Response to anonymous referee #4

General comments:

This work is a nice, extensive manuscript using an NO^+ CIMS (see below) to measure ambient alkanes in the PRD of China and evaluate their importance to SOA chemistry. The experimental methods are high quality and very well-documented. The importance of this manuscript is high, and I find it to be novel and useful.

It is, however, difficult to understand in places and suffers from some lack of precision in language. I recommend publication after these relatively minor, but common issues are fixed.

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.

Specific comments:

(1) Instrument name: The title of the paper and description of the instrument is not correct. PTR is a widely used term that refers to the transfer of a proton from H_3O^+ under controlled conditions. NO^+ ionization uses different ionization mechanisms, particularly charge transfer. I understand the instrument is a commercial PTR-MS, but the authors are now using a different reagent ion and the authors should change the name to something like NO^+ ToF-MS or NO^+ CIMS. Analytical chemistry acronyms are confusing enough as it is. Removing all meaning from them will make them unintelligible to everyone.

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) SOA Yields: There would appear to be a large amount of possible error in these measurements and calculations and it needs to be reflected when yields (SOA production) are displayed across the paper. Some yield calculations are presented with errors and some are not. Figure 7 and 8, in particular have issues with this.

Response: We included the errors when presenting the concentrations, SOA yields and SOA production. The errors displayed in this study refer to the standard deviations (1δ) over the averaging period during the campaigns.

(3) P2 L29: Is it novel? This method has previously been published (with GC comparisons) by some of the co-authors of this paper in Koss et al.

Response: We deleted the word “novel”.

(4) P12 L280: Is this really a surprise? Why? Do those references use different yields or inputs than this work?

Response: We deleted the word “interesting and the sentence was modified to **“The distribution of contributions from alkanes with different carbon number to SOA formation shown here is in good agreement with the previous results referred from volatility calculation for precursors (de Gouw et al., 2011;Liggio et al., 2016)**.”

(5) Figure 1: The mass-to-charge labels on the top of the graph are entirely illegible and the labels on the axes are too small to be conveniently legible. Please make larger. I understand that the authors used the default Tofware labels, but “IndivHRfitCurves” will not mean a lot to most readers. Please change the labels to something clearer in each graph.

Response: We modified this figure in the revised manuscript as follows.

