

Response to anonymous referee #1

Reviewer comments on acp-2020-145 revision

This manuscript, "Measurements of higher alkanes using 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.

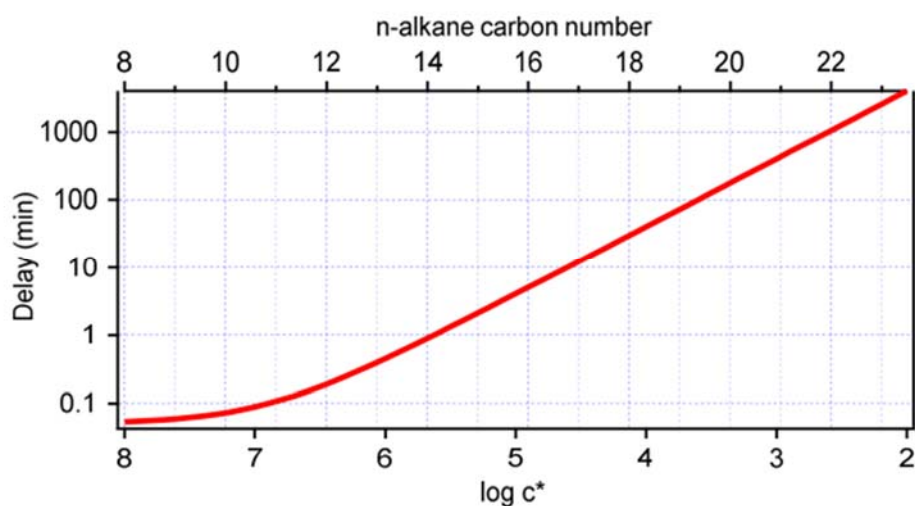
Response: Thank you very much for your valuable comments and suggestions on our revised manuscript. These comments are all helpful for improving our article. All the authors have seriously discussed about all these comments. According to your comments, we have tried best to modify our manuscript to meet 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.”

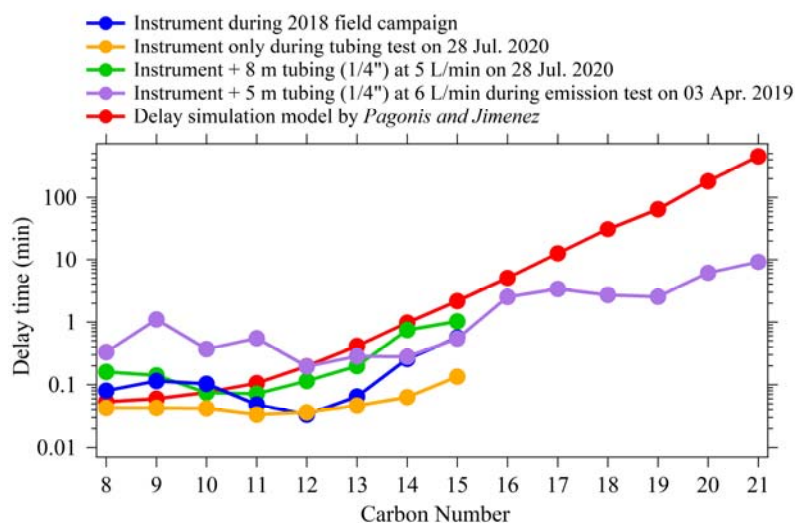


Figure S10. Delay times of higher alkanes for the field campaigns, emission source measurements and tubing losses test in the laboratory.

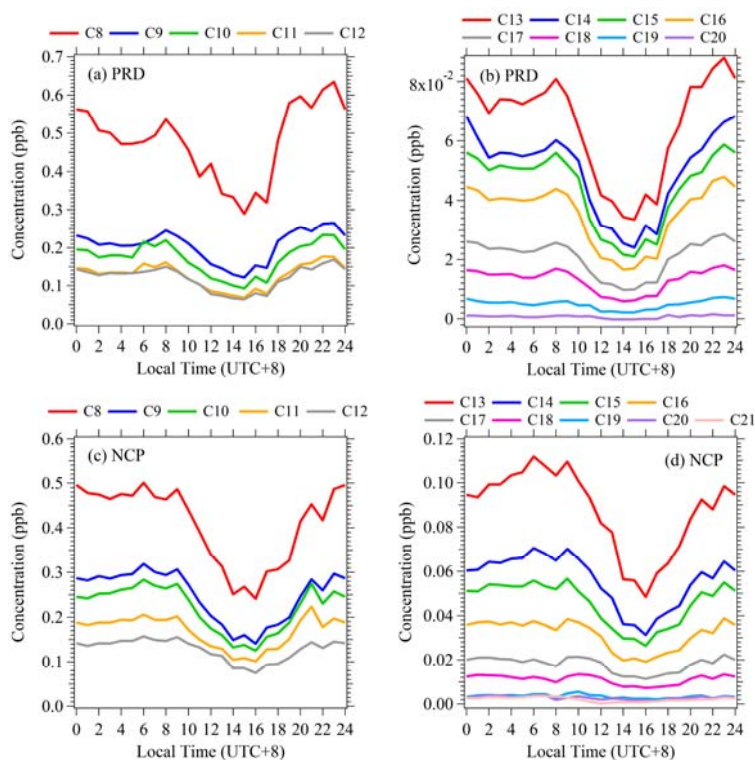


Figure S17. Similar diurnal profiles of C8-C21 alkanes during campaigns in PRD (a, b) and NCP (c, d).

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, Δt 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⁻³), Δt is the photochemical age. In this study, we calculate the [OH] × Δt (molecules cm⁻³ 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_x, *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:

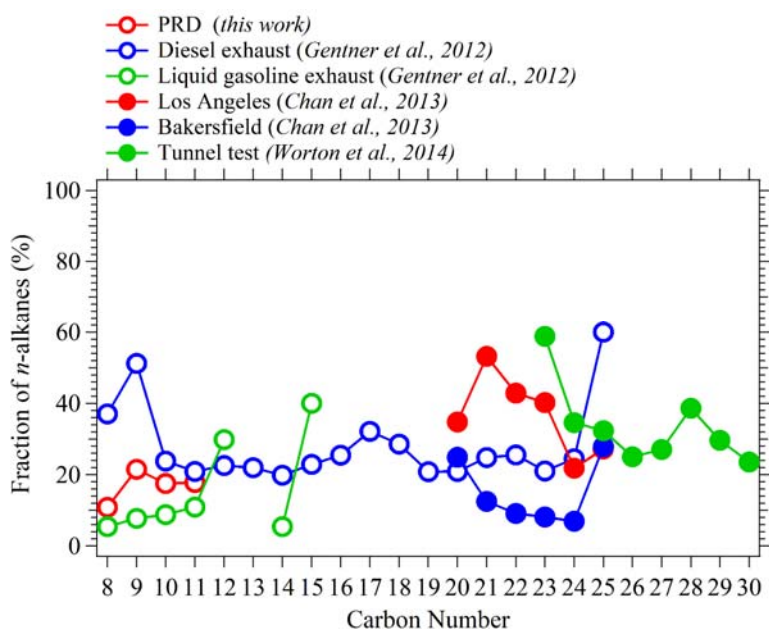


Figure 6. Fractions of *n*-alkanes in higher alkanes with same formulas in gas phase (hollow dots) and particle phase (solid dots) derived from this study, ambient air in Los

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 ^a	Los Angeles ^b	Bakersfield ^b	Caldecott Tunnel ^c	Diese exhaust ^d	Liquid gasoline exhaust ^d
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	/	/

^a:This work; ^b: Chan et al. (2013); ^c: Worton et al. (2014); ^d: 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⁺-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⁺ 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⁺ 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⁺ 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⁺ data in addition to the traditional PTR-MS data (e.g., what is the predicted SOA formation if only the H⁺ 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 NO^+ PTR-ToF-MS was analysed using Tofware software (Tofwerk AG) for high-resolution peak-fitting. Higher alkanes were detected through hydride abstraction by 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.

