Response to anonymous referee #2

Wang et al measured concentrations of VOC and IVOC alkanes in two locations in China. They use the measurement data to estimate the importance of alkanes to ambient SOA. Based on their estimates, these alkanes make up ~7% of ambient SOA in both sampling locations in north and south China. Overall the manuscript is topically relevant to ACP. It presents what seems to be a novel application of chemical ionization MS for estimating SOA production. However, I have several comments before I can recommend publication.

Response: Thank you very much for your valuable comments and suggestions on our 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.

Major Comments:

(1) I have an issue with calling the measurement technique NO^+ PTR-MS. The "P" in PTR stands for proton, which in this case you are switching out for NO^+ ions. So, the measurement technique is chemical ionization with NO^+ or selected ion mass spectrometry, but not PTR. An exception would perhaps be if you're using PTR-MS to indicate the instrument itself (e.g., an Ionicon PTR-MS) that has been modified.

Response: We understand the reviewer's concern. We use the NO^+ PTR-TOF-MS as the instrument name to reflect the fact that NO^+ chemistry has been mainly adopted from PTR-MS instruments as a switchable reagent ion technique (Jordan et al. 2009), which is also the case for this work. The first attempt to measure higher alkanes using NO^+ chemistry (Inomata et al., 2013) referred this method as NO^+ chemical ionization using proton-transfer-reaction mass spectrometry, which seems to reflect the reality of both the ion chemistry and also the instrumentation used for the method. As the result, we changed the title in the revised manuscript: "**Measurements of higher alkanes using NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China**".

In the main text (line 98-99) of the revised manuscript, we also reflect this information:

"In this study, we utilize NO^+ chemical ionization in PTR-ToF-MS (here referred as NO^+ PTR-TOF-MS) to measure higher alkanes at two different sites in China."

(2) Line 162-170 introduce that the PTR was run alternately with NO^+ and H_3O^+ every 10-20 minutes. This cycling requires more explanation. How was the cycling achieved? How long did the system take to re-equilibrate when the water flow was turned on and off? Even if the system only took 1-2 minutes to re-equilibrate after switching between ions, a large fraction of the data would be lost. Were data during the transition period considered for analysis? Were voltages and pressures changed or held constant in the NO^+ and H_3O^+ operating modes?

Response: We included more details about the automatic switches between H_3O^+ chemistry and NO^+ chemistry in the revised paper. The built-in software offers the possibility to program sequences where the instrument is switching between different settings. It usually takes ~10 s for H_3O^+ and ~60 s for NO^+ to re-stabilize after switching between the two measurement modes. The ambient measurement data during the transition period (~1 min) is discarded. The voltages of ion source and drift chamber are changed in H_3O^+ (Us=150 V, Uso=80 V; Udrift=920 V, Udx=46 V) and NO^+ (Us=40 V, Uso=100 V; Udrift=470 V, Udx=23.5 V) operating modes. The pressures of drift chamber are held constant at 3.8 mbar in both modes during the campaigns.

The added and modified sentences on line 199-205 of page 9 are listed below:

“Switching between H_3O^+ and NO^+ ion mode are provided by the PTR-MS Manager (v3.5) software developed by the Ionicon Anlytik (Table S1). The pressures of drift chamber are held constant at 3.8 mbar in both modes during the campaigns (Figure S10(a)). It usually takes <10 s for H_3O^+ ions and ~60 s for NO^+ ions to re-stabilize after automatically switching between the two measurement modes (Figure S10(b)). The ambient measurement data during the transition period (~1 min) was discarded.”

Table S1. The settings of the voltages of ion source voltages (Us, Uso), drift tube (Udrift, Udx) and pressure of drift tube (pDrift) during automatical switching between NO^+ mode and H_3O^+ mode, respectively.

