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Atmospheric Chemistry and Physics
Discussions

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 #2

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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.

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.

(2) Line 162-170 introduce that the PTR was run alternately with NO+ and H3O+ 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 H3O+ operating modes?

(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.

(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.

Minor comments:

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

humidity was also shown.

(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.

(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?

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

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.

(2) Line 160 - replace expect with except

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