2328-2334, 10.1021/es803389s, 2009.

Loza, C. L., Craven, J. S., Yee, L. D., Coggon, M. M., Schwantes, R. H., Shiraiwa, M., Zhang, X., Schilling, K. A., Ng, N. L., Canagaratna, M. R., Ziemann, P. J., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol yields of 12-carbon alkanes, *Atmospheric Chemistry and Physics*, 14, 1423-1439, 10.5194/acp-14-1423-2014, 2014.

Tkacik, D. S., Presto, A. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from Intermediate-Volatility Organic Compounds: Cyclic, Linear, and Branched Alkanes, *Environmental Science & Technology*, 46, 8773-8781, 10.1021/es301112c, 2012.

Figure 6. In their response to reviewers, the authors state that Worton et al. is not included because that work focused on particle-phase alkanes. However, I believe the same fact is true of the Chan et al. work, so I'm not sure that is a reasonable argument.

Response: Thank you very much for your correction. Yes, the higher alkanes data reported in Worton et al., 2014 and Chan et al., 2013 are both in particle phase. Hence, we also included the work from Worton et al., 2014 in the revised figure. We want to show the importance of contribution of branched isomers to higher alkanes concentrations at each carbon number whatever in gas phase and particle phase.

The Figure 6 is modified as follows:

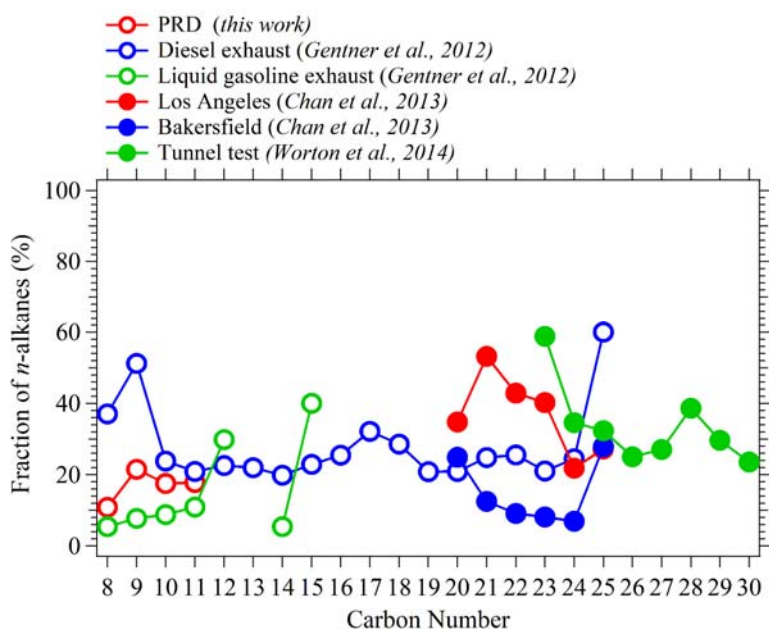


Figure 6. Fractions of *n*-alkanes in higher alkanes with same formulas in gas phase (hollow dots) and particle phase (solid dots) derived from this study, ambient air in Los

Angeles, Bakersfield, Caldecott Tunnel and in vehicle exhausts (Chan et al., 2013; Gentner et al., 2012; Worton et al., 2014).

The Table S2 are modified as follows:

Table S2. Fractions of *n*-alkanes in higher alkanes with same formulas derived from this study, ambient air in Los Angeles, Bakersfield, Caldecott Tunnel and in vehicle exhausts.