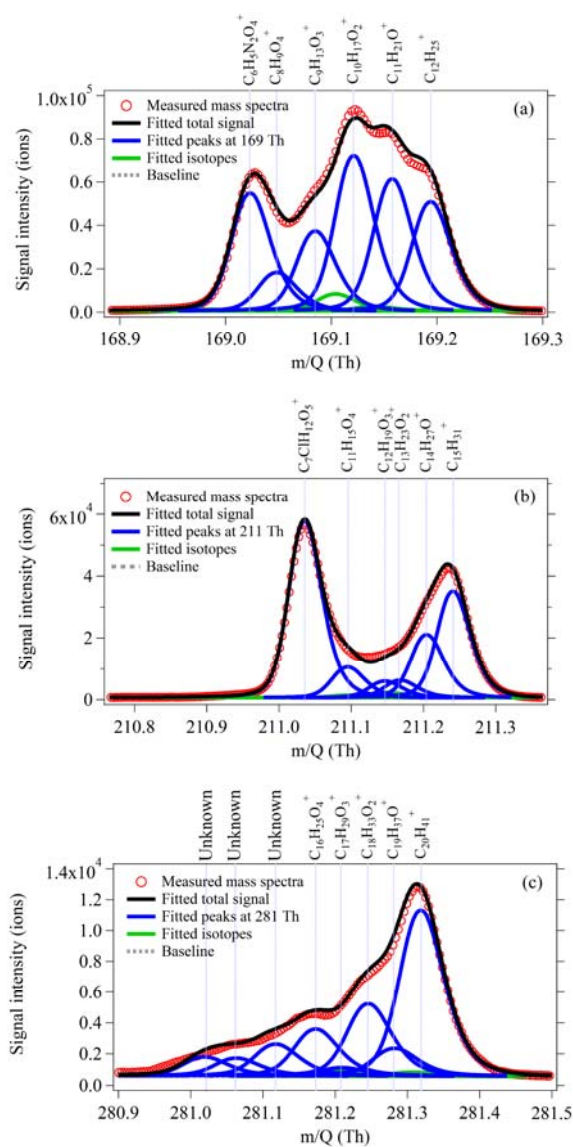


Figure 1. High-resolution (HR) peak-fitting to the averaged mass spectra on a typical day (12 October 2018) for m/z 169 (a), m/z 211 (b) and m/z 281 (c), at which masses

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.

1 **Measurements of higher alkanes using NO⁺ chemical**
2 **ionization in PTR-ToF-MS: important contributions of**
3 **higher alkanes to secondary organic aerosols in China**

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25 **Abstract:** Higher alkanes are a major class of intermediate-volatility organic compounds
26 (IVOCs), which have been proposed to be important precursors of secondary organic
27 aerosols (SOA) in the atmosphere. Accurate estimation of SOA from higher alkanes and
28 their oxidation processes in the atmosphere are limited, partially due to difficulty in their
29 measurements. High-time resolution (10 s) measurements of higher alkanes were performed
30 using NO^+ chemical ionization in proton transfer reaction time-of-flight mass spectrometer
31 (NO^+ PTR-ToF-MS) method at an urban site of Guangzhou in Pearl River Delta (PRD) and
32 at a rural site in North China Plain (NCP), respectively. High concentrations were observed
33 in both environments, with significant diurnal variations. At both sites, SOA production from
34 higher alkanes is estimated from their photochemical losses and SOA yields. Higher alkanes
35 account for significant fractions of SOA formation at the two sites, with average
36 contributions of $7.0 \pm 8.0\%$ in Guangzhou and $9.4 \pm 9.1\%$ in NCP, which are comparable or
37 even higher than both single-ring aromatics and naphthalenes. The significant contributions
38 of higher alkanes in SOA formation suggests that they should be explicitly included in
39 current models for SOA formation. Our work also highlights the importance of NO^+ PTR-
40 ToF-MS in measuring higher alkanes and quantifying their contributions to SOA formation.

41

42 1. Introduction

43 As important components of fine particles, secondary organic aerosols (SOA) not
44 only affect air quality and climate change, but also threaten human health (An et al.,
45 2019;Zhu et al., 2017;Chowdhury et al., 2018). Recent studies indicate large discrepancies
46 between simulations and observations for SOA (de Gouw et al., 2008;Dzepina et al.,
47 2009;Jiang et al., 2012), which are attributed to limited understanding of complicated
48 chemical and physical processes underlying SOA formation (Hallquist et al., 2009). A
49 volatility basis set (VBS) model was developed to advance SOA modeling by improving the
50 modeling of further multigenerational oxidation processes and incorporating numerous, yet
51 unidentified, low-volatility precursors of SOA (Donahue et al., 2006), which substantially
52 improved the agreement between SOA simulations and observations (Hodzic et al., 2010).
53 However, there are still large uncertainties in current VBS models, including rate constants
54 of oxidation reactions, the change of O/C ratio in oxidation, and the relative importance of
55 functionalization and fragmentation (Ma et al., 2017;Hayes et al., 2015). Explicit
56 consideration of individual or a group of important semi-volatile or intermediate volatile
57 organic compounds (S/I-VOCs) in the SOA model are urgently needed.

58 Higher alkanes as a major class of IVOCs (roughly corresponding to alkanes with
59 12-20 carbons) have been proposed as important SOA contributors in urban areas (Robinson
60 et al., 2007;Yuan et al., 2013;Zhao et al., 2014a). In the typical urban areas, higher alkanes
61 are reported to be mainly from vehicle emissions including diesel exhaust (Zhao et al., 2015)
62 and gasoline exhaust (Zhao et al., 2016), corresponding generally to ~4% of nonmethane
63 hydrocarbons (NMHCs) emissions from on-road vehicles. Higher alkanes are estimated to
64 produce as much as or even more SOA than single-ring aromatics and polycyclic aromatic
65 hydrocarbons from the oxidation of vehicle emissions, based on the chemical compositions

66 measurements of vehicle exhausts (Zhao et al., 2016, 2015). Based on vehicle exhaust tests,
67 higher alkanes were found to contribute ~37% to diesel exhaust-derived SOA and ~0.8% to
68 gasoline exhaust-derived SOA, respectively (Gentner et al., 2012). Previous model studies
69 suggested that SOA simulation can be significantly improved when higher alkanes were
70 considered in the model (Pye and Pouliot, 2012; Jathar et al., 2014; Wu et al., 2019). Although
71 the concentrations of higher alkanes might be lower than other VOCs classes (e.g. aromatics)
72 in the atmosphere, higher alkanes are found to have much higher SOA yields and the yields
73 increase steadily with carbon number (Lim and Ziemann, 2005; Lim and Ziemann,
74 2009; Presto et al., 2010b). For a given carbon number, SOA yields of higher alkanes reduce
75 with branching of the carbon chain, especially under high-NO_x conditions (Lim and Ziemann,
76 2009; Tkacik et al., 2012; Loza et al., 2014).

77 Higher alkanes have been mainly measured by gas chromatography-based techniques,
78 focusing on the compositions (Gong et al., 2011; Caumo et al., 2018), atmospheric
79 concentration levels (Bi et al., 2003; Anh et al., 2018) and gas-particle partitioning (Xie et al.,
80 2014; Sangiorgi et al., 2014). While most of previous studies collected offline samples
81 (usually 0.5 day-1 week) for GC-based analysis in the laboratory, hourly online
82 measurements of *n*-alkanes using GC-based thermal desorption aerosol gas chromatograph
83 for semi-volatile organic compounds (SV-TAG) was recently developed and applied in
84 ambient air (Zhao et al., 2013). Proton-transfer-reaction mass spectrometry (PTR-MS) using
85 H₃O⁺ as reagent ions are capable of measurements for many organic compounds with high
86 time response and sensitivity (de Gouw and Warneke, 2007; Jordan et al., 2009; Yuan et al.,
87 2017b). Although H₃O⁺ PTR-MS is responsive to large alkanes (>C₈), these alkanes usually
88 fragment into small masses with mass spectra difficult to interpret (Jobson et al.,
89 2005; Gueneron et al., 2015). Recently, PTR-MS using NO⁺ as reagent ions was
90 demonstrated to provide fast online measurement of higher alkanes (Koss et al.,

91 2016;Inomata et al., 2013). The high-time resolution measurements of higher alkanes
92 provide valuable information for SOA estimation, as the dependence of SOA yields on
93 organic aerosol concentrations and other environmental parameters (e.g. temperature) (Lim
94 and Ziemann, 2009;Presto et al., 2010b;Loza et al., 2014;Lamkaddam et al., 2017a) can be
95 taken into account in more detail.