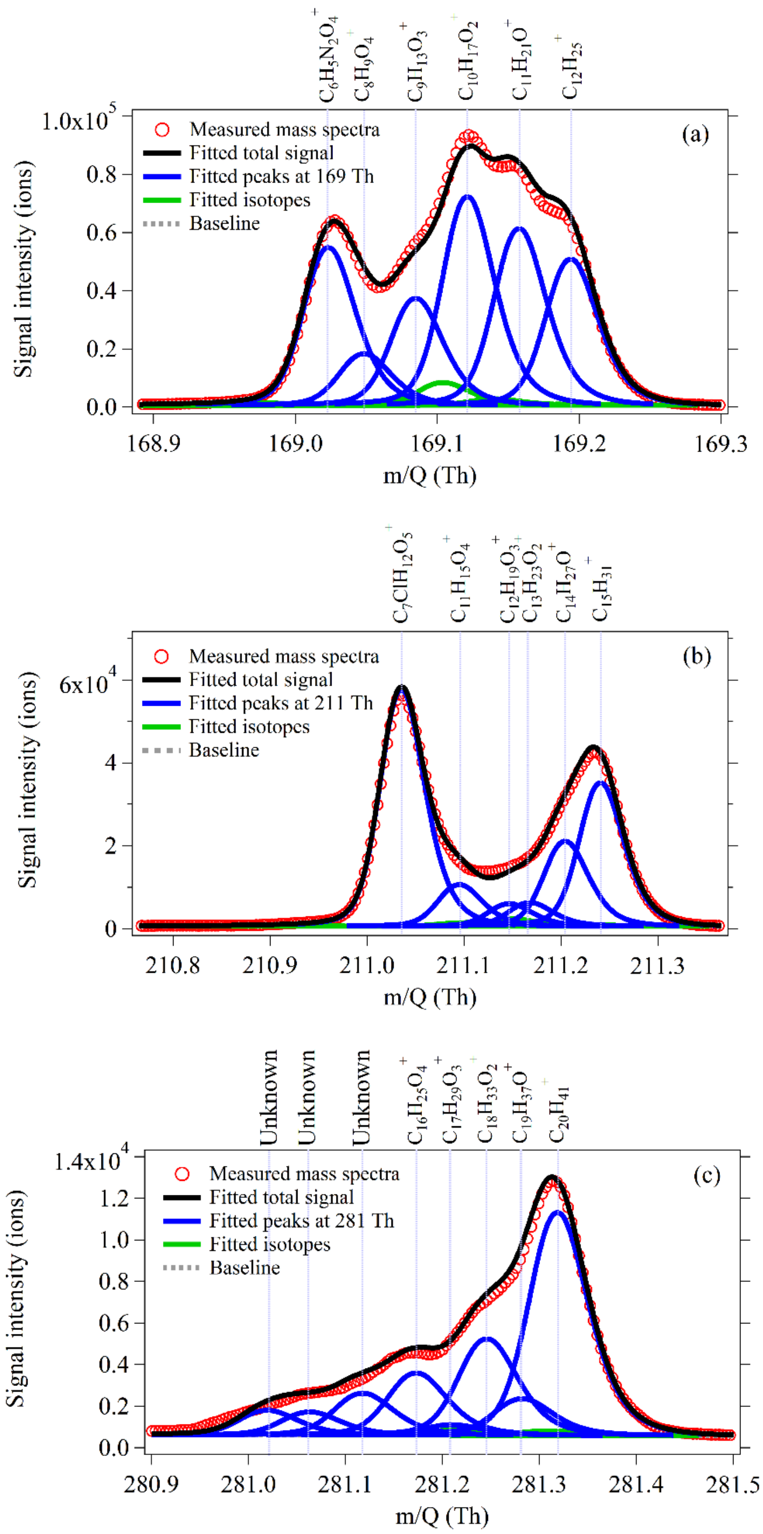

Figure 1. High-resolution (HR) peak-fitting to the averaged mass spectra on a typical day (12 October 2018) for m/z 169 (a), m/z 211 (b) and m/z 281 (c), at which masses produced by dodecane ($C_{12}H_{25}^+$), pentadecane ($C_{15}H_{31}^+$) and eicosane ($C_{20}H_{41}^+$) produced in NO$^+$ PTR-ToF-MS.

(6) Figure 5 gives the impression that the authors suggest the dominant source of alkanes in the region is diesel vehicles. Is that correct? If not, I'm not sure I understand the point of putting those traces on the graph with ambient measurements.

Response: This figure was used to emphasize the importance of contribution of branched isomers to higher alkanes concentrations at each carbon number. Linear alkanes and branched alkanes follow the same molecular formula: C_nH_{2n+2}. When using NO^+ PTR-ToF-MS, we measure the total concentrations of linear alkanes and branched alkanes with the same formulas since this technique doesn't differentiate isomers. We collected data from literatures which are derived from GC-based techniques to calculate the mass fractions of *n*-alkanes in higher alkanes with the same formula from various ambient and emission studies. Because of quite limited studies published about the emission sources of higher alkanes, we only collected few data about the vehicle exhaust. The other emission sources of higher alkanes are still unknown and are needed to study in the future.

