Author Responses to Referees and comments on

Gas-particle partitioning of toluene oxidation products: an experimental and modeling study

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We thank the reviewers for their comments and suggestions on the manuscript. We outline below responses to the points raised by each referee and summarize the changes made to the revised manuscript. We also provide a revised version of the manuscript with highlighted modifications.

We also thank the editor for his constructive comments and suggestions. In order to satisfy all requests, a new version of the response to the reviewers is provided. Additions to the previous version are highlighted in red. As requested, new versions of the manuscript and SI taking better account of comments are also provided. Changes have been made to the manuscript to correct grammatical and syntactical errors and to revise the style of citing tables and figures. The abstract has been modified to comply with the authors' guidelines, and new data tables with speciation (exp. and mod.) have been added to the SI.

Reponses to Referee #1

> *1. Before digging into the reason for the difference between modeled and measured composition, one need be sure that the difference is minimally influenced by the measurement artefacts. Is this possible that small compounds, particularly those less oxygenated C1-C4 compounds in particle-phase, are fragment of parent products or decomposition during heating in CHARON? It is surprising to see these compounds in the particle-phase due to their high volatility. It would helpful to elaborate the method used to exclude the artefacts and/or discuss their influence on the measured chemical composition.*

Thermal decomposition is typically not observed in CHARON PTR-ToF-MS instruments (except for hydroperoxides and labile sugars). It has, however, been shown in previous work (*e.g.*, Gkatzelis et al.,

2018; Leglise et al. 2019) that at the conditions used in this study (E/N = 105 Td) scission of the C-C bond may indeed occur. Therefore a fraction of the low C compounds found in the particle phase may thus be measurement artifacts (it is now introduced in the text in section 3.2, page 16).

> 2. In Fig. 2, no oligomers (C>7) compounds were shown. Are there any oligomers (C>7) detected? Can CHARON PTR MS see them?

Oligomers can be observed with CHARON PTR-ToF-MS instruments. It is, however, likely that at the operating conditions used in this study (E/N = 105 Td) oligomers fragment upon protonation (introduced in the text in section 3.2 at page 14).

> 3. I suggest adding a figure of reaction schemes of toluene+OH reaction highlight the new reaction mechanisms added to the model in SI so that readers can better follow.

The suggested figure was added to SI (Fig. S11) and is now mentioned in the text. The figure addresses the initial branching ratio of the toluene degradation process only.

> 4. L167, which data does this statement based on?

According to Jenkin et al. (2019) SAR, the $RO_2 + RO_2$ reactions mainly lead to the formation of alkoxy radicals as $RO_2 + NO$ reactions. Under atmospheric conditions, the $RO_2 + CH_3O_2$ (the most abundant RO_2 in atmosphere) reaction represents about 10 % of the RO_2 reactivity (Lannuque et al., 2018). If we have here decided to not consider all $RO_2 + RO_2$ reactions it is to limit the already relatively large size of our mechanisms. We are aware that this means ignoring the formation of certain minor secondary compounds, notably $C_{>7}$. This choice was made considering (1) the high NOx levels limiting the importance of $RO_2 + RO_2$ reactions and (2) the absence of detection of such compounds in our experiments.

About the assessment: "*These simplifications do not impact either the major species simulated or the simulations of the observed species.*": the removed reaction pathways only concern a minor fraction of matter. Tests were carried out with GECKO-A (without the modifications described in the article) considering more than 6 generations of stables species and RO2 reaction with other RO2 (not only CH3O2). These tests showed no significant variation in SOA mass and speciation because (i) lots of 6th-generation species are already in particles or too fragmented to be condensable or (ii) as mentioned above, RO2+RO2(≠CH3O2) reactions are negligible compared to reactions of RO2 with NO, HO2 or CH3O2 (especially NO in our case).Text was modified for more precisions (section 2.2.1 "the MCM/GECKO base mechanism", page 6).

> 5. L236, what does "long range interactions" mean? It would be helpful to briefly explain it.

Middle- and long-range interactions correspond to interactions between the organic compounds and charged molecules (especially inorganic ions, the only considered here) in water phase. This term is used in contrast to the interactions between the different uncharged organic molecules which occur at a shorter range. The text was modified accordingly, changing the terms used in "interaction between uncharged organic molecules" and "interaction of organic molecules with inorganic ions" (section 2.2.2 pages 8-9).

> 1. L35, it is not clear that what the "enhanced" is compared with.

It was compared to a reference mechanism using MCM and GECKO-A. Abstract were totally rewritten to comply with author's guidelines.

> 2. L287, "as" should be "and"?

The text was modified.

> *3. L407, "cercles" should be "circles". Also it would helpful to clarify that it is the diameter or area of circles that denotes the mass in Fig. 3.*

The area of the circles has been used. The text was modified and the legend of Fig. 3 was detailed.

> *In the caption of Fig. 3, there are no "pie charts". Please check.*

The mention to pie charts was removed.

> *1. L451, the "of" after "24 %" should be deleted.*

The text was modified.

> *2. L505, "47%", is this correct or should it be 28%?*

You are right, the mistake was corrected and 47% was replaced by 30% (28 + 2 %).