96 In this study, we utilize NO^+ chemical ionization in PTR-ToF-MS (here referred as
97 NO^+ PTR-ToF-MS) to measure higher alkanes at two different sites in China, one urban site
98 in Pearl River Delta region and one rural site in North China Plain region. We use the datasets
99 along with measurements of other pollutants to estimate contributions to SOA formation
100 from higher alkanes and other SOA precursors. The observation-constrained SOA formation
101 of this study is a step forward upon previous modelling studies, which proposed the
102 important roles of S/I-VOCs (Jiang et al., 2012;Yang et al., 2018;Wu et al., 2019) including
103 higher alkanes (Yuan et al., 2013) in SOA formation in China.

104 **2. Methods**

105 Field campaigns were conducted at an urban site of Guangzhou in the Pearl River
106 Delta (PRD) region during September-November 2018 and at a rural site of Baoding in North
107 China Plain (NCP) during November-December 2018, respectively. The detailed description
108 of the measurement sites can be found in Supporting Information (SI, Figure S1).

109 **2.1 NO^+ PTR-ToF-MS measurements**

110 Proton-transfer-reaction mass spectrometry (PTR-MS) is a technique that allows for
111 fast and sensitive measurements of volatile organic compounds (VOCs) at trace levels in air.
112 PTR-MS using H_3O^+ chemistry has been demonstrated to measure alkenes, aromatics, and
113 even oxygenated VOCs (Yuan et al., 2017a;Wu et al., 2020). Here, PTR-MS with NO^+

114 chemistry was used to detect higher alkanes, through hydride abstraction by NO^+ forming
115 mass (m-1) ions (m is the molecular mass) (Koss et al., 2016; Inomata et al., 2013).

116 A commercially available PTR-ToF-MS instrument (Ionicon Analytik, Austria) with
117 a mass resolving power of 4000 $m/\Delta m$ was used for this work. To generate NO^+ as reagent
118 ions, ultra-high-purity air (5.0 sccm) was directed into the hollow cathode discharge ion
119 source. The pressure of the drift tube was maintained at 3.8 mbar. Voltages of ion source and
120 drift chamber were explored (Figure S2) in the laboratory to optimize the generation of NO^+
121 ions relative to H_3O^+ , O_2^+ , and NO_2^+ and minimize alkane fragmentation. The intensities of
122 primary ion NO^+ and impurities (O_2^+ , H_3O^+ and NO_2^+) and the ratio of O_2^+ to NO^+ during two
123 campaigns are shown in Figure S3 and Figure S4, respectively. The ratio of O_2^+/NO^+ (Figure
124 S4 (a)) is basically stable at 2-4% during the PRD campaign except during Oct. 26-Nov. 2,
125 2018 (7-10%). For the NCP campaign, the ratio of O_2^+/NO^+ (Figure S4 (b)) fluctuates between
126 10-40% in the early stage of campaign and keeps stable at ~20% in the later stage of the
127 campaign. Such fluctuations are attributed to the humidity effect in the ambient air (Figure
128 S5). Ion source voltages of U_s and U_{so} were selected as 40 V and 100 V, while U_{drift} and
129 U_{dx} were set to 470 V and 23.5 V, resulting in an E/N (electric potential intensity relative to
130 gas number density of 60 Td. NO^+ PTR-ToF-MS data was analysed using Tofware software
131 (Tofwerk AG) for high-resolution peak-fitting. A description of the algorithm can be found
132 in Stark et al. (2015) and Timonen et al. (2016). Figure 1 shows the high-resolution peak
133 fitting to the averaged mass spectra on a typical day (12 October 2018) for m/z 169, m/z 211
134 and m/z 281, at which masses produced by dodecane ($\text{C}_{12}\text{H}_{25}^+$), pentadecane ($\text{C}_{15}\text{H}_{31}^+$) and
135 eicosane ($\text{C}_{20}\text{H}_{41}^+$) are detected. It is observed that the ions from higher alkanes lie at the right-
136 most position at each nominal mass, with signals either the largest or among the largest ions
137 at these nominal masses, which help to achieve high precision for determined signals of higher
138 alkanes from high-resolution peak fitting (Cubison and Jimenez, 2015; Corbin et al., 2015).

139 In this study, we normalize the raw ion count rate of higher alkanes to the primary ion
140 (NO^+) at a level of 10^6 cps to account for fluctuations of ion source and detector. Calibrations
141 were conducted every 1-2 days under both dry conditions ($\text{RH}<1\%$) and ambient humidity
142 conditions using a gas standard with a series of *n*-alkanes (Apel Riemer Environmental Inc.)
143 during NCP campaign (Figure 2(a)). Sensitivities of *n*-alkanes (C8-C15) standards were
144 obtained during the campaign (Figure S6), which is defined as the normalized signal of hydride
145 abstraction ions for each higher alkane at 1 ppbv with a unit of ncps/ppb. The fluctuations of
146 sensitivities during the NCP campaign may be influenced by the variations of O_2^+ signals
147 (Figure 2), because the reactions of O_2^+ with alkanes can be proceeded by both charge transfer
148 and hydride abstraction (Amador et al., 2016) that may affect the ion signals of alkanes with
149 NO^+ reactions. Therefore, we use the daily ambient calibrations results to quantify the
150 concentration of higher alkanes during the NCP campaign to reflect the variations of sensitivity
151 from day to day. For the measurements without daily calibrations, we used closest calibration
152 results according to corresponding ambient O_2^+/NO^+ ratios and ambient humidity. Since we got
153 the alkanes standard at the very late period of the PRD campaign, we did not have the daily
154 calibrations for this campaign. Therefore, we use the sensitivity of each alkane under
155 corresponding O_2^+/NO^+ condition obtained from lab experiments after this campaign and also
156 consider the humidity effects (Figure 3(b, c)) to quantify the concentration of higher alkanes
157 during the PRD campaign. Humidity-dependent behaviours of *n*-alkanes (C8-C15) were
158 performed in the laboratory under different humidity (0-33 mmol/mol) by diluting higher
159 alkanes standard into humidified air to reach approximately 1 ppb mixing ratio. As shown in
160 Figure 3(b, c) and Figure S7 (a), the normalized signal of all product ions (*m*-1) and the
161 fragment ions of *n*-alkanes (C8-C15) standards are decreasing with the increase of humidity.
162 These decreasing patterns are probably due to the decreasing primary reagent ions (NO^+ and

163 O₂⁺) as the humidity increases Figure S7(b). Thus, the humidity correction should be applied
164 for the quantitation of higher alkanes using NO⁺ PTR-ToF-MS.

165 The fragmentation patterns for selected *n*-alkanes and their branched isomers are
166 measured with NO⁺ PTR-ToF-MS by introducing commercially acquired pure chemicals
167 (Figure S8). Figure 4(a) shows the fractions of hydride abstraction m-1 ions in the mass
168 spectra of C8-C20 *n*-alkanes in NO⁺ PTR-ToF-MS. Generally, larger *n*-alkanes show less
169 degree of fragmentation in the mass spectra with higher fractions contributed by m-1 ions.
170 The fractions of m-1 ions account for more than 60% of total ion signals for >C12 *n*-alkanes.
171 We also observe good correlation between the fractions of m-1 ions in mass spectra and the
172 determined sensitivities for C8-C15 *n*-alkanes. As C16-C21 *n*-alkanes exhibit similar degrees
173 of fragmentation as C15, sensitivities of the alkanes were assumed to be same as that of C15
174 *n*-alkane (Figure 4(b)). Comparison of the degree of fragmentation between *n*-alkanes and
175 their branched isomers (Figure S9) show the substituted groups affect little on the degrees of
176 fragmentations for product ions, at least for branched isomers with up to 4 substituted methyl
177 groups. Previous studies demonstrated that the branched alkanes from emissions of fossil fuel-
178 related sources are primarily with one or two alkyl branches (Chan et al., 2013; Isaacman et
179 al., 2012). Therefore, we conclude that the branched isomers of higher alkanes should have
180 similar response factors to their normal analogues. As a result, the concentration of higher
181 alkanes by NO⁺ PTR-ToF-MS should be regarded as the summed concentrations of *n*-alkanes
182 and branched alkanes that have the same chemical formulas.