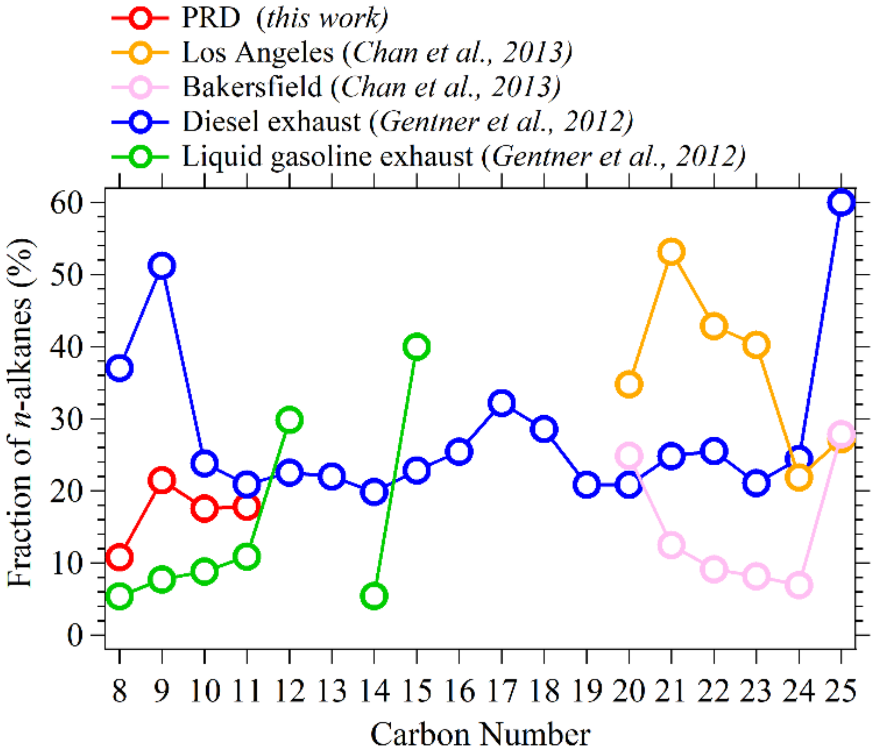

Figure 6. Fractions of *n*-alkanes in higher alkanes with same formulas derived from this study, ambient air in Los Angeles, Bakersfield and in vehicle exhausts.

(7) Figure 7a needs error bars on the calculated SOA yields. There would appear to be a large amount of possible error in these measurements and calculations and it needs to be reflected when yields are displayed in this work

Response: We included the error bars on the calculated SOA yields in Figure 8 in the revised manuscript as follows. In this study, SOA yield data for higher alkanes (Lim and Ziemann, 2009;Presto et al., 2010;Loza et al., 2014;Lamkaddam et al., 2017b) were summarized from reported values in the literature, with the consideration of the influence of organic aerosol concentration to SOA yields (Figure S20). The error bars in Figure 8(a) refer to standard deviations (1δ) over the averaging period of calculated SOA yields. The error bars in Figure 8(b) refer to standard deviations (1δ) over the averaging period of calculated SOA production during the campaigns.

