

Interactive comment on “Measurements of higher alkanes using NO⁺ PTR-ToF-MS: significant contributions of higher alkanes to secondary organic aerosols in China” by Chaomin Wang et al.

Anonymous Referee #5

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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

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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.

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.
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.
3. Lines 58-61: It might be worthwhile to talk about the differences in the various SOA precursor classes between gasoline and diesel exhaust.
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).
5. Line 80: ‘is response’ should be ‘responds’.
6. Line 105: grammatical mistake in ‘makes possible of quantitative of alkenes’.
7. Lines 147-148: grammatical mistake in ‘group affect little on the degrees of fragmentation for product ions’.
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?

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9. Line 212: Should be 'This decreasing pattern'.

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?

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?

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 NO_x-dependence on SOA modeled? No NO_x data at either of those sites was presented, nor any argument was made for the use of high NO_x SOA parameters.

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

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

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?

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2020.