183 Detection limits are calculated as the concentrations at which signal counts are 3 times
184 of standard deviation of measured background counts (Bertram et al., 2011; Yuan et al., 2017b).
185 As shown in Table 1, detection limits are determined to be on the order of 0.7-1.3 ppt for
186 higher alkanes for 1 min integration times. Delay time is calculated as the time it takes for the
187 signal to drop to 10% of its initial value caused by the step-function change in sample

188 concentration (Pagonis et al., 2017). The delay times of higher alkanes for the field
189 measurements in this study and some other measurements (e.g. emission source
190 measurements and tubing losses test in the laboratory are summarized in Figure S10. It is
191 found that delay times for various alkanes are in a range of few seconds to few minutes, among
192 of which, higher-volatility alkanes (C8-C15) are better than 1 min and lower-volatility alkanes
193 (C16-C21) are relatively long reaching several minutes. These results suggest that alkanes
194 with higher carbon number, especially C20 and C21 might be influenced by the tubing delay
195 effect during the measurements. However, as shown later in section 3.1, the lower-volatility
196 alkanes exhibit very similar diurnal variations as higher-volatility alkanes during both
197 campaigns in PRD and NCP, implying that the tubing effects should not significantly affect on
198 temporal variations of higher alkanes reported in this study.

199 During these two campaigns, PTR-ToF-MS automatically switches between H_3O^+ and
200 NO^+ chemistry every 10-20 minutes with a 10 s resolution of measurement. Switching
201 between H_3O^+ and NO^+ ion mode are provided by the PTR-MS Manager (v3.5) software
202 developed by the Ionicon Analytik (Table S1). The pressures of drift chamber are held constant
203 at 3.8 mbar in both modes during the campaigns (Figure S11(a)). It usually takes <10 s for
204 H_3O^+ ions and ~60 s for NO^+ ions to re-stabilize after automatically switching between the
205 two measurement modes (Figure S11(b)). The ambient measurement data during the transition
206 period (~1 min) was discarded. Ambient air was continuously introduced into PTR-ToF-MS
207 through a Teflon tubing (1/4") with an external pump at 5.0 L/min, with tubing length of ~8
208 m and ~3 m during the PRD and the NCP campaign, respectively. The inlet tubing was heated
209 all the way to the sampling inlet to avoid water vapour condensation by an insulating tube
210 with a self-controlled heater wire (40 °C) wrapping outside. The calculated residence time for
211 the inlet was ~3 s for PRD campaign and ~1 s for NCP campaign, respectively. The tubing
212 loss experiments were conducted in the laboratory by introducing standards of higher alkanes

213 (*n*-C8-C15), monoaromatics (benzene, toluene, *o*-xylene, 1,2,4-trimethylbenzene),
214 isoprenoids (isoprene, α -pinene) and naphthalene into PTR-ToF-MS through a 8 m Teflon
215 tubing (1/4") at room temperature with an external pump at 5.0 L/min (Figure S12). The
216 tubing loss of these compounds is found to be <5% except *n*-C15 (~8%) and naphthalene
217 (~10%). Background measurement of 3 minutes was conducted in each cycle of NO⁺ and
218 H₃O⁺ measurements by introducing the ambient air into a catalytic converter with a
219 temperature of 367 °C.

220 **2.2 Other measurements**

221 During the Guangzhou campaign, an online GC-MS/FID system was used to measure
222 C2-C11 *n*-alkanes, alkenes and aromatics with a time resolution of one hour (Yuan et al.,
223 2012). Non-refractory components in particulate matter with diameter less than 1 μ m (PM₁)
224 including nitrate, sulfate, ammonium, chloride, and organics were measured with an
225 Aerodyne high-resolution time-of-flight aerosol mass spectrometric (HR-ToF-AMS) and a
226 time-of-flight aerosol chemical speciation monitor (ToF-ACSM) in PRD and NCP,
227 respectively. Trace gaseous species (CO, NO, NO₂, O₃, and SO₂) were measured using
228 commercial gas analyzers (Thermo Scientific). Photolysis frequencies were measured using
229 a spectroradiometer (PFS-100, Focused Photonics Inc.). In addition, temperature, pressure,
230 relative humidity and wind were continuously measured during two campaigns.

231 **3. Results and Discussion**

232 **3.1 Ambient concentrations and diurnal variations of higher alkanes**

233 Although NO⁺ chemistry has been shown to be valuable in measuring many organic species,
234 the applications in real atmosphere of different environments are still rare (Koss et al., 2016).
235 Here, we compared the measurements of various VOCs from NO⁺ PTR-ToF-MS with both

236 H₃O⁺ PTR-ToF-MS and GC-MS/FID during the two campaigns. Overall, good agreements
237 between PTR-ToF-MS (both H₃O⁺ and NO⁺ chemistry) and GC-MS/FID are obtained for
238 aromatics and oxygenated VOCs except benzene (Figure S13, S14). Benzene measurements in
239 H₃O⁺ chemistry show large difference with benzene measured from NO⁺ chemistry in the
240 earlier period of PRD campaign (11 Sep.-14 Oct. 2018), but good agreement was obtained for
241 the rest of measurement period. Considering good agreement of benzene between NO⁺ PTR-
242 ToF-MS and GC-MS/FID, we used benzene data from NO⁺ measurement in this study. The
243 time series and diurnal variations of alkanes (C8-C11) between NO⁺ PTR-ToF-MS and GC-
244 MS/FID are shown in Figure 5 (and Figure S15). Similar temporal trends for these alkanes are
245 observed from the two instruments. However, the diurnal patterns of total alkanes from NO⁺
246 PTR-ToF-MS have a deeper afternoon trough than the *n*-alkanes measured by GC-MS,
247 implying that *n*-alkanes may have different temporal variations compared with those of total
248 alkanes. The concentrations at each carbon number from NO⁺ PTR-ToF-MS are ~3-6 times
249 those from GC-MS/FID. This is expected, as dozens to hundreds of isomers exist for alkanes
250 with carbon number at this range (Goldstein and Galbally, 2007) and GC-MS/FID only
251 measured one or a few isomers. Based on measurements from NO⁺ PTR-ToF-MS and GC-
252 MS/FID, we compute the molar concentration fractions of *n*-alkanes for each carbon number
253 (Figure 6 and Table S1). We found the fractions are in the range of 11%-21% for carbon
254 number of 8-11, which are comparable with results of ambient air in California, tunnel test and
255 vehicle exhausts (Figure 6 and Table S2) (Chan et al., 2013; Worton et al., 2014; Gentner et
256 al., 2012). These results indicate the importance of branched alkanes in concentrations of
257 higher alkanes and their potential contributions to SOA formation. It also has strong
258 implication for the merits of NO⁺ PTR-ToF-MS in measuring sum of the alkanes with the same
259 formula for estimation of SOA contributions, as discussed later.

260 Table 2 summarizes means and standard deviations of concentrations of C8-C21
261 higher alkanes measured in PRD and in NCP, respectively. The mean concentrations of *n*-
262 alkanes measured at a suburban site in Paris (Ait-Helal et al., 2014) and an urban site in
263 Pasadena, U.S. are also included in Table 1 for comparison. According to the fraction of *n*-
264 alkanes, the mean concentrations of *n*-alkanes in China are found to be comparable to that
265 from Paris and higher than in Pasadena. In general, concentrations of higher alkanes
266 concentration decrease with the increase of carbon number, with octanes (C8) at ~0.5 ppb and
267 heneicosanes (C21) at ~0.002 ppb. This decreasing pattern of carbon distribution are as the
268 results of lower emissions from sources (Gentner et al., 2012), larger reactivity towards OH
269 radicals (Atkinson et al., 2008;Keyte et al., 2013) and larger fractions partitioning to particles
270 (Liang et al., 1997;Xie et al., 2014;Zhao et al., 2013) in the atmosphere.

271 The diurnal variations of selected higher alkanes are shown in Figure 7. C12 alkanes
272 and C15 alkanes exhibit similarly strong diurnal variations at both sites, with a relatively
273 high levels at night and minimum concentrations detected in the late afternoon at both sites.
274 Such diurnal patterns are consistent with other primary VOCs species (e.g. aromatics). In
275 PRD, the diurnal variations of higher alkanes were as the result of faster chemical removal
276 in the daytime and shallow boundary layer heights at night. Since OH concentrations in NCP
277 during winter were much lower than that in PRD during autumn (Figure S16), diurnal
278 variations of higher alkanes in NCP were mainly influenced by the change of boundary layer.
279 The diurnal profiles of other higher alkanes are similar to C12 and C15 alkanes (Figure S17).