Setting	NO^+ mode	H_3O^+ mode
Us	40 V	150 V
Uso	100 V	80 V
Udrift	470 V	920 V
Udx	23.5 V	46 V
pDrift	3.8 mbar	3.8 mbar

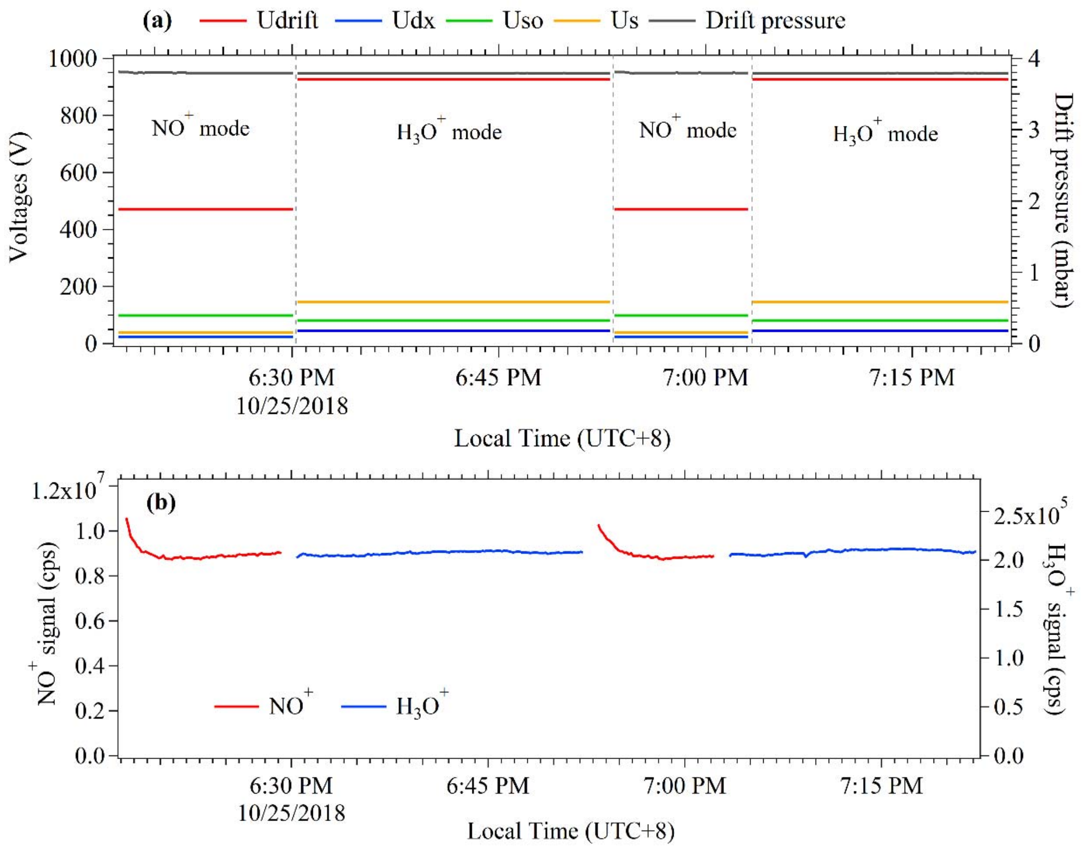

Figure S10. An example of the voltages of ion source voltages (Us, Uso), drift tube (Udrift, Udx) and pressure of drift tube (a), and the signal changes of primary ions (b) during automatical switching between NO$^+$ mode and H_3O^+ mode, respectively.

(3) This paper relies on predicted SOA production to compare the importance of alkanes versus aromatics and other compound classes. However, the SOA estimates rely on a number of assumptions (e.g., SOA yields) that are uncertain. There are other ways to compare the importance of alkanes to other compounds. There is very little discussion of absolute concentrations, which is one way to make the comparison. The authors could also compare something like OH reactivity.

Response: We included the comparison of average concentrations from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) in PRD and NCP in the revised supporting information. Compared to monoaromatics, higher alkanes have lower average concentrations. But due to the high SOA yields, higher alkanes also play an important role in SOA formation.

We added sentences on line 354-356 of page 15 in the revised manuscript as follows:

"Compared to monoaromatics, higher alkanes are associated with lower concentrations (Figure S26). However, higher alkanes play an important role in SOA formation due to their high SOA yields (Figure S27)."

