Response to anonymous referee #5:

Wang et al. report on measurements of higher alkanes made with a PTR-ToF-MS in an urban and rural location in China. They find relatively abundant quantities of higher alkanes and, based on estimates of OH concentrations and SOA mass yields, argue that they also contribute meaningfully to SOA formation in both regions. Measuring the chemical composition and complexity of VOCs in the atmosphere is an important step in studying the potential of those VOCs to form SOA and identify the sources of fine particulate matter. The study is well motivated and mostly well written (some detailed comment about technical communication can be found below). I am not overtly familiar with the online mass spectrometry measurements so the editor should rely on the other reviews to make a judgement about that. The data analysis and modeling sections require some additional detail to better communicate the inputs and assumptions. I generally favor publication of this work in ACP but after the authors have had a chance to respond to my comments.

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.

Comments:

1. Line 2: After reviewing the manuscript, I did not find that the word 'significant' was appropriate in the title. The authors find that alkanes are probably as important as aromatics and biogenic VOCs but the model currently still underestimates the total SOA production in both studied regions. The word 'significant' could be misconstrued to mean that alkanes explain the majority of the SOA in urban and rural china.

Response: We replaced the word "significant" with "important".

2. Lines 47-53: This introduction to SOA modeling is not well described and does accurately represent the historical approaches used to model SOA formation. For instance, precursor lumping has been used prior to the volatility basis set.

Response: We modified this part of introduction as follows. "**A volatility basis set (VBS) model was developed to advance SOA modeling by improving the modeling of further multigenerational oxidation processes and incorporating numerous, yet unidentified,**

low-volatility precursors of SOA, which substantially improved the agreement between SOA simulations and observations."

3. Lines 58-61: It might be worthwhile to talk about the differences in the various SOA precursor classes between gasoline and diesel exhaust.

Response: We included the introduction about the differences in the various SOA precursor classes between gasoline and diesel exhaust on line 69-71 of page 4 in the revised manuscript.

"Based on vehicle exhaust tests, higher alkanes were found to contribute ~37% to diesel exhaust-derived SOA and ~0.8% to gasoline exhaust-derived SOA, respectively (Gentner et al., 2012)."

4. Lines 61-63, lines 314-316: A recent study by Akherati et al. (ACP, 2019) also modeled SOA formation from higher alkanes but did not find them to be as important when compared to aromatics, especially after accounting for the effects of vapor wall losses (see #12).

Response: The estimation of SOA formation from higher alkanes in this study is calculated based on the field measurements in the urban and rual regions of China, which is different from the model study in Akherati et al. (ACP, 2019). According to the calculated SOA yield biases for a variety of VOCs when considering the potential influence of vapour wall losses (Table S4), the literature reported SOA yields are low by factors of ~1.1-2.2 for the high NO_x conditions (Zhang et al., 2014). This suggests the SOA calculations in our study might be correspondingly underestimated. However, we still can find the importance of higher alkanes to SOA formation in our study.

Table S4. Average biases in SOA yields due to vapour wall losses for various VOCs under high-NO_x conditions from Zhang et al. 2014.

VOC	**R_{wall}**
Benzene	1.25±0.1
Toluene	1.13±0.06
m-xylene	1.2±0.1
Naphthalene	1.2±0.1
Isoprene	2.2±0.5
α-pinene	1.3±0.1
n-dodecane	1.16±0.08
2-methylundecane	1.4±0.2

5. Line 80: ‘is response’ should be ‘responds’.

Response: We corrected it to “responsive”.

6. Line105: grammatical mistake in ‘makes possible of quantitative of alkenes’.

Response: We corrected this sentence.

7. Lines 147-148: grammatical mistake in ‘group affect little on the degrees of fragmentation for product ions’.

Response: We corrected this sentence.

8. Lines 193-195: I don’t see why the PTR measurement should be higher than the GC. Shouldn’t the GC measurement be close to the PTR if the unresolved mixture is accounted for?

Response: In this study, the higher alkanes standards used by online GC-MS are just linear alkanes (*n*-alkanes) without branched ones. Therefore, the quantification of branched alkanes by GC-MS is not available in this study. While, the higher alkanes measured by PTR-ToF-MS include linear and branched isomers for each carbon number.

