

Responses to the comments of anonymous referee #1

We thank the referee for the additional comments. Please find below our responses (in black) after the referee comments (in blue). The changes in the revised manuscript are written in *italic*.

The authors seem to have responded to both sets of comments and questions posed by the two reviewers. I have specific concerns on a few of the responses (see below) but should note that most of my concerns are centered around the description of the methods (and not the results). I am generally okay with the response and changes made to the manuscript and recommend publication of this paper in GMD after the authors have had a chance to review my additional concerns below.

Continuing comments:

1 Reviewer 1, point 1:

- a. Thanks for providing additional details on the PTR data but I still think the paper would benefit from a brief description of the PTR measurements, speciation information, and how those species were aggregated for use in the model, including the rationale (e.g., reduced-form?) and limitations (e.g., highly lumped?) of this approach. This detail is limiting comprehension of the modeling sections in 2.2 and 2.3 and could be done in the SI if there are issues with space.

We added a brief description about the measurements and the approach to group the species in section 2.1 and section 2.2.

“The PTR-ToF-MS was operated under standard conditions in H_3O^+ mode, as introduced in Stefenelli et al. (2019). A common set of 263 ions was extracted from the measurements, and among these ions, 86 showed clear decay with time and were identified as potential SOA precursors. These are listed in Table S1 of Stefenelli et al. (2019).” (P3, L90–L93, section 2.1)

“CAMx includes four types of precursors from anthropogenic sources, i.e. toluene, xylene, benzene, and IVOC which includes all the other unspciated organic gases. According to our measurements, the traditional anthropogenic precursors toluene, xylene and benzene only account for ~15% of the total organic gases. To facilitate the implementation of the optimized parameters in CAMx, all the measured SOA precursors including the traditional ones were lumped into one surrogate as IVOC with the same reaction rate and volatility distribution. In comparison, Stefenelli et al. (2019) have assigned the same set of compounds to six different classes according to their properties (reaction rates, expected SOA yields...) and origins/occurrence in the emissions. These included furans and methoxy-phenols from the pyrolysis of cellulose and lignin, respectively, single-ring and poly-aromatic hydrocarbons from flaming combustion, and oxygenated non-aromatic compounds with lower and higher than six carbon chains. The current lumping approach of all these species into one surrogate, despite variations in their properties is more adapted for the implementation into CAMx and for assessing vapor wall losses, where additional parameters are included in the box model.” (P4, L100–L111, section 2.2)

- b. Can you show how the measurements were used to calculate the OH reaction rate constant?

Is there a citation for this calculation?

The k_{OH} was calculated following the Eq (1) in Stefenelli et al. (2019) shown as follows, where P represents the production of oxidized condensable gases (OG) in the chamber, k_{dil} is the dilution rate, and k_{other} is the loss rate of OG by other processes.

$$\frac{d[OG]}{dt} = P - \left(\sum k_{dil} \times [OG] + k_{OH} \times [OH] \times [OG] + k_{other} \times [OG] \right).$$

We added the citation in P7, L217–L218.

“The reaction rate with OH (k_{OH}) was calculated based on the measurements following Stefenelli et al. (2019)”

2. Reviewer 1, point 2: I still maintain that determining SVOC and IVOC emissions from POA emissions (that are susceptible to vagaries of partitioning) is a poor choice. It should be fine for this work but needs to be discussed in light of arguments made in earlier work, e.g., Lu et al. (2018; <https://doi.org/10.5194/acp-18-17637-2018>).

More discussion about the S/IVOC calculations are added in the introduction section.

“In order to compensate the effects from missing precursors, various modeling studies treated the POA as semi-volatile and adopted different scaling approaches to calculate the S/IVOC emissions. The most commonly used method is to increase the POA emissions by a factor of 3 (Ciarelli et al., 2017a; Fountoukis et al., 2014; Jiang et al., 2019b; Tsimpidi et al., 2010), while recent studies have also developed new profiles based on the nonmethane organic compounds (NMOCs) (Lu et al., 2018; Cai et al., 2019). However, increasing number of laboratory experimental studies found that the S/IVOC emissions are of high variability depending on different burning conditions and fuel types (Hatch et al., 2015; Hatch et al., 2017; Jen et al., 2019; Koss et al., 2018; Sekimoto et al., 2018), and the estimation of S/IVOC in modeling studies remains to be improved.” (P2, L46–L53)

...

“Despite considerable variability of the SVOC emissions from biomass burning according to recent studies, the VBS_3POA is supposed to be a reference case representing the commonly used approach without vapor wall loss, and therefore we adopted the routine approach of multiplying the POA emissions by a factor of 3 to offset the influence of missing SVOC emissions.” (P7, L206–L209)

Lu, Q., Zhao, Y., and Robinson, A. L.: Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions, Atmos. Chem. Phys., 18, 17637-17654, 10.5194/acp-18-17637-2018, 2018.

Cai, S., Zhu, L., Wang, S., Wisthaler, A., Li, Q., Jiang, J., and Hao, J.: Time-Resolved Intermediate-Volatility and Semivolatile Organic Compound Emissions from Household Coal Combustion in Northern China, Environ. Sci. Technol., 53, 9269-9278, 10.1021/acs.est.9b00734, 2019.