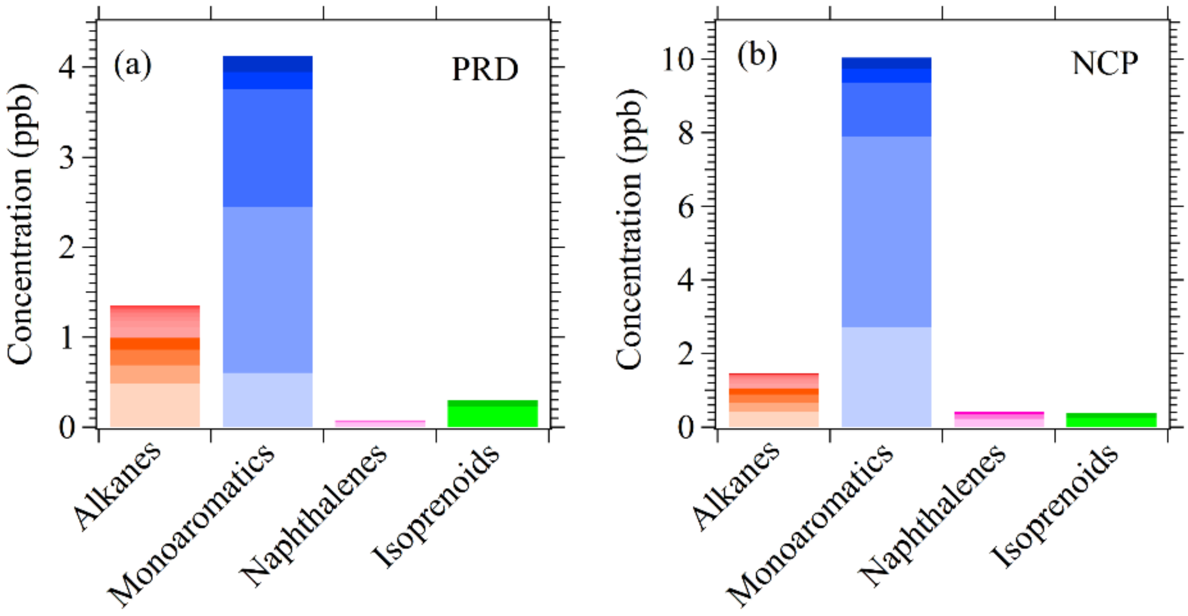

Figure S26. The average concentrations from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) in PRD (a) and NCP (b), respectively.

