Interactive comment on "Influence of the vapor wall loss on the degradation rate constants in chamber experiments of levoglucosan and other biomass burning markers"

by Amelie Bertrand et al.

We thank the Referee for the careful revision and comments which helped to improve the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the referee‘s remarks (in the *italic typeset*) follows, while changes to the manuscript are indicated in blue font. In the following document, lines references refer to the manuscript version reviewed by the anonymous referee.

Anonymous Referee #2 Received and published: 1 March 2018

General Comments: In this manuscript the authors present results of an experimental/modeling study aimed at evaluating the effects of gas-wall partitioning on estimates of gas-phase oxidation rate constants for organic compounds, especially levoglucosan, used as atmospheric markers for biomass burning. The approach was to add biomass burning emissions into a Teflon chamber, expose them to OH radicals generated by HONO photolysis, measure the decay of the marker compounds present in particles, and then simulate the decay using a simple first-order model with corrections for particle wall loss and then a more complex model that includes various parameters for partitioning of vapors to the particles, particle wall loss, gas-phase reaction with OH, and gas-wall partitioning.

The complex model was run many times using values of parameters that fell within a reasonable range based on previous knowledge and the results were then compared to the measured particle-phase concentrations of levoglucosan and some other markers to determine optimum parameter values. The results demonstrate that vapor wall loss is the major mechanism for loss of markers in the chamber and that one cannot accurately determine the gas-phase OH rate constant for loss of markers in the chamber because of its minor effect on decay.

These results are important for interpreting results of chamber aging experiments on biomass burning emissions and also field data on biomass burning markers. I think the manuscript is concise and well written, and the technical aspects and interpretations are reasonable. I recommend it be published in ACP after the following minor comments are addressed.

Specific Comments

1. *It seems that the model assumes that the chamber is in steady state. Is that a good approximation, and how might it affect the results?*

The chamber was not operated under steady state conditions, as emissions from the combustion were only injected once and prior to the oxidation. We assume that the anonymous reviewer #2 refers to the section of the manuscripts in which we define several variables as a change of concentration (in the gas phase, particulate phase) at steady state conditions (i.e. line 14 page 6, line 17 page 6). This is a mistake on our part, and these variables should not have been defined in such manner. We removed these descriptions from the manuscript. The modified text reads as follow:

$C_{i,g}$ is the gas phase concentration of a compound i in µg m-3, $Ceq_{i,g/p}$ is the gas phase concentration at equilibrium in µg.m-3

and

Taking into account the reactivity of the compound, its partitioning, and the deposition to the wall of the vapors; we can express the change in the concentration of a gas phase marker $C_{i,g}$ using Equation 7:

and

The change in the concentration is expressed using Equation 10:

2. *Page9, lines1–5: There are some more recent references that give useful estimates for timescales for gas-wall partitioning and accommodation coefficients for gas-particle partitioning (Krechmer et al., Env. Sci. Technol., 2016, 2017).*

These references were added in the manuscript.

In other works, Julin et al., (2014) and Krechmer et al. (2017) determined a coefficient of near 1.

and

Authors have determined residence time comprised between several hours and down to a few minutes in the case where the chamber is equipped with an active mixing system (McMurry and Grosjean, 1985; Ye et al., 2016; Krechmer et al., 2016, 2017).

1. *Page 11–12: It is probably worth mentioning that calculation of the OH rate constant using the structure-activity relationships of Atkinson and co-workers(e.g. Ziemann and Atkinson, Chem. Soc. Revs.,2012) yields a value at the gas-kinetic limit(>10(–10)cm3 molecule–1 s–1).*

We thank anonymous reviewer #2. We have added this clarification in line 9 page 9 of the manuscript.

Finally, the rate constant k_{OH} was varied between 5 × 10^{-12} and an upper limit of 1 × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} according to the collision theory of reaction rates (Seinfeld and Pandis, 2006) although, we note that in their work based on structural-activity relationship, Ziemann and Atkinson (2012) yield a value at the gas-kinetic limit > 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}.

2. *How do the optimized C* values compare to those calculated using a method such as SIMPOL.1?*

As mentioned line 34, page 2, the SIMPOL model determines a C* of 8 µg m-3 at 298 K for levoglucosan or about 0.5 µg m-3 at 275 K. We determine a C* of 3 µg m-3 at 275 K. Discrepancy between the values yielded by the SIMPOL model and other methods have been commented on before (Kurtén et al., 2016)

Technical Comments

1. *Page 6, line 24: "Fuks" should be "Fuchs". 2. Page 13, line 19: "makers" should be "markers".*

Corrected as suggested.

References

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Ye, P., Ding, X., Hakala, J., Hofbauer, V., Robinson, E. S. and Donahue, N. M.: Vapor wall loss of semi-volatile organic compounds in a Teflon chamber, Aerosol Sci. Technol., 50(8), 822–834, doi:10.1080/02786826.2016.1195905, 2016.

Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41(19), 6582, doi:10.1039/c2cs35122f, 2012.