9. Line 212: Should be ‘This decreasing pattern’.

Response: We corrected this sentence.

10. Lines 239-242: It isn’t clear to me why different pairs of species are used to estimate OH concentrations for the anthropogenic and biogenic species separately. Can the equation for the OH estimation be provided? Also, is there confounding in the OH estimation associated with emissions being added to the air parcel while the selected pairs are oxidized?

Response: We included the details about the calculations of OH exposure in the revised supporting information. During the PRD campaign, since biogenic species (i.e. isoprene and monoterpenes) have different emission sources and patterns from the anthropogenic species, the photochemical oxidation processes are quite different in these species. Therefore, we use different methods to calculate the OH exposures for anthropogenic species and biogenic species during PRD campaign. For the anthropogenic species, the observed ratio between m+p-xylene and ethylbenzene was used to estimate the OH exposure ($[OH]\times\Delta t$) by Roberts et al. (1984) :

$$[OH]\times\Delta t=\frac{1}{k_{\mathrm{m+p-xylene}}-k_{ethylbenzene}}\times[ln(\frac{\mathrm{m+p-xylene}}{ethylbenzene})_{t=0}-ln(\frac{\mathrm{m+p-xylene}}{ethylbenzene})_{t}]$$

Where the initial emission ratios of m+p-xylene/ethylbenzene were estimated according to the correlation of m+p-xylene with ethylbenzene during campaigns. The ratio of 4 and 1.5 were used in the PRD campaign and the NCP campaign, respectively (Figure S29).

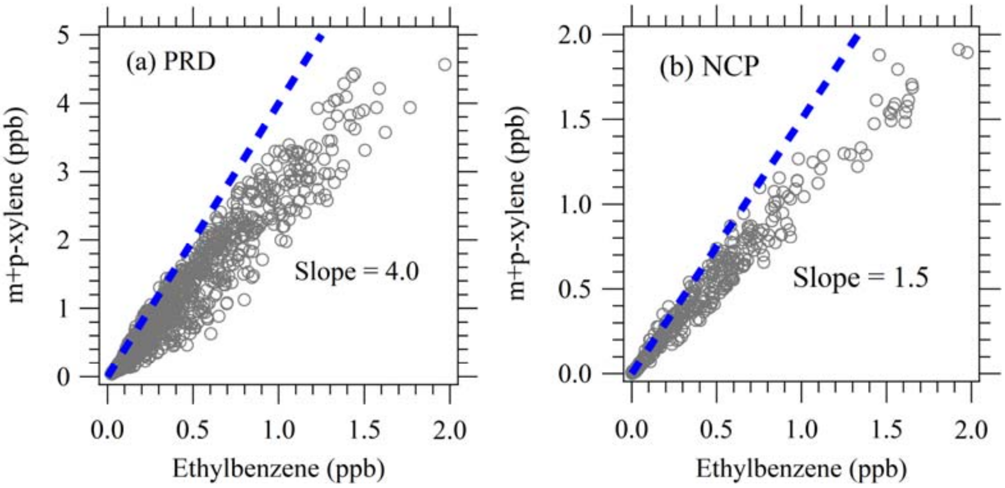

Figure S29. Correlation of m+p-xylene with ethylbenzene in PRD (a) and NCP (b). The dashed lines in both graphs indicate the estimated initial mission ratio of m+p-xylene/ethylbenzene.

The OH exposure of biogenic emissions are estimeted based on isoprene chemistry for PRD campaign. The calculation method can be found in Roberts et al. (2006). Isoprene are mainly photo-oxidized through the reactions with OH radical in the atmosphere and its primary first-generation reaction products are formaldehyde, MVK and MACR (Apel et al., 2002) . The reaction processes of isoprene oxidized by OH radical are mainly as follows:

$$Isoprene + OH \rightarrow 0.63HCHO + 0.32MVK + 0.23MACR \quad k_1=1.0\times10^{-10}\,cm^{-3}\,s^{-1} \; (Eq.\ S1)$$

$$MVK + OH \rightarrow Products \quad k_2=1.9\times10^{-11}\,cm^{-3}\,s^{-1} \; (Eq.\ S2)$$

$$MACR + OH \rightarrow Products \quad k_3=3.3\times10^{-1\,1}cm^{-3}s^{-1} \; (Eq.\ S3)$$

