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Comment on amt-2022-147

Anonymous Referee #2

Referee comment on "Real-time measurement of phase partitioning of organic compounds using a proton-transfer-reaction time-of-flight mass spectrometer coupled to a CHARON inlet" by Yarong Peng et al., Atmos. Meas. Tech. Discuss.,
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Review

Realtime measurement of phase partitioning of organic compounds using a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer coupled to a CHARON inlet

by Yarong Peng et al.

General:

The authors conducted month-long ambient SVOC measurements in East China using a CHARON-PTR-TOF-MS. This instrument measures the gas-particle partitioning of organic molecules and is a still relatively new technique that is not widely used. Peng et al. find that fragmentation inside the PTR instrument is a major challenge in the correct representation of gas-particle partitioning of SVOCs. I think the validation of the data obtained by CHARON-PTR-MS by a model that the authors provide here, and the lessons learnt on the challenges in interpreting the ion signals, are very useful for the community. The paper is written in a concise and clear language.

I recommend publication of the manuscript in AMT after the following comments have been addressed.

I. 112: Can you specify the typical wind direction and what kind of sources (broadly) are in the fetch?

I. 173 ff: The authors used a standard gas mixture where the component with the highest mass is α -pinene (136 amu), although later on, they report compounds with masses over 200 amu and even 342 amu. It would be good practice to calibrate the PTR transmission and sensitivity for the whole mass range you measure. Nowadays, gas standards of siloxanes e.g. with mass 370 amu or 444 amu are available. Please comment on the added uncertainty due to the lower mass range covered in calibrations.

Equation 2: what does "a" stand for?

I. 187 ff & Fig. S2a: The ToF transmission efficiency is generally expected to follow a root function if not corrected for duty cycle. The reason that it doesn't look like a root function here is probably that the authors used duty cycle correction in ToFWare (please specify in the methods description if you did). What I do not fully understand is why there still seems to be a reduced transmission in low masses – is this instrument equipped with a low-mass filter (e.g. a quadrupole) that lowers the transmission of lower mass molecules? If not, the duty cycle correction should, in my understanding, have brought all masses on the line where relative mass discrimination = 1. The data in Fig. S2a look like the sigmoidal fit makes sense for your transmission function, I am just asking why, because the method description isn't clear on that. Please specify the instrument model that you used and explain why your transmission curve looks like it does. And please plot the sigmoidal fit function in the figure, too.

I. 267 ff: Can you give an estimate of the total uncertainty of the gas/particle partitioning propagated from the uncertainties for both gas and particle concentration and the assumption on saturation vapor pressures? Mentioning somewhere in the methods the separate uncertainty of gas and particle phase concentrations would be interesting as well (or are they both the same?).

I. 137: Why did you run the TDU at 140°C, even though your desorption temperature variation experiments showed that even at 70°C-80°C all the SVOCs are transferred to the gas phase?

I. 327: I wonder if this plot might be more instructive if you showed the ratios of parent masses vs their fragments and clusters? From the way the data is presented, I find it hard to see whether the fragment ions really are stable or if they just look stable because of the log scale. Please deliberate more on what can be seen in Fig. 2. For example, it looks like some fragments or parent masses have a dip in the middle temperatures, while others

decrease and others increase with temperature. Is this just scatter or is there a physical/chemical explanation? (If it is just scatter: error bars would help.)

I. 353: I wouldn't describe a correlation of $r=0.6-0.8$ ($r^2 = 0.36-0.64$) as "well". Maybe "reasonable"?

I. 354 ff: How can loss of H₂O cause a lower total carbon mass? (There is no carbon in H₂O.)

I. 363: Why the focus on compounds below 250 Th? Please add a half sentence. (Instrument limitation?)

I. 381: Since Fig. S7 is so deliberately discussed here, I think it should be part of the main manuscript instead of the supplement.

Fig. S7: The y-axes should be more correctly labeled as C_xH_y, C_yH_yO₄, etc., instead of "CH", "CHO₄" which is chemically incomplete.

I. 442: It is not true that 140 Td is very common. The Yuan et al. review that you cite here states "The drift tube in PTR-MS has been commonly run with an E/N of 100–120 Td."

Section 3.3:

- What is the uncertainty of the modeled gas-particle partitioning? (How much of the difference between measurements and model could be due to model uncertainty?)
- Is the discrepancy in the gas-particle partitioning between the model and the TAG data smaller? (Thereby you could show that the reason for the mismatch is indeed a fragmentation issue in the PTR.)
- Would there be a way to optimize a combination of the four loss mechanisms to find an optimal correction?
- Gkatzelis et al (<https://doi.org/10.1029/2020GL091351>) reported that small aldehydes, acids and alcohols significantly contributed to the particle phase during a campaign in Beijing. Is it possible that part of the low mass particle phase contribution that you see is because of aqueous-phase uptake of such small OVOCs?