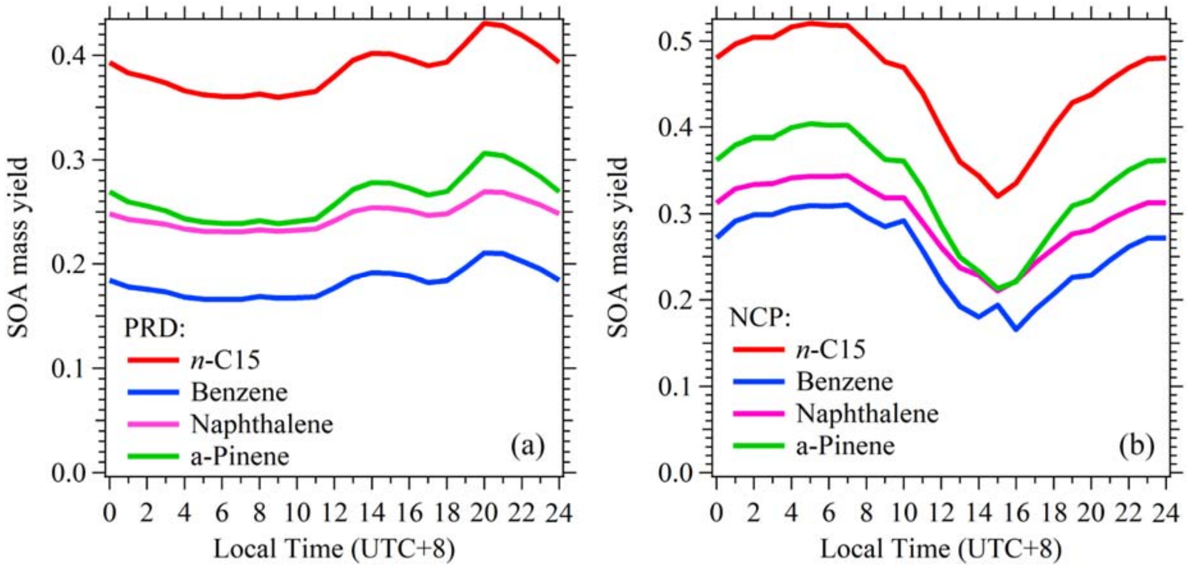

Figure S27. Diurnal variations of SOA yields of *n*-C15 alkane, benzene, naphthalene and α-pinene in PRD (a) and NCP (b).

(4) The comparisons in Figure 8 (and associated discussion) do not seem to place alkanes and aromatics on equal footing. The alkane signal is essentially the sum of all C_x alkanes (i.e., C12 is the sum of dodecane, cyclododecane, and all branched isomers). This is analogous to integrating individual peaks in the GC along with the entire C12 "bin" of UCM (unresolved complex mixture) as shown by Zhao et al (2016a, b) and others. However, the authors only consider specific aromatics (e.g., BTEX) but not the aromatic UCM of larger substituted benzenes. A more complete comparison of alkanes to aromatics would include these species as well.

Response: Many thanks for your nice suggestion. Since we didn't have the measurement of aromatic UCM of larger substituted benzenes during these two campaigns, we only consider the specific aromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene) in this study. The aromatics used in this study are also the most considered aromatic hydrocarbon species in current SOA research. We agree that if the aromatic UCM of larger substituted benzenes are included, the contribution of aromatics to SOA may be even greater. However, in this study we want to emphasize the importance of higher alkanes to SOA formation, which is at least comparable to these common aromatic species, rather than figure out which VOCs class contribute most to SOA. The measurement of aromatic UCM of larger substituted benzenes and their contributions to SOA will also be considered in our future studies.

Minor comments:

(1) Lines 131-136 and Figure 2 - The figure would be easier to interpret if the relative humidity was also shown.

Response: The relative humidity is relative to the temperature. During the campaigns, especially in the NCP campaign, the relative humidity varies a lot due to the temperature changes. While, the sensitivities of higher alkanes are depended on the water vapour content in the sampling air. Previous studies indicate that water vapour in the gas phase can lead to the formation of hydrated hydronium ions ($(H_2O)_n$ H_3O^+) in the drift chamber (Blake et al., 2009). These hydrated hydronium ions can then themselves act as regent ions. Moreover, these hydrated hydronium ions can result in additional reactions (e.g. ligand switching) other than proton transfer in the drift chamber (Midey et al., 2000). Therefore, we use the absolute humidity to present the humidity dependence of higher alkanes in this paper.

(2) Line 192, in the comparison of GC-MS and NO^+ ionization for alkanes: "Similar temporal trends for these alkanes are observed from the two instruments." I can’t really tell this from the figure. The diurnal trends suggest that the PTR-derived measurements have a deeper afternoon trough than the GC-MS, which seems to show a flatter concentration profile.

Response: We modified the figures to make the comparison clearer and easier to read. Since we don’t have sufficient data and evidence, the deeper diurnal trends of higher alkanes in the afternoon from the PTR-derived measurements compared to GC-MS measurements are not discussed in this study.