where k_1, k_2, k_3 are the rate constants of the reactions. According to above reactions, the relationship between MVK/Isoprene, MACR/Isoprene, (MVK+MACR)/Isoprene and the reaction time Δt can be decribed as follows (Apel et al., 2002):

$$\frac{MVK}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)\,[OH]\Delta t)\right) \qquad (Eq.S\ 4)$$

$$\frac{MACR}{Isoprene} = \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)\,[OH]\Delta t)\right) \qquad (Eq.\ S5)$$

$$\frac{MVK+MACR}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)\,[OH]\Delta t)\right) + \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)\,[OH]\Delta t)\right) \quad (Eq.\ S6)$$

where $\frac{MVK+MACR}{Isoprene}$ can be derived from the measurements by PTR-ToF-MS. Then the OH exposure ($[OH]\Delta t$) of isoprenoids can be obtaind from Eq. S6.

The OH exposure values in this study represent the average "photochemical age" that are calculated by some properly chosen VOCs ratios. Parrish et al. (2007) compared the calculated photochemical age of different NMHCs species with the transport time calculated by a back trajectory model, and concluded that the calculated photochemical age could better describe the average transport time of VOCs species by selecting suitable hydrocarbon species pairs.

11. Lines 242-246: If the isoprene and monoterpenes are of anthropogenic origin, shouldn't the biogenic VOCs be oxidized based on the OH determined from the anthropogenic VOCs?

Response: In this study, we think the isoprene and monoterpenes are of anthropogenic origin in NCP. Thus, we use the OH exposure estimated from the anthropogenic VOCs for isoprenoids in NCP campaign. While, because the isoprenoids in PRD campaign are of biogenic origin, we estimate the OH exposure of isoprenoids based on isoprene chemistry method as mentioned above.

12. Lines 253-onwards: While I commend the authors for relying on a lot of historical data to determine SOA parameterizations for the VOCs measured in this work, the toluene parameterizations do not use the more recent work of Zhang et al. (PNAS, 2014) that account for the influence of vapor wall losses in chambers. On a related note, were the SOA mass yields adjusted for vapor wall losses? Alternatively, some of the parameterizations can also be found in Eluri et al. (ACP, 2018). Finally, how was the NOx-dependence on SOA modeled? No NOx data at either of those sites was presented, nor any argument was made for the use of high NOx SOA parameters.

Response: Thank you for the nice suggestion. We agree with that the vapour wall losses might influence the calculation of SOA formation by using SOA yields from previous chamber studies where the wall losses were rarely corrected. Cappa and Wilson (2012) developed a Statistical Oxidation Model (SOM) to simulate the multigenerational chemistry and gas-particle partitioning of organic compounds. This SOM has been used to interpret chamber experiments to examine the influence of chamber-based vapour wall losses on yields of SOA (Zhang et al., 2014). According to the calculated SOA yield biases for a variety of VOCs when considering the potential influence of vapour wall losses (Table 1 in this reference), the literature reported SOA yields are low by factors of ~1.1-2.2 for the high NO_x conditions (Zhang et al., 2014). This suggests the SOA calculations in our study might be correspondingly underestimated. In the revised manuscript on line 370-374 of page 16, we added sentences to mention this influence as follows:

"The influence of chamber-based vapour wall losses on SOA yields was examined in previous studies (Zhang et al., 2014) and the results show that the literature reported SOA yields are low by factors of ~1.1-2.2 for the high NO_x conditions (Table S4). This suggests that the SOA estimations in this study might be correspondingly underestimated."

Table S4. Average biases in SOA yields due to vapour wall losses for various VOCs under high-NO_x conditions from Zhang et al. 2014.

VOC	**R_{wall}**
Benzene	1.25±0.1
Toluene	1.13±0.06
m-xylene	1.2±0.1
Naphthalene	1.2±0.1
Isoprene	2.2±0.5
α-pinene	1.3±0.1
n-dodecane	1.16±0.08
2-methylundecane	1.4±0.2

We included the NO_x data in the revised supporting information (Figure S22). The average concentrations of NO_x are 42.6±33.7 ppb in PRD and 81.7±57.0 ppb in NCP, respectively. Under such high NO_x levels, the RO_2 mainly reacts with NO (Bahreini et al., 2009). Thus, we used the high SOA parameters in this study.