280 **3.2 Estimation of the contributions of higher alkanes to SOA formation**

281 A time-resolved approach based on consideration of photo-oxidation processes with
282 OH radical (Ait-Helal et al., 2014) was applied to estimate contributions of higher alkanes
283 to SOA during these two campaigns. In order to evaluate the relative importance to SOA

284 from different precursors, the same method was also used for monoaromatics, naphthalenes,
285 and isoprenoids.

286 This method considers the amount of chemical removal based on the parameterized
287 photochemical age, which was widely used to quantify contributions of different VOC
288 precursors to SOA formation (Zhao et al., 2014a; Ait-Helal et al., 2014; de Gouw et al., 2009).

289 The contributions to SOA formation from different compounds are determined by the ratios
290 of calculated SOA production amounts from individual precursors (SI, Appendix 2) and
291 SOA concentrations derived from factor analysis of OA measurements by AMS (SI,
292 Appendix 3). In this method, SOA formation for a given compound can be estimated by

$$293 [SOA_i]_t = [VOC_i]_t \times (e^{k_{VOC_i} \times [OH] \times \Delta t} - 1) \times Yield_i \quad (1)$$

294 where $[SOA_i]_t$ is the calculated SOA production ($\mu\text{g m}^{-3}$) for a given specific compound VOC_i
295 at time t , $[VOC_i]_t$ is the VOC_i concentration measured at time t ($\mu\text{g m}^{-3}$), $Yield_i$ is the SOA
296 yield data summarized from chamber studies, k_{VOC_i} is the rate constant of VOC_i with the OH
297 radical ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). $[OH]$ is the OH concentration (molecules cm^{-3}), Δt is the
298 photochemical age. In this study, we calculate the $[OH] \times \Delta t$ ($\text{molecules cm}^{-3} \text{ s}$), which was
299 considered as OH exposure in some studies (Jimenez et al., 2009). The OH exposure is
300 estimated by the ratio m+p-xylene and ethylbenzene with different reactivity for anthropogenic
301 VOCs and by the oxidation processes of isoprene for biogenic VOCs, respectively (Apel et al.,
302 2002; Roberts et al., 2006) (see details in SI, Appendix 4 and Figure S18). Since biogenic
303 emissions were pretty weak during cold winter (mean temperature 0.5 ± 3.6 °C) during NCP
304 campaign, measured concentrations of isoprene and monoterpenes are attributed to be of
305 anthropogenic origin during the winter campaign in NCP campaign, especially given the fact
306 that they showed similar variations, diurnal profiles and strong correlation with CO and
307 anthropogenic VOCs species (Figure S19). A previous study in Helsinki also found the

308 importance of anthropogenic emission in monoterpene concentrations (Hellén et al., 2012).

309 Based on equation (1), SOA production from higher alkanes (C8-C21 alkanes),
310 monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics, styrene), naphthalenes
311 (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene,
312 monoterpenes) were calculated. The concentration data of higher alkanes, isoprenoids and
313 benzene were taken from measurements of NO⁺ PTR-ToF-MS. The concentration data of
314 naphthalenes (Figure S20) and monoaromatics except benzene were taken from
315 measurements of H₃O⁺ PTR-ToF-MS. The detail about the H₃O⁺ PTR-ToF-MS measurements
316 can be found in Wu et al. (2020). The OH reaction rate constant of each compound was taken
317 from literature (Atkinson, 2003). SOA yield data used here for higher alkanes (Lim and
318 Ziemann, 2009;Presto et al., 2010a;Loza et al., 2014;Lamkaddam et al., 2017b),
319 monoaromatics (Li et al., 2016;Ng et al., 2007;Tajuelo et al., 2019), naphthalenes (Chan et al.,
320 2009) and isoprenoids (Ahlberg et al., 2017;Carlton et al., 2009;Edney et al., 2005;Kleindienst
321 et al., 2006;Pandis et al., 1991) were summarized from reported values in the literature, with
322 the consideration of the influence of organic aerosol concentration (Figure S21) to SOA yields
323 (Donahue et al., 2006) (Figure S22-23). SOA yields under high NO_x conditions are used in
324 this study, as relatively high NO_x concentrations in PRD (42.6±33.7 ppb) and in NCP
325 (81.7±57.0 ppb) (Figure S24) would cause RO₂ radicals from organic compounds mainly
326 reacting with NO (Bahreini et al., 2009).

327 Both OH reaction rate constants and SOA yields of *n*-alkanes reported in the literature
328 are applied for higher alkanes, as most of the chamber studies have focused on *n*-alkanes.

329 Considering the SOA yields of branched alkanes are lower than *n*-alkanes, which is depending
330 on chemical structures of the carbon backbone (Lim and Ziemann, 2009;Tkacik et al.,
331 2012;Loza et al., 2014), the estimation of SOA from alkanes in this study might be a little
332 overestimated. As shown above, temperature (mean temperature 0.5±3.6 °C) in NCP winter

333 campaign was significantly lower than the temperature (usually 25 °C) at which SOA yields
334 are derived from chamber studies. Temperature can significantly influence SOA yields, with
335 higher yields at lower temperature (Takekawa et al., 2003; Lamkaddam et al., 2017b). It might
336 cause underestimation of SOA production from various precursors in winter of NCP.

337 The calculated results of SOA production for different higher alkanes are shown in
338 Figure 8. Although lower concentrations of heavier alkanes were observed for both
339 campaigns, the calculated SOA production are largest for C12-C18 (Figure 8(b)). This is
340 because of two reasons: (1) Alkanes with larger carbon number have larger SOA yields. The
341 calculated average SOA yields (Table S3) during the two campaigns are both larger than 0.2
342 for >C12 alkanes and increase to near unity for C20-C21 alkanes. (2) Larger alkanes are
343 relatively more reactive than lighter ones, which results in larger proportions of calculated
344 concentrations that have been chemically consumed in the atmosphere (the concentrations
345 labelled “consumed” in Figure 8(a)). The distribution of contributions from alkanes with
346 different carbon number to SOA formation shown here is in good agreement with the
347 previous results referred from volatility calculation for precursors (de Gouw et al.,
348 2011; Liggio et al., 2016). The peaks in alkanes SOA productions occur around C15 in both
349 campaigns of PRD and NCP, which is a great result that shows the importance of IVOCs on
350 SOA.

351 Along with higher alkanes, SOA production for monoaromatics, naphthalenes and
352 isoprenoids are shown in Figure 9 (and Figure S25-27). Compared to monoaromatics, higher
353 alkanes are associated with lower concentrations (Figure S28). However, higher alkanes play
354 an important role in SOA formation due to their high SOA yields (Figure S29). The total
355 average SOA production from C8-C21 alkanes are $0.6 \pm 0.8 \mu\text{g m}^{-3}$ and $0.7 \pm 0.8 \mu\text{g m}^{-3}$ in PRD
356 and NCP, respectively. The formed SOA from higher alkanes account for $7.0 \pm 8.0\%$ and
357 $9.4 \pm 9.1\%$ of SOA formation in PRD and NCP, respectively. The contributions of

358 monoaromatics to SOA formation are $6.2\pm 7.7\%$ and $9.4\pm 17.4\%$ in PRD and NCP,
359 respectively. Naphthalenes have been proposed to be important precursors of SOA from
360 laboratory chamber studies (Kleindienst et al., 2012). In this study, we determine $2.8\pm 4.6\%$
361 of SOA in PRD and $11.1\pm 14.3\%$ of SOA in NCP are contributed by naphthalenes. The SOA
362 contribution from naphthalenes determined for NCP is comparable to the results ($10.2\pm 1.0\%$)
363 obtained during haze events in Beijing in a recent study (Huang et al., 2019). Significant
364 contribution from monoterpenes to SOA ($8.7\pm 14.6\%$) is observed in NCP. As mentioned
365 above, we attribute these isoprene and monoterpenes to anthropogenic emissions in this region.
366 The SOA precursors considered in this study in total could explain 14.9%-29.0% and 16.4-
367 125.3% of SOA formation in PRD and NCP, respectively. The influence of chamber-based
368 vapour wall losses on SOA yields was examined in previous studies (Zhang et al., 2014) and
369 the results show that the literature reported SOA yields are low by factors of ~ 1.1 -2.2 for the
370 high NO_x conditions (Table S4). This suggests that the SOA estimations in this study might
371 be correspondingly underestimated. The low explained percentages of SOA formations in
372 both of PRD and NCP (Figure 9(c, d)) imply that some other SOA precursors (e.g.
373 alkylcyclohexanes, alkylbenzenes, cyclic and polycyclic aliphatic materials) (Zhao et al.,
374 2015; Drozd et al., 2019) or formation pathways (e.g. aqueous reactions) (Kuang et al., 2020)
375 are contributing significantly to SOA formation. Compared to a previous study in northern
376 China (Yuan et al., 2013), the missing gap of SOA formation declined after explicitly
377 considering higher alkanes and naphthalenes in SOA production.