Carbon Number	Fraction of <i>n</i> -alkanes in higher alkanes with same formulas					
	PRD <sup>a</sup>	Los Angeles <sup>b</sup>	Bakersfield <sup>b</sup>	Caldecott Tunnel <sup>c</sup>	Diese exhaust <sup>d</sup>	Liquid gasoline exhaust <sup>d</sup>
8	10.82	/	/	/	37.04	5.39
9	21.48	/	/	/	51.22	7.71
10	17.56	/	/	/	23.81	8.81
11	17.81	/	/	/	20.91	10.88
12	/	/	/	/	22.54	29.82
13	/	/	/	/	21.98	/
14	/	/	/	/	19.84	5.41
15	/	/	/	/	22.86	40
16	/	/	/	/	25.44	/
17	/	/	/	/	32.16	/
18	/	/	/	/	28.57	/
19	/	/	/	/	20.83	/
20	/	34.78	24.85	/	20.87	/
21	/	53.16	12.47	/	24.82	/
22	/	42.85	9.11	/	25.51	/
23	/	40.24	8.14	58.82	21.05	/
24	/	21.85	6.92	34.62	24.44	/
25	/	27.17	27.87	32.35	60	/
26	/	/	/	25	/	/
27	/	/	/	27.03	/	/
28	/	/	/	38.64	/	/
29	/	/	/	29.63	/	/
30	/	/	/	23.53	/	/

<sup>a</sup>:This work; <sup>b</sup>: Chan et al. (2013); <sup>c</sup>: Worton et al. (2014); <sup>d</sup>: Gentner et al. (2012)

We also modified the sentences on lines 253-255 of page 11 as follows:

**“We found the fractions are in the range of 11%-21% for carbon number of 8-11, which are comparable with results of ambient air in California, tunnel test and vehicle exhausts (Figure 6 and Table S2) (Chan et al., 2013; Worton et al., 2014; Gentner et al., 2012).”**



Reference:

Chan, A. W. H., Isaacman, G., Wilson, K. R., Worton, D. R., Ruehl, C. R., Nah, T., Gentner, D. R., Dallmann, T. R., Kirchstetter, T. W., Harley, R. A., Gilman, J. B., Kuster, W. C., deGouw, J. A., Offenberg, J. H., Kleindienst, T. E., Lin, Y. H., Rubitschun, C. L., Surratt, J. D., Hayes, P. L., Jimenez, J. L., and Goldstein, A. H.: Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: Insights into emission sources, atmospheric processing, and secondary organic aerosol formation, *Journal of Geophysical Research-Atmospheres*, 118, 6783-6796, 10.1002/jgrd.50533, 2013.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, *Proceedings of the National Academy of Sciences of the United States of America*, 109, 18318-18323, 10.1073/pnas.1212272109, 2012.

Worton, D. R., G. Isaacman, D. R. Gentner, T. R. Dallmann, A. W. H. Chan, C. Ruehl, T. W. Kirchstetter, K. R. Wilson, R. A. Harley and A. H. Goldstein: Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles. *Environmental Science & Technology*, 48(7): 3698-3706, 10.1021/es405375j, 2014.

## Response to anonymous referee #2

The authors addressed all of my comments from the first round of review, and seem to have addressed the comments of the other reviewers as well. I have a few minor comments below.

Response: Thank you very much for your valuable comments and suggestions on our revised manuscript. These comments are all helpful for improving our article. All the authors have seriously discussed about all these comments. According to your comments, we have tried best to modify our manuscript to meet with the requirements for the publication in this journal. Point-by-point responses to the comments are listed below.

The only major issue with the revised manuscript is in Figure 8. I generally like this figure, but I don't understand the shaded parts of the bars labelled "consumed", as it is not explained in the text. Please clarify. Also, why are there two different lines for SOA yield in part (a)? I think part (b), which shows that the peak in alkane SOA production occurs around C15, is a great result that shows the importance of IVOCs on SOA.

Response: We clarified the "consumed" on lines 798-800 of page 41 in the revised manuscript as follows:

**"The consumed concentrations represent the chemical losses of higher alkanes, which are calculated by using the estimated SOA from each alkane dividing the corresponding SOA yields."**

We also modified the sentences on lines 342-345 of page 15 as follows:

**"Larger alkanes are relatively more reactive than lighter ones, which results in larger proportions of calculated concentrations that have been chemically consumed in the atmosphere (the concentrations labelled "consumed" in Figure 8(a))."**

The two different lines for SOA yields represent the yields that we used in PRD and NCP campaigns, respectively. SOA yield data used in this study for higher alkanes were summarized from reported values in the literature, with the consideration of the influence of organic aerosol concentration (Figure S20) to SOA yields (Donahue et al., 2006) (Figure S21). Since the organic aerosol concentrations are quite different in these two campaigns, the SOA yields of high alkanes are correspondingly different.