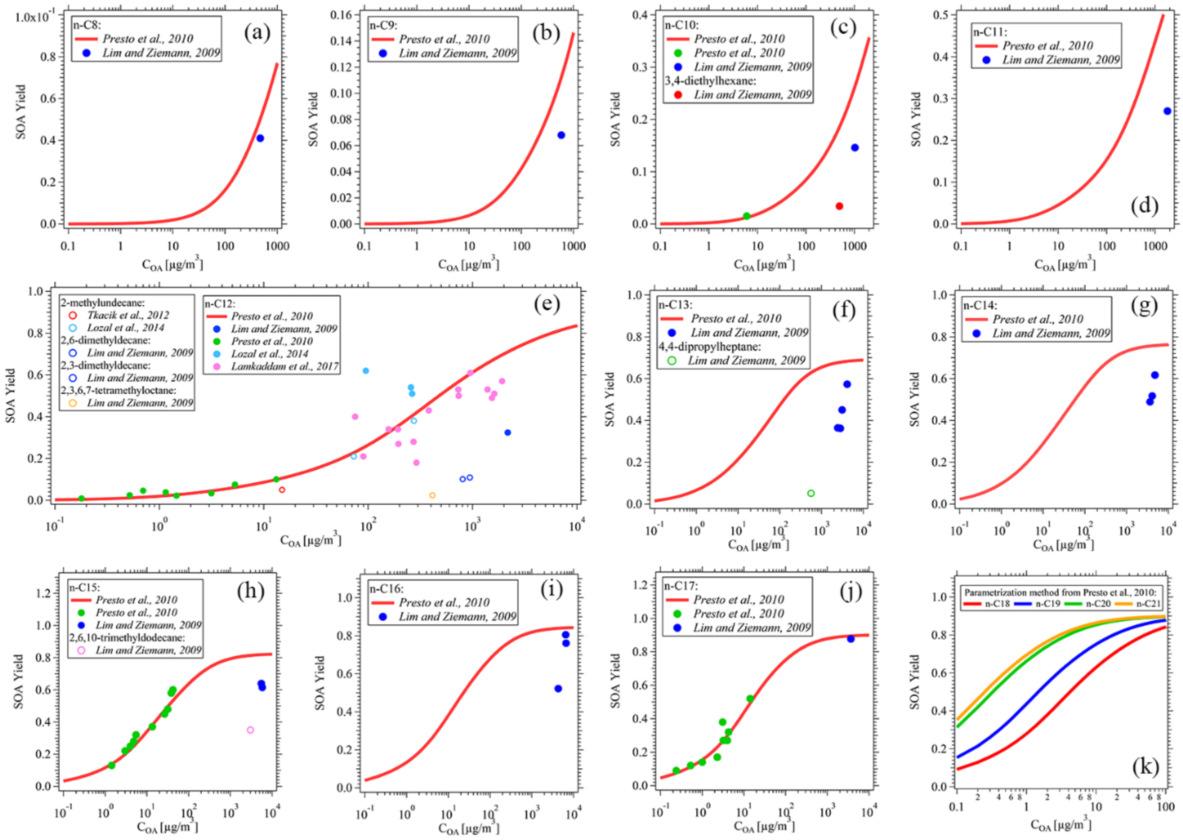

Figure S20. The reported SOA yields as a function of OA concentrations for higher alkanes (C8-C21 alkanes) (a-k) under high-NOx condition from chamber studies.

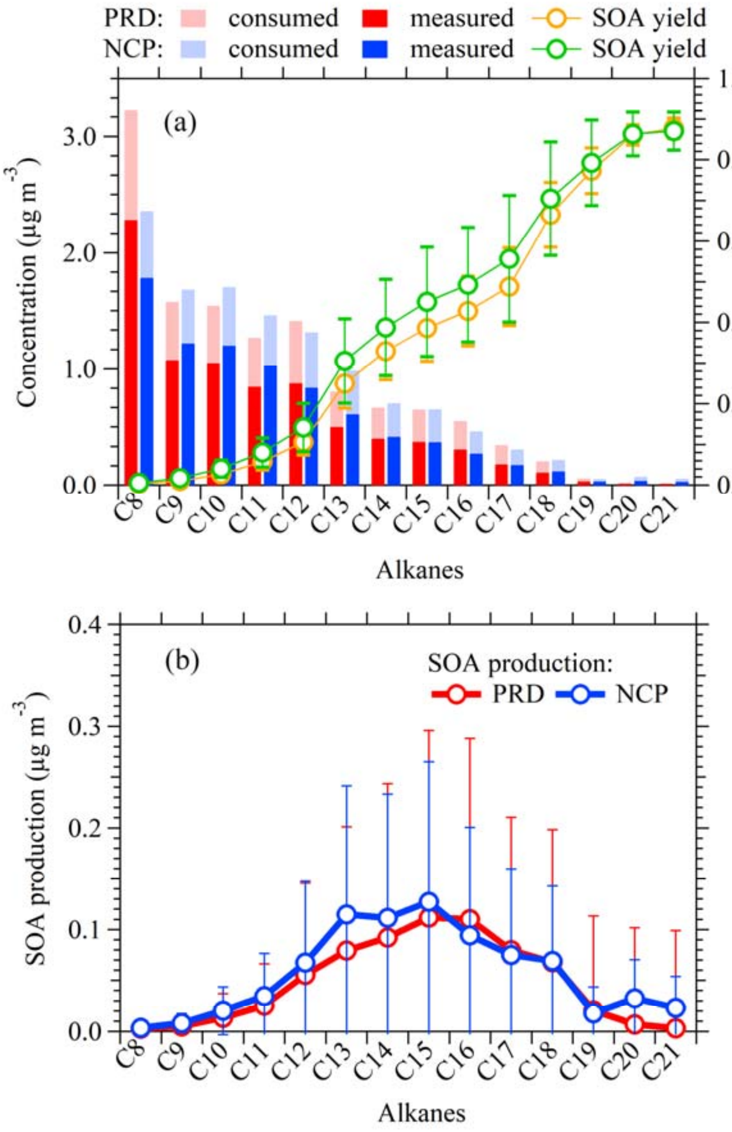

Figure 8. (a) Measured concentrations by NO^+ PTR-ToF-MS, calculated consumed concentrations and average SOA yields for C8-C21 alkanes in PRD and NCP. **The error bars represent standard deviations (1δ) over the averaging period of calculated SOA yields** (b) Calculated average SOA productions for C8-C21 alkanes in PRD and NCP. **The error bars represent standard deviations (1δ) over the averaging period of calculated SOA production**.

Technical corrections:

P4 L80: should be “is responsive” P4 L82: Not PTR-MS. See above. P4 L88: “in more detail.” P5 L102: See above. Not PTR-MS P5 L110: “mass resolving power” instead of resolution P5 L111: “source” P15 L343: “While: : :” this sentence needs to be re-written for grammatical clarity

Many small language clarity issues throughout the manuscript.

Response: Thanks. We corrected all these technical issues and checked the language clarity issues throughout the manuscript.

Reference:

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.