We added sentences on line 321-324 of page 14 in the revised manuscript as follows:

"SOA yields under high NO_x conditions are used in this study, as relatively high NO_x concentrations in PRD (42.6±33.7 ppb) and in NCP (81.7±57.0 ppb) (Figure S22) would cause RO_2 radicals from organic compounds mainly reacting with NO (Bahreini et al., 2009)."

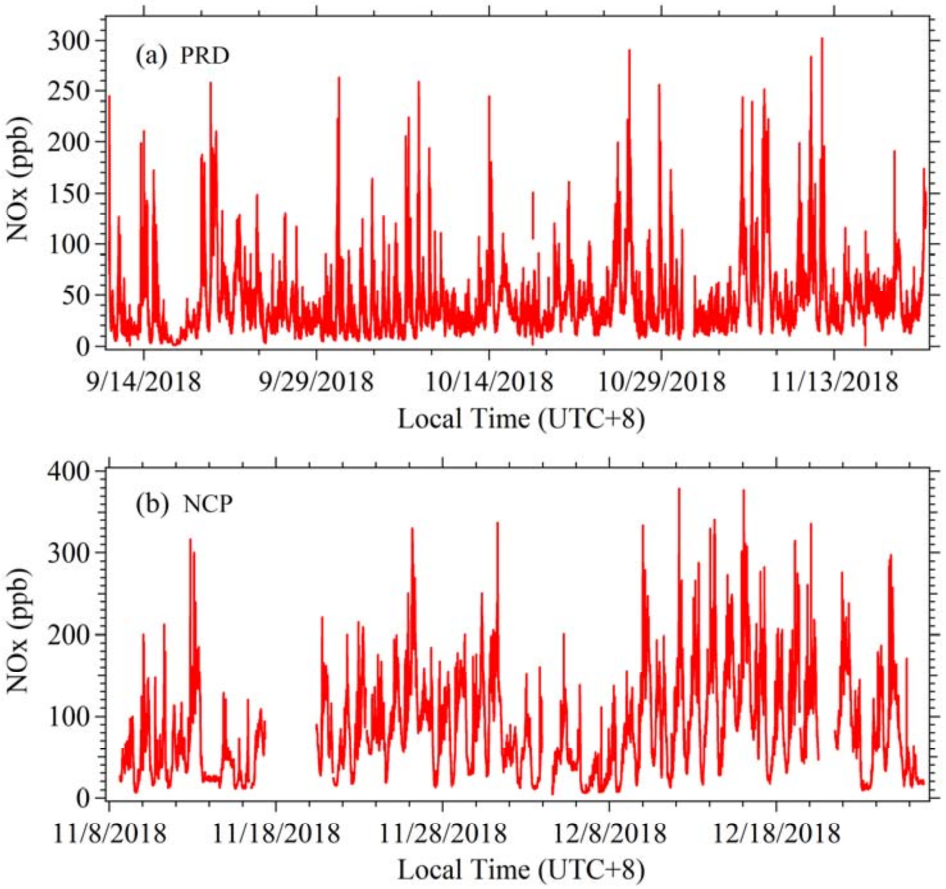

Figure S22. Time series of NO$_x$ during the PRD (a) and the NCP (b) campaigns, respectively.

13. Lines 299-300: The sentence reads as if isoprene and monoterpenes are emitted in vehicle exhaust. Please correct.

Response: We deleted "including vehicle exhausts and biomass combustions in this region". The sentence is modified to **"As mentioned above, we attribute these isoprene and monoterpenes to anthropogenic emissions in this region."**

14. Line 312: Can you describe how this is 'independent'?

Response: We replaced the "independent" with "another".

15. Line 332: The previous literature that has examined alkanes in more detail (Gentner et al., 2012; Zhao et al., 2015,2016; Drozd et al., 2019) have found a strong contribution of cyclic alkanes, especially in vehicular exhaust. Were these specifically measured/estimated in this work and can the authors comment on their role in contributing to SOA formation?

Response: In this study, we didn't estimate the contribution of cyclic alkanes to SOA formation. We are trying to establish the quantification method of these cyclic alkanes.

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