378 As shown in Figure 9, we find that C8-C21 higher alkanes contribute significantly to
379 SOA formation at both an urban site in autumn of PRD and a rural site in winter of NCP.
380 The contributions from higher alkanes are either comparable or higher than both
381 monoaromatics and naphthalenes. Another estimation method by considering SOA
382 instantaneous production rates obtained similar results (Figure S30), which confirms the

383 results from the photochemical age based on parameterization method shown above. The
384 importance of higher alkanes in SOA formation has been also proposed in several previous
385 SOA modelling studies (Pye and Pouliot, 2012;Zhao et al., 2014b). These results, along with
386 our results from observations in ambient atmosphere, underline that the inclusion of higher
387 alkanes in SOA models in the atmosphere should be considered if possible.

388 **4. Concluding remarks**

389 In this study, we utilized a NO^+ PTR-ToF-MS to measure C8-C21 alkanes in two different
390 environments in China. Based on a series of laboratory experiments, we show that NO^+ PTR-
391 ToF-MS can provide online measurements of higher alkanes with high accuracy and fast
392 response. The measured concentrations of higher alkanes were relatively high during the two
393 campaigns. The diurnal profiles of higher alkanes are similar to anthropogenic VOCs,
394 implying they are emitted from anthropogenic sources.

395 On the basis of measurements of higher alkanes by NO^+ PTR-ToF-MS, we successfully
396 take into account their contributions in SOA formation. The time-resolved measurements of
397 higher alkanes by NO^+ PTR-ToF-MS provide the opportunity to accurately apply the
398 photochemical age-based parameterization method. As there is no separation before detection
399 in PTR-ToF-MS, the measured concentrations of NO^+ PTR-ToF-MS represent all of the
400 compounds that contribute to the product ions ($m-1$ ions), which include concentrations from
401 both *n*-alkanes and branched alkanes. With the total concentration of both *n*-alkanes and
402 branched alkanes quantified, the contribution from higher alkanes at each carbon number can
403 be estimated as a whole. This is an important supplementary method to the traditional
404 analytical method by GC techniques for higher alkanes, as fully chemical separation and
405 detection of numerous isomers of higher alkanes remain as a challenge, even using the most
406 advanced GC \times GC-ToF-MS instruments (Chan et al., 2013;Alam et al., 2016).

407 Higher alkanes were found to have significant contributions to SOA in both PRD and
408 NCP regions with a similar or even higher contributions than that of monoaromatics and
409 naphthalenes. The importance of higher alkanes to SOA formation also call for more work
410 to investigate emissions and chemistry of these compounds in the atmosphere. It was shown
411 that fossil-related combustions such as vehicle exhausts are major sources for higher alkanes
412 (Zhao et al., 2016). While, recent studies have shown that non-combustion sources, such as
413 the use of solvents, have a potentially significant impact on high-alkane emissions
414 (McDonald et al., 2018;Khare and Gentner, 2018). However, such quantitative information
415 on emissions of higher alkanes is still limited. The measurements of higher alkanes by NO⁺
416 PTR-ToF-MS with fast response could help to fill these research gaps.

417

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429 **Data availability**

430 Data is available from the authors upon request

431 **Competing interests**

432 The authors declare that they have no conflicts of interest

433 **Author contributions**

434 BY and MS designed the research. CMW, CHW, SHW, JPQ, BLW, WC, CW, WS and
435 WYX contributed to data collection. CMW performed the data analysis, with contributions
436 from ZLW, WWH, SXY and CSY. CMW and BY prepared the manuscript with contributions
437 from other authors. All the authors reviewed the manuscript.

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755

756 **Table 1.** Fractions of product ions (m-1) ions in mass spectra, sensitivities and detection
 757 limits of higher alkanes in NO⁺ PTR-ToF-MS.

Compounds	Ions	Fractions of	Sensitivities	Detection limit for	Detection limit for
		(m-1) ions (%)	(ncps/ppb)	10 s integration (ppt)	1 min integration (ppt)
<i>n</i> -Octane	C ₈ H ₁₇ ⁺	24	104.6	3.5	1.3
<i>n</i> -Nonane	C ₉ H ₁₉ ⁺	32	106.3	3.2	1.2
<i>n</i> - <i>n</i> -Decane	C ₁₀ H ₂₁ ⁺	39	120.9	3.5	1.3
<i>n</i> -Undecane	C ₁₁ H ₂₃ ⁺	44	140.9	3.3	1.2
<i>n</i> -Dodecane	C ₁₂ H ₂₅ ⁺	62	156.3	2.4	0.9
<i>n</i> -Tridecane	C ₁₃ H ₂₇ ⁺	61	186.6	2.1	0.8
<i>n</i> -Tetradecane	C ₁₄ H ₂₉ ⁺	64	220.7	1.9	0.7
<i>n</i> -Pentadecane	C ₁₅ H ₃₁ ⁺	84	205.5	1.7	0.6
<i>n</i> -Hexadecane	C ₁₆ H ₃₃ ⁺	95	/	1.6	0.6
<i>n</i> -Heptadecane	C ₁₇ H ₃₅ ⁺	82	/	1.8	0.7
<i>n</i> -Octadecane	C ₁₈ H ₃₇ ⁺	90	/	1.8	0.7
<i>n</i> -Nonadecane	C ₁₉ H ₃₉ ⁺	71	/	1.2	0.4
<i>n</i> -Eicosane	C ₂₀ H ₄₁ ⁺	86	/	1.9	0.7
<i>n</i> -Heneicosane	C ₂₁ H ₄₃ ⁺	/	/	2.0	0.7

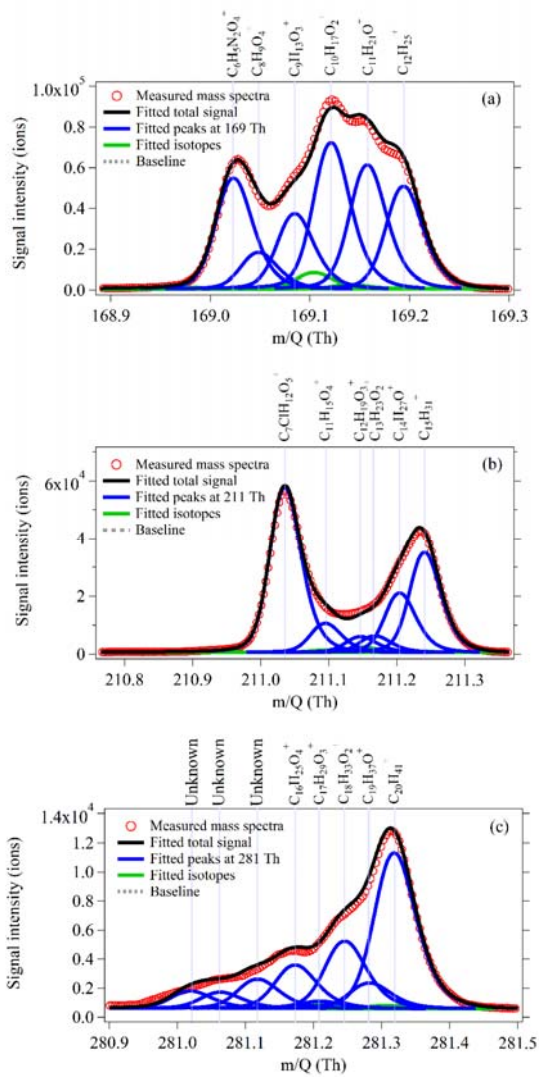
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759

760 **Table 2.** Mean concentrations of alkanes (C8-C21) in different sites worldwide.

