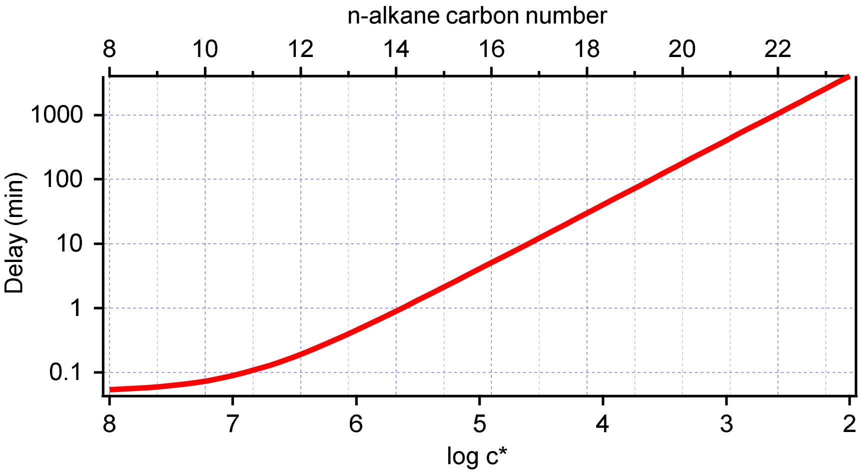
Reviewer comments on acp-2020-145 revision

This manuscript, "Measurements of higher alkanes using NO+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China," is a revision of a manuscript I previously reviewed. In it the authors study the contribution of high-molecular-weight gas-phase alkanes to SOA formation, specifically at two sites in China. The authors seem to have addressed most of my original concerns, though I note below a few things that are still of general concern and could be addressed better. I think the manuscript is generally suitable for publication, but would encourage the authors to consider some of these comments and suggests.

General comments:

1) The authors provide much improved discussion of the sampling inlet design, and present data (Figure S11) demonstrating that the 8 meter length of tubing does not impact C8-C15 alkanes. I would note, however, that there are some limitations to their tests that leave me only partly convinced. For example, the C15 cal curve is not completely linear: 2 ppb gives a response below 200 ncps though 1 ppb gives a response of 100 ncps, but the same non-linearity is not observed for C10. There is also a clear time lag in the 8-meter tube that grows with carbon number, though it remains fast. Furthermore, the true sampling set up has many valves in line between the ambient sample and the instrument (6, by my count), which could substantially increase the surfaces and thus the time lag, and this effect is not considered in the tubing test.

Unfortunately, only up to C15 is tested, but these issues are likely to get much worse for up to C21. This effect can be modeled using the work of Pagonis et al. (Atmos. Meas. Tech., 10, 4687–4696, 2017). I have included a figure of this model belo for the sampling system here (8 meter tube with 5 lpm flow), but roughly, C10 and smaller alkanes have essentially no lag, and up to C15 have lags on the order of a minute or so. Notably, for larger alkanes, time delays increase, with C21 having a lag of hours; while this is likely a worst case, I would note that the estimates for C8-15 are more or less in agreement with Figure S11, so the model seems to be working to some degree. In addition to potential losses, this might have significant impacts on measured diurnals, etc.



Because much of the results of this work are not dependent on the diurnals or time-dependent measurements of higher-alkanes, I don't know that this issue is fatal. However, if the authors intend to continue these types of measurements, they will need to convince themselves (and reviewers) that their measurements of these lower-volatility gases are reliable. One option would be to show that diurnals for lower-volatility alkanes exhibit similar time dependence as higher-volatility alkanes, another would be to measure the time constant for step-function changes in concentrations of low-volatility alkanes even if quantitative concentrations can't be reliably generated.

2) The new detail and discussion around OH expsoure calculations are much improved. One suggestion I would make, though, is to change the language a little around this topic. I think many of us think of "OH exposure" as a feature of an air mass, so it is a bit confusing to talk about different OH exposure for different components, e.g., aromatics vs biogenics. The authors discussion in their response to reviewers of the reasons for this (differences in timing of the different emission sources) is helpful in understanding this. I think it might help to think of these calculations as "photochemical age", which could be described as the time between emission and detection - it might be more intuitive that this is different between components, and some inclusion of this discussion might help with interpretation of Figure S16.

Specific comments:

Line 315. It is not really true that branched alkanes react faster than normal alkanes with OH in the gas phase. Though Isaacman et al. showed this was true in the particle phase (Environ. Sci. Technol. 2012, 46, 10632−10640), structure activity relationshops do not predict the same effect in the gas-phase. Roughly speaking, branching increases the number of tertiary carbons, but concomitantly increases the number of primary carbons - these effects balance out at the estimated OH rate constant is mostly unchanged. For example, Kwok and Atkinson methods estimate kOH=2.44e11 for 2,6,10,14-tetramethylpentadecane ("pristane") and kOH=2.38e11 for n-nonadecane, a difference of less than 3%, well within uncertainty. The lower estimated yields for branched alkanes are consequently expected to "win out" in these calculations, since the effect of branching on yields is likely more substantial (Gentner et al. estimated branched yields were roughly half that of normal alkanes).

Figure 5. In their response to reviewers, the authors state that Worton et al. is not included because that work focused on particle-phase alkanes. However, I believe the same fact is true of the Chan et al. work, so I'm not sure that is a reasonable argument.