We added sentences on lines 348-350 of page 15 in the revised manuscript to mention the peaks of SOA production from alkanes as follows:

**“The peaks in alkanes SOA productions occur around C15 in both campaigns of PRD and NCP, which is a great result that shows the importance of IVOCs on SOA.”**

One comment on Figure 5c - the diurnal pattern of total alkanes from NO<sup>+</sup>-PTR has a deeper afternoon trough than the n-alkanes measured by GC-MS. This suggests that the n-alkanes cannot be used as tracers for the total alkane signal at each carbon number.

Response: Thank you very much for your nice suggestion. We added sentences in the revised manuscript to mention this result on lines 245-248 of page 11 as follows:

**“However, the diurnal patterns of total alkanes from NO<sup>+</sup> PTR-ToF-MS have a deeper afternoon trough than the *n*-alkanes measured by GC-MS, implying that *n*-alkanes may have different temporal variations compared with those of total alkanes.”**

We also discussed the importance of NO<sup>+</sup> PTR-ToF-MS in measuring higher alkanes on lines 256-259 of page 11 as follows:

**“These results indicate the importance of branched alkanes in concentrations of higher alkanes and their potential contributions to SOA formation. It also has strong implication for the merits of NO<sup>+</sup> PTR-ToF-MS in measuring sum of the alkanes with the same formula for estimation of SOA contributions, as discussed later.”**

Figure 9 - the authors do not seem to comment on the poor SOA mass closure. This of course could be due to several factors (yield estimates, unmeasured species, etc). I would like to see the mass closure issue commented on before publication. I'm also interested to know how much better the mass closure is when using the NO<sup>+</sup> data in addition to the traditional PTR-MS data (e.g., what is the predicted SOA formation if only the H<sup>+</sup> PTR-MS data was available?).

Response: Thank you very much for your comment and nice suggestion. We modified the sentences on lines 371-377 of page 16 in the revised manuscript to mention the SOA mass closure as follows:

**“The low explained percentages of SOA formations in both of PRD and NCP (Figure 9(c, d)) imply that some other SOA precursors (e.g. alkylcyclohexanes, alkylbenzenes, cyclic and polycyclic aliphatic materials) (Zhao et al., 2015; Drozd et al., 2019) or formation pathways (e.g. aqueous reactions) (Kuang et al., 2020) are contributing significantly to SOA formation. Compared to a previous study in northern China (Yuan et al., 2013), the missing gap of SOA formation declined after explicitly considering higher alkanes and naphthalenes in SOA production.”**

Reference:

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Oliver Chang, M. C., Maldonado, H., Sardar, S., Weber, R. J., Robinson, A. L., and Goldstein, A. H.: Detailed Speciation of Intermediate Volatility and Semivolatile Organic Compound Emissions from Gasoline Vehicles: Effects of Cold-Starts and Implications for Secondary Organic Aerosol Formation, *Environ. Sci. Technol.*, 53, 1706-1714, <https://doi.org/10.1021/acs.est.8b05600>, 2019.

Kuang, Y., He, Y., Xu, W., Yuan, B., Zhang, G., Ma, Z., Wu, C., Wang, C., Wang, S., Zhang, S., Tao, J., Ma, N., Su, H., Cheng, Y., Shao, M., and Sun, Y.: Photochemical Aqueous-Phase Reactions Induce Rapid Daytime Formation of Oxygenated Organic Aerosol on the North China Plain, *Environmental Science & Technology*, 10.1021/acs.est.9b06836, 2020.