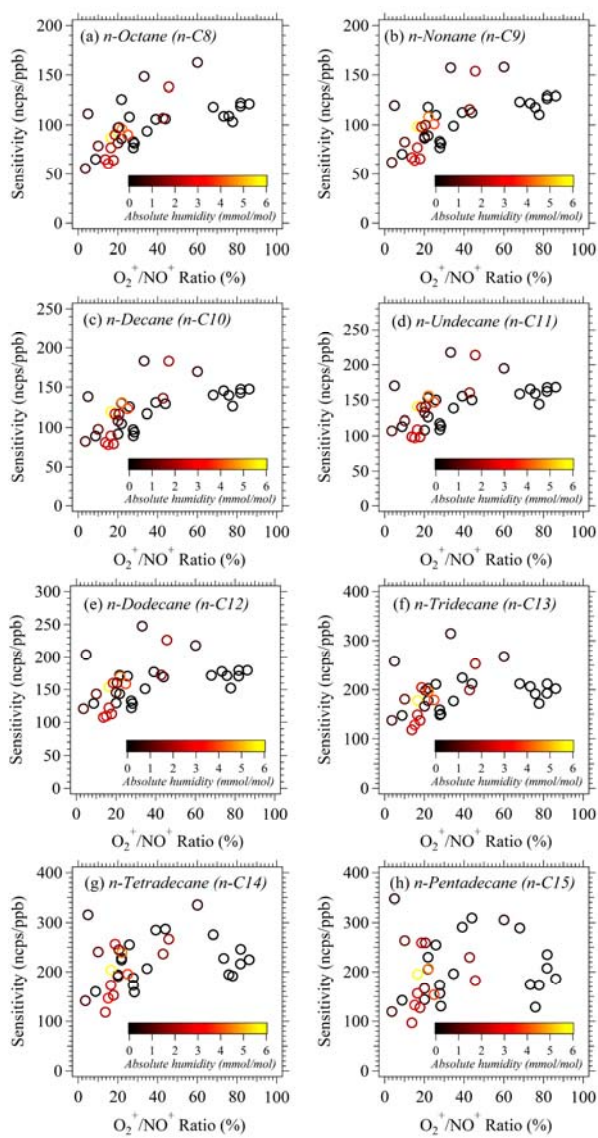
Compounds	Formula	PRD, China ^a (ppt)	PRD, China ^b (ppt)	NCP, China ^a (ppt)	Paris, France ^c (ppt)	Pasadena, US ^d (ppt)
Octane	C ₈ H ₁₈	482±488	50±49	412±270	/	/
Nonane	C ₉ H ₂₀	208±186	43±32	252±162	14±13	/
Decane	C ₁₀ H ₂₂	174±199	29±28	224±147	24±22	/
Undecane	C ₁₁ H ₂₄	129±138	21±17	170±119	19±16	/
Dodecane	C ₁₂ H ₂₆	122±120	/	129±86	22±21	8±1
Tridecane	C ₁₃ H ₂₈	66±60	/	89±59	13±12	6±1
Tetradecane	C ₁₄ H ₃₀	50±47	/	57±39	27±23	9±2
Pentadecane	C ₁₅ H ₃₂	45±42	/	46±33	23±18	5±0.8
Hexadecane	C ₁₆ H ₃₄	36±33	/	32±24	22±19	4±1
Heptadecane	C ₁₇ H ₃₆	21±20	/	18±14	/	3±0.4
Octadecane	C ₁₈ H ₃₈	13±14	/	11±9	/	1.6±0.5
Nonadecane	C ₁₉ H ₄₀	5±9	/	4±7	/	0.7±0.2
Eicosane	C ₂₀ H ₄₂	0.7±4	/	3±6	/	0.24±0.08
Heneicosane	C ₂₁ H ₄₄	0.5±5	/	2±5	/	0.15±0.1

761 ^a: alkanes measured with NO⁺ PTR-ToF-MS; ^b: *n*-alkanes measured with GC-MS; ^c: *n*-alkanes from Ait-Helal762 et al. (2014); ^d: *n*-alkanes from Zhao et al. (2014a).



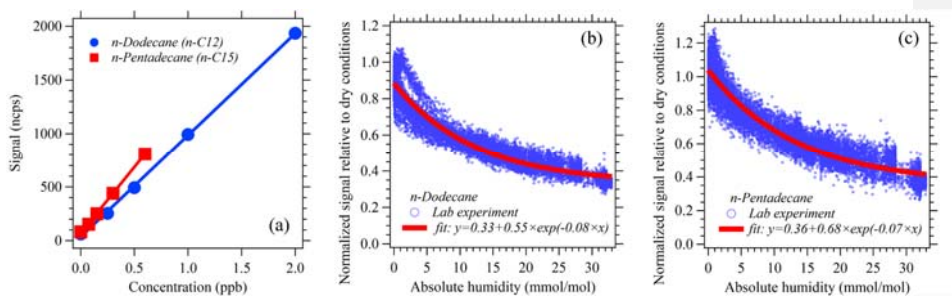
763

764 **Figure 1.** High-resolution (HR) peak-fitting to the averaged mass spectra on a typical day (12
 765 October 2018) for m/z 169 (a), m/z 211 (b) and m/z 281 (c), at which masses produced by
 766 dodecane (C₁₂H₂₅⁺), pentadecane (C₁₅H₃₁⁺) and eicosane (C₂₀H₄₁⁺) in NO⁺ PTR-ToF-MS.



767

768 **Figure 2.** The relationship of sensitivities of *n*-alkanes (C8-C15) versus O_2^+ / NO^+ ratios during
 769 the NCP campaign. The data points are color-coded using absolute humidity during the
 770 calibration.

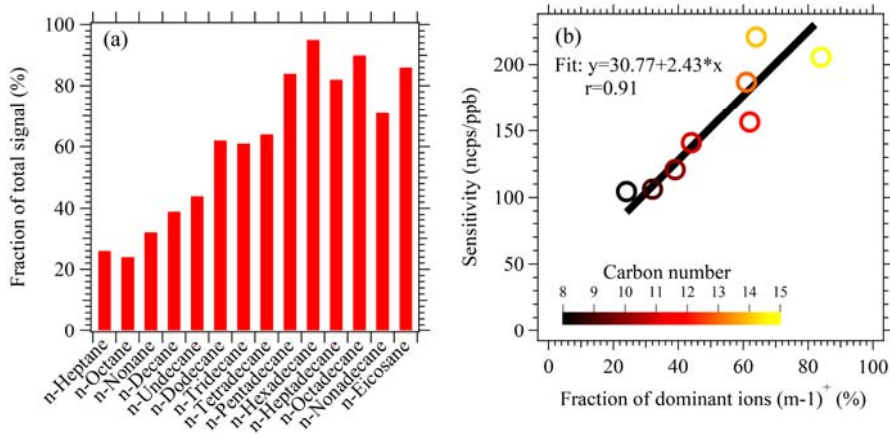


771

772 **Figure 3.** (a) Calibrations of *n*-Dodecane and *n*-Pentadecane under dry conditions; (b)

773 Humidity dependence of *n*-Dodecane. (c) Humidity dependence of *n*-Pentadecane.

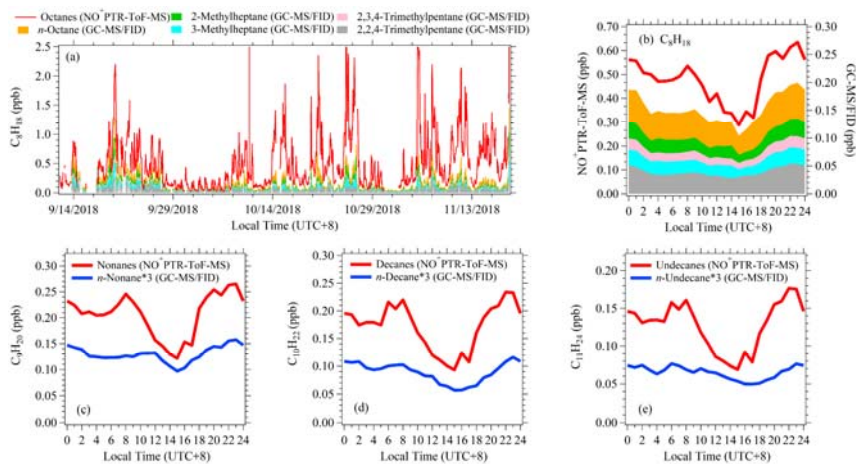
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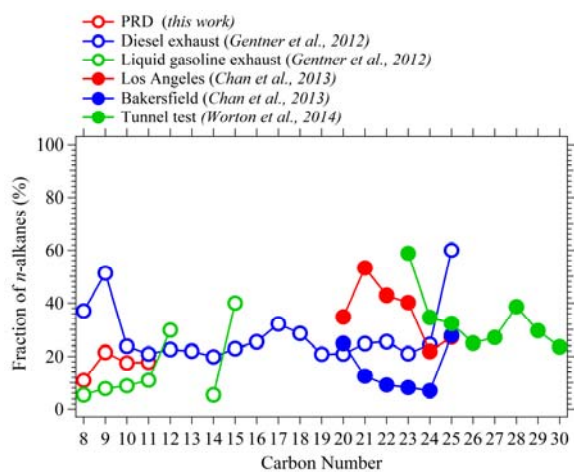
776 **Figure 4.** (a) The fractions of product ions (m-1) from hydride abstraction of C8-C20 *n*-alkanes
 777 in NO⁺ PTR-ToF-MS. (b) Scatterplot of sensitivities under dry conditions versus the fractions
 778 of hydride abstraction ions for C8-C15 *n*-alkanes.