> *3. L545, a comma is missing after "(a).*
> *4. L482, a space is missing after "distribution".*

The text was corrected.

References :

Gkatzelis, G. I., Tillmann, R., Hohaus, T., Müller, M., Eichler, P., Xu, K.-M., Schlag, P., Schmitt, S. H., Wegener, R., Kaminski, M., Holzinger, R., Wisthaler, A., and Kiendler-Scharr, A.: Comparison of three aerosol chemical characterization techniques utilizing PTR-ToF-MS: a study on freshly formed and aged biogenic SOA, Atmos. Meas. Tech, 11, 1481–1500, https://doi.org/10.5194/amt-11-1481-2018, 2018.

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Reponses to Referee #2

> *Line 98: Additional experimental details such as the rate and residence time of the gas flow in the OFR and the initial concentrations of toluene should be provided in the experimental section.*

Experiments were carried out using a total flow varying from 1.3 to 1.8 L/min corresponding to a residence time of approximately 10-13 minutes. In total 24 oxidations experiments were carried out for initial concentrations of toluene ranged from 8 to 162 ppbv. A list of the experimental conditions is provided in Table S1 in the supplementary information (SI). These details have been introduced in the experimental section (page 4).

> *Line 132: Have any experiments been done to verify that all the organics in SOA are thermally desorbed at a temperature of 413 K in the CHARON inlet? Was the fragmentation of organic compounds during the thermal desorption of SOA significant?*

During the toluene experiments we did not carry out any tests on thermal desorption of the organic compounds. However, it has been shown in the literature that at the temperatures used in this study SVOCs, LVOCs and even ELVOCS are vaporized (Piel et al., 2021). It is important to note that vaporization is affected on the walls of the thermal desorption unit at reduced at reduce pressure (few mbar).

Piel et al. (2021) also mention that certain types of thermal decomposition such as the decarboxylation of organic acids does not occur at the temperatures used in this study. This is confirmed in Table S2 where ion distribution of 15 reference compounds (CHARON analysis) is shown. Succinic acid shows only water loss only. Piel et al. 2021 found evidence for the thermal decomposition of hydroperoxides in the CHARON inlet. A comment of fragmentation of compounds has been introduced at page 15.

> *Line 145: Are the C* values calculated from the measured partitioning coefficients using Equation 2? What are the influences of the potential non-equilibrium phase partitioning (for example under low RH conditions) and non-ideality of the condensed phase on such calculations?*

The C^* were calculated using equations 1 and 2. According to Shiraiwa and Seinfeld (2012): the equilibrium time is achieved from seconds to minutes for relatively high volatility organic compounds into liquid particles. However, equilibrium time can increase to hours or days for organic aerosol when the particles are large, semi-solid particles, of low volatility, and low mass loadings. Instantaneous equilibrium partitioning may lead to substantial overestimation of particle mass concentration and underestimation of gas-phase concentration.

In our study most of the identified SOA compounds identified are semi-volatile (Table 1). Moreover, monodispersed seeds+SOA had a size was about 150-216 nm so our particles are quite small to establish an equilibrium with the gas phase. In addition, the total mass concentration was on average 13.9 ± 3.4 µg m^{-3} for the experiments at 295 K and 17.4 ± 4.9 µg m^{-3} for the experiments at 280 K, the mass loading is high enough for the establishment of the equilibrium. Indeed according to Figure 4 of Shiraiwa and Seinfeld (2012), for semi-solid SVOCs with a diameter of 150 nm and organic mass concentration 14-17 µg m^{-3} the equilibrium timescale of SOA partitioning is about 10 min. Given the fact that the residence time in the OFR was about 11-13 minutes we conclude that particle and gas phases were practically in equilibrium. Furthermore, in preliminary modeling tests, gas-particle partitioning was represented using both methods: one considering thermodynamic equilibrium at each time step, and one following a dynamic phase transfer approach. The two methods showed no significant differences in partitioning under our simulation conditions.

The non-ideallity, for individual organic compounds in different mixtures is quantified by the activity coefficient γ. Liu at et. (2020) found that the γ of bulk SOA (produced by OH oxidation of a mixture