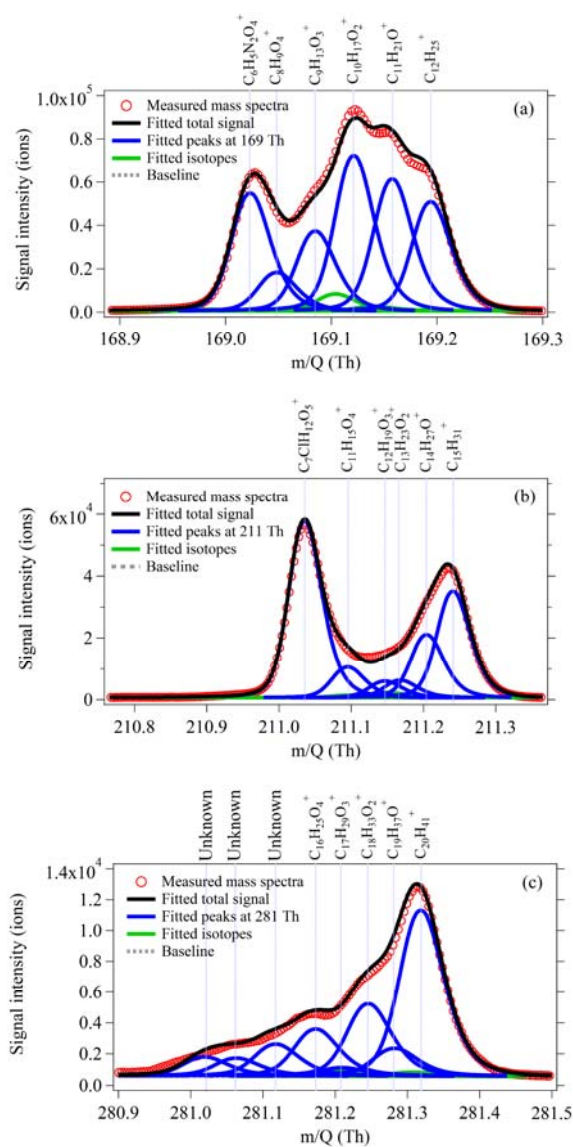
Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate Volatility Organic Compound Emissions from On-Road Diesel Vehicles: Chemical Composition, Emission Factors, and Estimated Secondary Organic Aerosol Production, *Environ Sci Technol*, 49, 11516-11526, 10.1021/acs.est.5b02841, 2015.

Line 62 - define NMHCs

Response: We defined NMHCs on lines 62-63 of page 3 in the revised manuscript as follows: **“nonmethane hydrocarbons (NMHCs)”**.

Lines 136-138 - I do not understand what the authors mean by "with signals either the largest or among the largest ions at these nominal masses, which help to achieve high precision for determined signals of higher alkanes from high-resolution peak fitting ."

Response: In this study, the measured mass spectra from  $\text{NO}^+$  PTR-ToF-MS was analysed using Tofware software (Tofwerk AG) for high-resolution peak-fitting. Higher alkanes were detected through hydride abstraction by  $\text{NO}^+$  forming mass ( $m-1$ ) ions ( $m$  is the molecular mass) (Koss et al., 2016; Inomata et al., 2013). As shown in the attached Figure 1, the product ions ( $m-1$ ) of higher alkanes have relatively high signals at these nominal masses, for example, the signal of  $\text{C}_{20}\text{H}_{41}^+$  produced by eicosane is the highest at  $m/z$  281, which helps in getting precise peak-fitting results (Cubison and Jimenez, 2015; Corbin et al., 2015). That is to say, if the signals of product ions ( $m-1$ ) of higher alkanes are too small, then the peak-fitting results may have large uncertainties.



**Figure 1.** High-resolution (HR) peak-fitting to the averaged mass spectra on a typical day (12 October 2018) for  $m/z$  169 (a),  $m/z$  211 (b) and  $m/z$  281 (c), at which masses

produced by dodecane ( $C_{12}H_{25}^+$ ), pentadecane ( $C_{15}H_{31}^+$ ) and eicosane ( $C_{20}H_{41}^+$ ) in  $NO^+$  PTR-ToF-MS.

Reference:

Corbin, J. C., Othman, A., D. Allan, J., R. Worsnop, D., D. Haskins, J., Sierau, B., Lohmann, U., and A. Mensah, A.: Peak-fitting and integration imprecision in the Aerodyne aerosol mass spectrometer: effects of mass accuracy on location-constrained fits, *Atmos. Meas. Tech.*, 8, 4615-4636, 10.5194/amt-8-4615-2015, 2015.

Cubison, M. J., and Jimenez, J. L.: Statistical precision of the intensities retrieved from constrained fitting of overlapping peaks in high-resolution mass spectra, *Atmos. Meas. Tech.*, 8, 2333-2345, 10.5194/amt-8-2333-2015, 2015.