Review of gmd-2020-189

Suciu et al., "A zero-dimensional view of atmospheric degradation of levoglucosan using numerical chamber simulations"

Summary:

The authors presents a numerical study investigating the atmospheric degradation of levoglucosan, which itself isn't necessarily new, but adding the explicit chemical mechanisms and the effect of levoglucosan chemistry on trace gases is not something that I've seen previously, so those are nice additions. Arguably, this is a modeling framework that can be integrated directly into a chemical transport model, so it has substantial potential for utility in the modeling world. I don't have a large number of comments, but I do have one that is fairly significant (Major Comment), one related comment (General Comment), three others that are more towards clarification (Specific Comments), and one suggestion.

Overall, this is a good manuscript, and it will be valuable for the community. Therefore, my recommendation is to reconsider after at least the Major Comment and Specific Comments have been addressed (the authors can take or leave my suggestion).

I have never "signed" a review previously, but I felt that it was necessary here due to the relationship of this manuscript with my previous work. I will also add that I am happy to continue this discussion, as needed, if the authors require any clarification. I am uncertain of the protocol here, but I imagine that we could have an "offline" discussion over email that could ultimately be included as part of the Interactive Discussion.

Major Comment:

- There appears to be a fundamental error regarding the volatility (C_i^*) of levoglucosan in this modeling framework.
    - Table S1 shows that $C_i^* = 3 \times 10^{-3}$ kg m^{-3} = 3×10^{6} μg m^{-3}, which would imply that that vast majority of the levoglucosan should be in the gas phase (e.g., if $C_{OA} = 30$ μg m^{-3}, 99.999% would be in the gas phase). This does not match with the initial distribution of the gas-phase and aerosol-phase concentration in Table S1.
    - Experimentally, we showed that this was more like 13 μg m^{-3} in May et al. (2012).
        - We speculated that this was why Hennigan et al. (2010) observed uptake coefficients (γ) greater than 1, and this could be a plausible explanation for the results in Knopf et al. (2011) for NO_3 radicals.
    - Moreover, a structure-activity relationship (Mansouri et al., 2018) predicts a vapor pressure that yields $C_i^* \approx 1$ μg m^{-3}.
    - Perhaps this issue with C_i^* is the reason why α = 0.0001 is required to demonstrate good agreement in Figure 1?

General Comment:

- Related to the Major Comment, Kulmala and Wagner (2001) provide a theoretical relationship between mass accommodation coefficients (α) and γ. One key point that they make is that $\alpha \geq \gamma$ (depending on the Knudsen number). In this work, $\gamma >> \alpha$, based on Table 2. Therefore, the authors should either constrain $\alpha > 0.1$ or provide some justification for $\alpha << \gamma$.
    - I suspect that this issue may work itself out once the Major Comment has been resolved, but it is worth noting in the event that it does not.

Specific Comments:

- Lines 198-203: As I'm reflecting on this after having read the full draft, it seems like these "F" values could be related to the mass fraction of levoglucosan in the particles. For example, F = 0.03 is the slope of "*m*/*z* 60" (proxy for anhydrosugars in the Aerosol Mass Spectrometer world) vs. OA concentration in Figure 7 in Sullivan et al. (2014). I haven't carefully read through Lai et al. (2014), but conceivably, they could have used lower mass-mixing ratios of levoglucosan in their particles. I bring this up because as written, F essentially sounds like a "fudge factor" to get the model to agree with observations. Maybe something like "We expect F to be, at a maximum, 0.1 due to observed mass fractions in biomass burning organic aerosol, and this value may decrease due to different levoglucosan sources or experimental conditions"

- Lines 203-204: I have no recollection of making this claim regarding α in May et al. (2013), and quickly reviewing that paper, it appears that the closest thing to that is that there appeared to be no mass transfer limitations for the evaporation of biomass burning smoke. In May et al. (2012), we did include some discussion of this in the online supporting information, but that was more focused on the fact that even if we decrease $\alpha < 1$, the evaporation timescale is shorter than heterogeneous chemistry timescale. I guess that my point here is that my previous work has been mis-interpreted.

  These results, coupled with $\gamma \approx 1$ (presumably, based on Kessler et al. (2010)?) and Kulmala and Wagner (2001) suggesting that $\alpha \geq \gamma$, seem to imply that $\alpha \approx 1$.

- Section 3.2 and Figure 4: I am a bit confused by this discussion about yield, which is perhaps based on an *a priori* expectation that SOA yield increases with increased photochemical aging. Is the implication that initially, many of the oxidation products remain in the particle phase ($t < \sim 6$ hr) but as the chemistry continues, heterogeneous oxidation results in more volatile products until a steady-state is reached (at $t \sim 24$ -36 hrs?

Suggestion

- Another dataset to consider would be that from Pratap et al. (2019). They also modeled their own data, explicitly accounting for gas-particle partitioning and chamber wall loss in addition to oxidation chemistry, in predicting particle-phase levoglucosan concentrations. If nothing else, these data can provide another valuable test set at colder temperatures than Hennigan et al. (2010) and Lai et al. (2014).

References

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