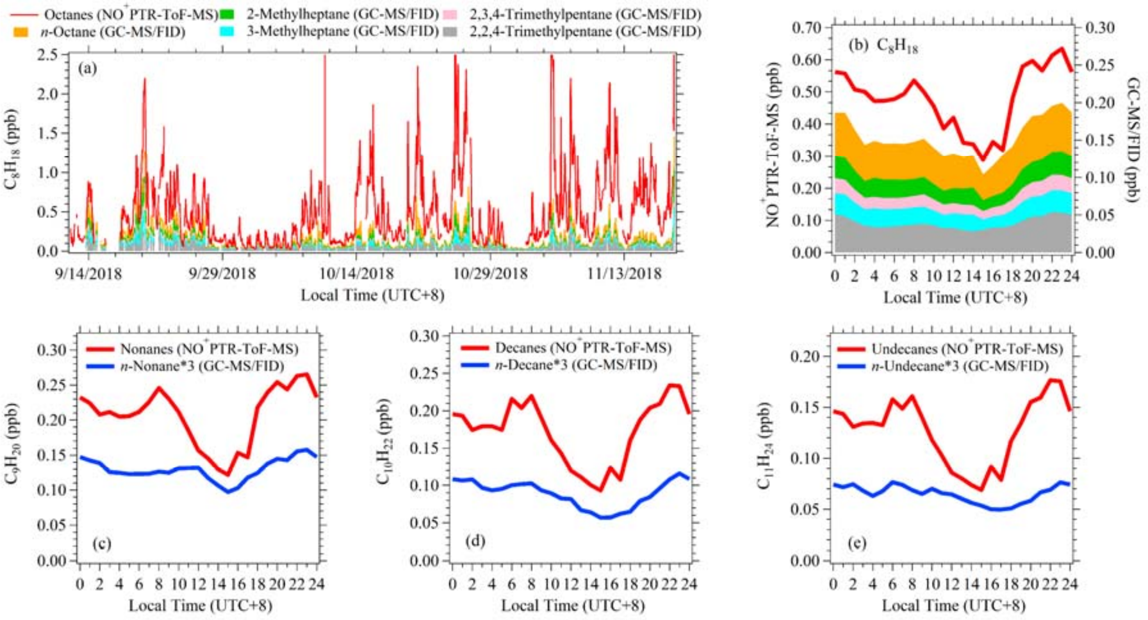

Figure 5. Comparisons of times series and diurnal variations of alkanes measured by NO^+ PTR-ToF-MS and GC-MS/FID in PRD. **(a)** Time series of C8 alkanes measured by NO^+ PTR-ToF-MS, C8 *n*-alkane and four branched isomers measured by GC-MS/FID. **(b)** Diurnal variations of C8 alkanes. **(c-e)** Diurnal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

(3) Line 193-194 - PTR data are a factor of 3-6 higher than the GC data. It looks like the GC data were only analyzed for species that are resolved by the GC (e.g., no UCM). How does the closure look if the entire chromatogram (or the entire m/z 57 signal) is binned and analyzed, similar to Zhao et al's (2016a, b) work?

Response: During the 2018 PRD campaign, the online GC-MS/FID system was operated in the selected ion monitoring (SIM) mode without scanning m/z 57 all the time. Therefore, we are not able to do the work as you suggested here.

(4) Why does Figure 5 only show PRD data for carbon numbers 8-11? The instrument measured up to C21.

Response: The online GC-MS/FID system we used in this campaign can only measure alkanes up to C11. So, we compared only C8-C11 alkanes, which were measured by both GC-MS/FID and NO^+ ToF-MS.

Grammar:

(1) Line 80 states that PTR "is response to large alkanes" - please edit. I think the authors mean that PTR responds to large alkanes.

Response: We modified “is response to large alkanes” to “is responsive to large alkanes”.

(2) Line 160 - replace expect with except

Response: We replaced expect with except.

Reference:

Blake, R. S., Monks, P. S. and Ellis, A. M. Proton-Transfer Reaction Mass Spectrometry. Chemical Reviews 2009, 109(3): 861-896.

Inomata, S., Tanimoto, H., and Yamada, H.: Mass Spectrometric Detection of Alkanes Using NO^+ Chemical Ionization in Proton-transfer-reaction Plus Switchable Reagent Ion Mass Spectrometry, Chemistry Letters, 43, 538-540, 10.1246/cl.131105, 2013.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Herbig, J., Maerk, L., Schottkowsky, R., Seehauser, H., Sulzer, P., and Maerk, T. D.: An online ultra-high sensitivity Proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR+SRI-MS), International Journal of Mass Spectrometry, 286, 32-38, 10.1016/j.ijms.2009.06.006, 2009.

Midey, A. J., Arnold, S. T. and Viggiano, A. A.. Reactions of $H_3O^+(H_2O)_n$ with Formaldehyde and Acetaldehyde. The Journal of Physical Chemistry A, 2000, 104(12): 2706-2709.