3. Why is the sum of the molar yields in Table 1 for IVOCs larger than 1?

We have constrained the total mass yields in the volatility range X-Y to be equal 1 (using normal distribution kernel functions). This does not have a great effect on the resulting yields as the

normal distribution center and width are allowed to vary/adjust. The sum becomes larger than 1 when converting the mass yields to molar yields. The default molar yields in CAMx also have a sum larger than 1 as the VBS scheme accounts for both oxygenation and fragmentation (Koo et al., 2014). We added a sentence in P7, L215–L217 to clarify it.

“The optimized mass yields in the box model were converted to molar yields using the default molecular weights in CAMx (Table 1). Both the optimized and default molar yields have a sum larger than 1 as the VBS scheme accounts for both oxygenation and fragmentation (Koo et al., 2014).”

Koo, B., Knipping, E., and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmos. Environ., 95, 158-164, 10.1016/j.atmosenv.2014.06.031, 2014.

4. Reviewer 1, point 2: If I understand this correctly, the model assumes that there is only a single IVOC-like precursor that reacts with OH to form biomass burning SOA and that all other precursors (e.g., single-ring aromatics) are ignored. When the IVOC emissions are determined and adjusted to remove other more traditional SOA precursors in CAMx, a few assumptions are being made but none are explained. It assumes that benzene, toluene, and xylenes are the only other traditional SOA precursors. What about larger aromatics, isoprene, monoterpenes, and the likes? It assumes that the yields of the now-removed traditional SOA precursors are identical to the IVOC-like SOA precursor that is being added. On a related note, why weren't the traditional precursors explicitly accounted for in the box model so parameters specific to the IVOC-like SOA precursor could be directly determined and applied in CAMx?

As we mentioned in the response to point 2, CAMx has benzene, toluene, xylene and IVOC as the traditional SOA precursor species from **anthropogenic** emissions. Isoprene and monoterpenes are included in CAMx but mainly from the biogenic sources. We do not find them in our biomass burning emissions. As the modification of parameters in this study is on the biomass burning sector, the biogenic precursors were not specifically mentioned in the method section. We rephrased the sentence to clarify that these are traditional precursors for biomass burning in P7, L220–L221.

“... among which the traditional precursors in CAMx from biomass burning (toluene, xylene and benzene) accounting for ~15% of the total emissions.”

Separating the traditional precursors and the IVOCs in the box model would mean that we need to determine their yield, which increases the parameter space substantially. Therefore, we decided to lump all the species into one surrogate, IVOC, in the box model and optimize their yield parameters. We have then implemented these parameters in CAMx for biomass burning emissions and excluded the traditional precursors. We modified P4, L100–L111 to better explain that the traditional precursors were not separated in the box model.

“CAMx includes four types of precursors from anthropogenic sources, i.e. toluene, xylene, benzene, and IVOC which includes all the other unspciated organic gases. According to our measurements, the traditional anthropogenic precursors toluene, xylene and benzene only account for ~15% of the total organic gases. To facilitate the implementation of the optimized parameters in CAMx, all the measured SOA precursors including the traditional ones were

lumped into one surrogate as IVOC with the same reaction rate and volatility distribution. In comparison, Stefenelli et al. (2019) have assigned the same set of compounds to six different classes according to their properties (reaction rates, expected SOA yields...) and origins/occurrence in the emissions. These included furans and methoxy-phenols from the pyrolysis of cellulose and lignin, respectively, single-ring and poly-aromatic hydrocarbons from flaming combustion, and oxygenated non-aromatic compounds with lower and higher than six carbon chains. The current lumping approach of all these species into one surrogate, despite variations in their properties is more adapted for the implementation into CAMx and for assessing vapor wall losses, where additional parameters are included in the box model.”

5. Reviewer 1, point 8: Sinha et al. (2018) heated the aerosol and heating itself could change the mass accommodation coefficient through changes in the viscosity/bulk diffusion coefficient. So, I don't see that study as directly refuting the findings from Cappa and Akherati that used isothermal dilution to probe changes in POA.

As mentioned in our earlier response, by considering the POA volatility distributions from May et al. (2013) our results indicate little evaporation of the POA (~20%), which is in line with Cappa and Akherati. We cannot completely exclude kinetic limitations. Considering lower accommodation coefficients would increase the wall loss effects and would result into higher SOA yields. Therefore, our results using accommodation coefficient = 1 are lowest estimates of the wall loss effects and SOA yields. We have added these considerations in the modified version of the manuscript.

6. Reviewer 1, point 9: The different k_w seem to scale inversely with chamber size. This fact could be mentioned.

We added a sentence about the k_w and chamber size in P4, L127–L128.

“The k_w varies significantly depending on the chamber conditions such as the chamber size, relative humidity, etc.”

7. Reviewer 1, point 11: See Figure 4 and Figure S10 in Krechmer et al. (2016).

In Figure 4 and S10, Krechmer et al. (2016) shows a dependence of the particle accommodation coefficients, α , not C_w on C^* . They have mentioned in the text that their C_w has been parameterized in a previous work based on the decay of compounds with different C^* , therefore is not independent from C^* in their analysis. We note that this dependence of α on C^* is not large (within 50%) compared to other sources of uncertainties, with $\alpha < 1$ for more volatile compounds with higher C^* . Krechmer et al. (2016) noted that the reason for this dependence is not well understood and might be related to effects that were not considered in their model. Therefore, we have not taken this dependence into account in our analysis. We have considered $\alpha = 1$ and as mentioned above this would result in a lower estimate of the vapor wall loss effect and thereby of SOA yields.