Atmospheric
Chemistry
and Physics

Open Access

EGU

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 #3

Received and published: 15 May 2020

Comments on acp-2020-145

In their manuscript, "Measurements of higher alkanes using NO+ PTR-ToF-MS: significant contributions of higher alkanes to secondary organic aerosols in China," the authors tackle an important but often overlooked issue: the contribution of high-molecular-weight gas-phase alkanes to SOA formation. A relatively large body of work over the last decade has provide a fairly thorough examination of the composition of vehicle emissions and the importance of branched (and cyclic) alkanes; this manuscript uses this work as a starting place to explore their contribution to SOA in China. The work is made possible in large part by the recent development of the NO+ PTR. Overall,

I think this work addresses interesting questions, and makes real efforts to tackle the complexity of calibrating a new instrument for compound classes that may contain hundreds of isomers. However, there are a few scientific weakspots that need to be addressed before this work is ready for publication. These larger comments include some needs for clarification, and some more fundamental issues with how OH exposure and SOA potential are being calculated. I commend the authors for taking a step into some unknown territory, but some additional discussion (and possibly work) needs to be included.

General comments:

1) There are some typo and english issues throughout. It is not sufficient to seriously detract from the science, but it is to the degree that the authors should have a native english speaker review and edit this manuscript.

2) Considering the focus of this work is on large alkanes, and the semi-volatile nature of these components, particularly at the lower temperatures of some of these measurements, this manuscript really does not provide enough detail on the sample line and inlet. How long is this sample line? Is it heated all the way to the sample inlet, or just in the room? If it is not heated all the way to the inlet, I would have some misgivings about alkanes about C14 or so, there could be substantial losses or time lags for larger alkanes. Is there any evidence (observations or models) that suggest line losses and delays can be ignored? If the authors want to focus on gas-phase measurements of S/IVOC alkanes, more detail needs to be provided for the sampling.

3) In the discussion around "sensitivity", is that the response per mass of the m-1 ion, or the sum of all ions? If the former, it should be discussed in some of the relationships shown, as discussed in comments below. If the latter, how are those ions summed and attributed in the complex real-world data? Understanding of this terminology is critical for interpreting some of the figures.

4) More detail is necessary on how they calculate OH exposure. I'm not familiar with

the isoprene chemistry method - please include a description. And for the ratio-of-aromatics method, don't you need to start by assuming some ratio at the time of emissions? What is assumed here? Why does the OH exposure diurnal (Figure S9) look very different for the biogenics and the anthropogenics? Notably, in the NCP campaign this is also a large missing daytime source, could this be related to a "mistiming" of SOA caused by a bias in the OH exposure calculation? Or what might be the missing source?

The math on Eq. 1 makes sense, but I'm not sure the assumptions do. This assumes that the air behaves like a plug flow reactor from some emissions source, and then just oxidizes until the measurement site. Wouldn't local emissions (that perhaps have a different oxidation history) change things dramatically? Given that benzene and TMB aren't present in diesel or motor oil (which is the source of higher alkanes), this might be an issue. Though they are both from vehicle emissions, so maybe not. This might all be more compelling with more detail on how OH exposure is calculated.

Specific comments:

Line 135. The relationship between humidity and sensitivity seems fairly robust, so correctable, but I'm not sure a would classify a 50% drop in sensitivity as a "slight" decrease. If the "sensitivity" is to m-1, is the drop due to a change in fragmentation, or a drop in all ions? As it also due to a shift of NO+ to H3O+ as water content increases, or does increasing humidity not increase H3O+?

Line 144. Is this slope between fraction of m-1 and sensitivity just due to the decrease m-1? In other words, is the total ion count produced the same, and just the fragmentation different, or is the total ion count lower for lower alkanes?

Line 144-145. Are calibrations of C16-C21 not available directly just because it is hard to get them into the gas phase, or was there some other reason?

Line 160. Should be "except" instead of "expect"

C3

Line 162. How was this switching achieved? Was it just a change in voltages? Are there residual effects observed, and/or do some transitional data need to be removed?

Line 167. I'm not quite sure what the "insulated tube" is - do they mean heater rope or something?

Line 185. Do the authors mean there are limitations to its application? Or just that it hasn't been applied very often?

Line 187-190. The comparison between H3O+ and NO+ and GC-MS/FID is very encouraging. There are some significantly non-unity slopes though (0.47 for benzene) - do the authors have an explanation for this?

Line 276. A Table of SOA yields used would be helpful for the SI

Line 301-304. Are there emissions sources for only alkanes? I would guess not, in which case these alkanes must be getting emitted alongside cyclic saturated hydrocarbons (e.g., cycloalkanes), which actually contribute similar or more to petroleum fuels (e.g., Gentner et al., 2012, Table S5). These compounds are expected to have broadly similar (or slightly higher) SOA yields. This would have you substantially overestimating SOA in NCP at night - the authors should comment on possible explanations or biases.

Figure 5. I'm not quite sure what data is being shown here. Gentner provides diesel fuel data in table S5 of that publication (this is used to approximate exhaust in that manuscript). That data doesn't agree with what is shown here though - for C8 it is 37%, and all the values are near or above 21%. The Isaacman paper is actually just a single fuel sample that is included in the Gentner data set, so could probable be excluded. That paper also provides gasoline data, which is not shown. In Figure 9 of the Chan paper, the branched-to-normal ratios are given for vehicle exhaust, which convert to between 13 and 41% normal for C24 through C21, which are fairly different than those shown. Similarly, in Figure 5, the branched-to-normal ratios for LA are shown at

C4

multiple oxidation times, and reach levels of 20 to 50% for those same carbon numbers - this is simlar to the values shown, but I think not quite right. I think the numbers for Bakersfield (based on Figure 4 from that paper) should be much lower, 5-10%, for all carbon numbers. Values should also be included for direct vehicle emissions from Worton et al., 2014, dx.doi.org/10.1021/es405375j. Basically, some explanation for how these numbers were all compiled is necessary (even if it's just in the SI), because they don't look quite right to me.

C5