779



780

781 **Figure 5.** Comparisons of times series and diurnal variations of alkanes measured by NO⁺
 782 PTR-ToF-MS and GC-MS/FID in PRD. **(a)** Time series of C8 alkanes measured by NO⁺ PTR-
 783 ToF-MS, C8 *n*-alkane and four branched isomers measured by GC-MS/FID. **(b)** Diurnal
 784 variations of C8 alkanes. **(c-e)** Diurnal variations of C9-C11 alkanes with NO⁺ PTR-ToF-MS
 785 and C9-C11 *n*-alkanes with GC-MS/FID.

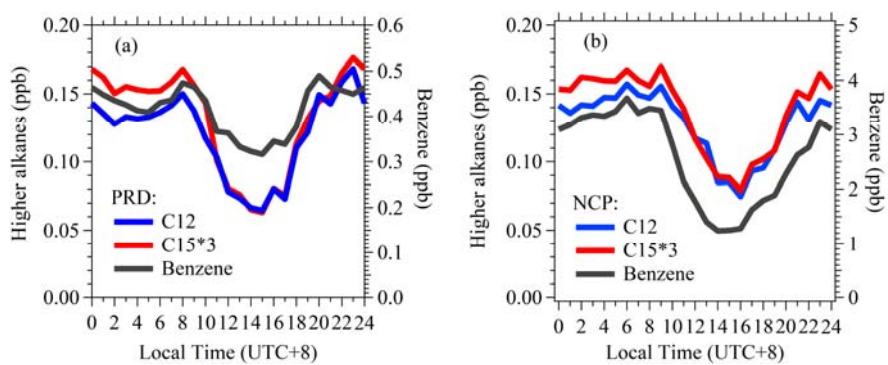


786

787 **Figure 6.** Fractions of *n*-alkanes in higher alkanes with same formulas in gas phase (hollow
 788 dots) and particle phase (solid dots) derived from this study, ambient air in Los Angeles,
 789 Bakersfield, Caldecott Tunnel and in vehicle exhausts (Chan et al., 2013; Gentner et al., 2012;
 790 Worton et al., 2014).

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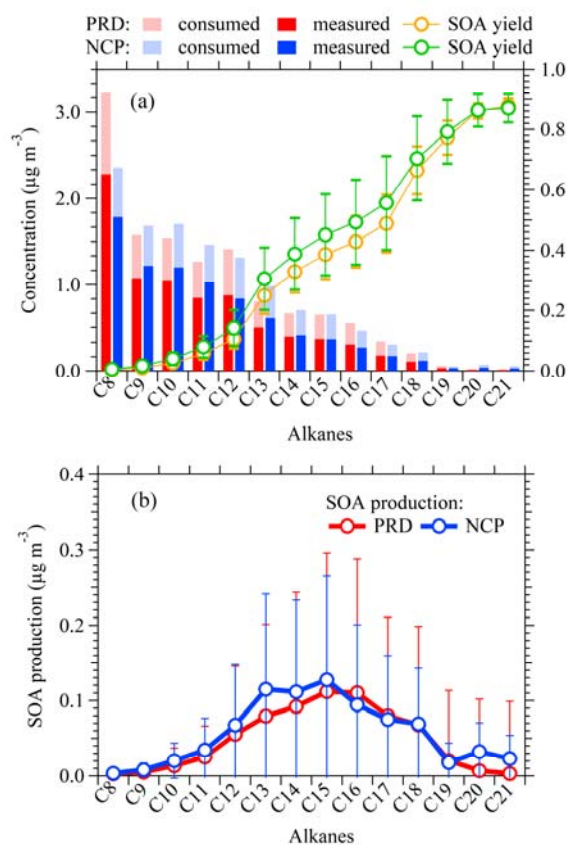
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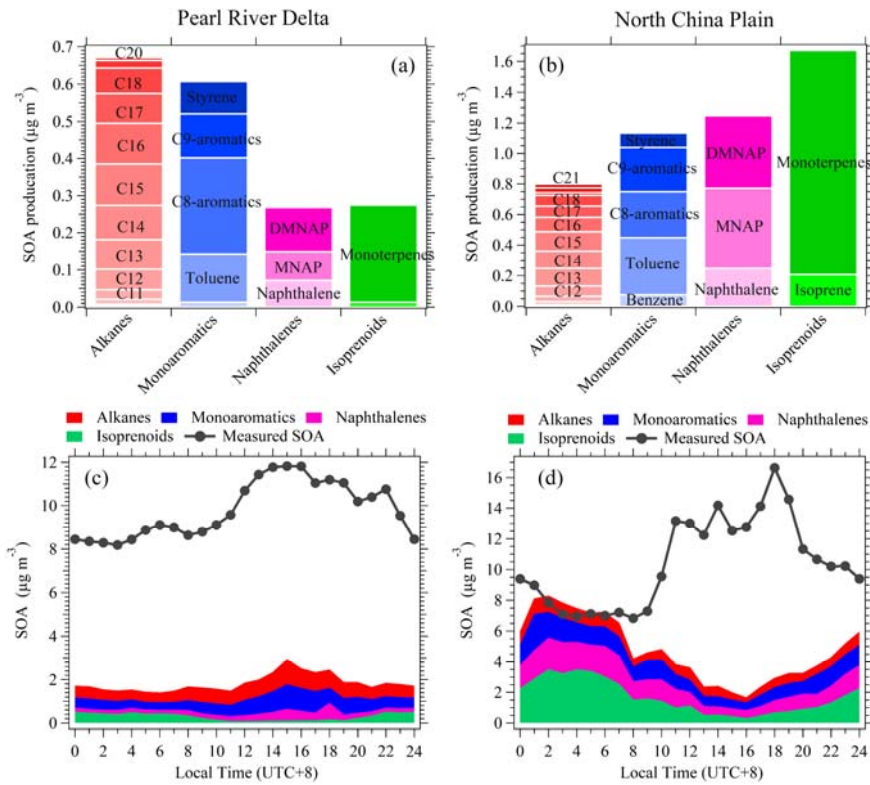
794 **Figure 7.** Diurnal variations of C12 alkanes, C15 alkanes and benzene in PRD (a) and NCP

795 (b).



796

797 **Figure 8.** (a) Measured concentrations by NO^+ PTR-ToF-MS, calculated consumed
 798 concentrations and average SOA yields for C8-C21 alkanes in PRD and NCP. The consumed
 799 concentrations represent the chemical losses of higher alkanes, which are calculated by using
 800 the estimated SOA from each alkane dividing the corresponding SOA yields. The error bars
 801 represent standard deviations (1δ) over the averaging period of calculated SOA yields. (b)
 802 Calculated average SOA productions for C8-C21 alkanes in PRD and NCP. The error bars
 803 represent standard deviations (1δ) over the averaging period of calculated SOA production.



805

806 **Figure 9.** The mean concentrations of SOA produced from higher alkanes (C8-C21 alkanes),
 807 monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes
 808 (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and
 809 monoterpenes) in PRD (a) and NCP (b). Diurnal variations of SOA production from higher
 810 alkanes, monoaromatics, naphthalenes and isoprenoids as well as the measured SOA
 811 concentrations in PRD (c) and NCP (d).