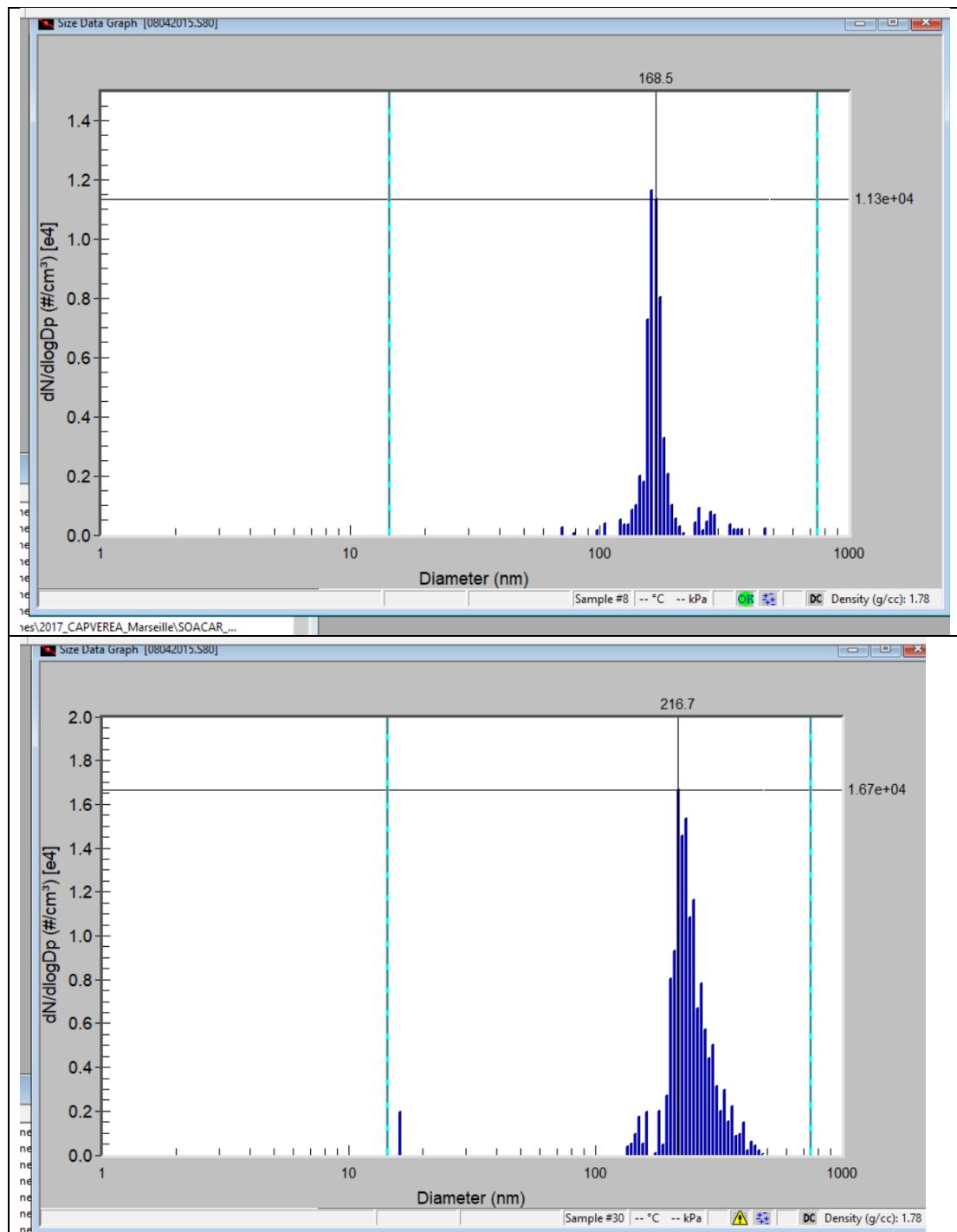
of 1-alkanols) increased from near 1 to 5 as the seeds and the SOA have more differing polarities. A high γ value of 74 was found for a wet ammonium sulfate-SOA system indicating phase separation. Ammonium sulfate is a polar compound. We have to check the polarity of the SOA compounds, if the majority of their mass have polarities close to ammonium sulfate, then we say that γ is around 1 and we are close to ideality. If the polarity is quite different, then the seeds are less hospitable to the condensing vapors and the compounds tend to stay in the gas phase increasing the C^* by up to 5 times (and so $logC^*$ will increase half an order of magnitude).

Tests on non-ideality carried out in the modeling section clearly show the effect that interactions can have on the partitioning of different compounds. However, these tests highlight the large uncertainties that remain in the calculation of non-ideality, with effects that can be contrary depending on the phases and compounds. The lack of interaction data between the different functional groups adds even more uncertainties. It is partly for this reason that we have chosen not to take non-ideality into account for the experimental C* in Fig. 3.

> Line 210-214: The formation pathways of highly oxygenated organic molecules (HOMs) from toluene photooxidation are also included in the newly developed mechanism. Do they make a significant difference to the speciation of the gaseous and particulate organic species, especially for those with high oxygen numbers?

In our study, the species referred as "HOMs" correspond to stable species that have undergone at least two successive autoxidation steps after the addition of a first OH radical. Other highly oxygenated compounds (which could have higher oxygen number than these "HOMs") are formed in a more conventional way by successive oxidation with OH, O_2 and then NO or HO_2. "HOMs" are negligible in our simulations. This observation is not discussed too much in the article, as it could be due to the high concentrations of radicals (NO and HO_2) in our experimental conditions, which are unfavorable to successive autoxidation pathways. In line with this, recent use of the mechanism in simulations under atmospheric conditions shows that "HOMs" are not negligible in SOA formation when there are few radicals (which is not, however, the most common case for toluene, generally emitted at the same time as many NOx).

> Line 280: What are the size distributions of toluene SOA formed under typical experimental conditions? Are the formed SOA particles monodispersed as assumed here? Given the low pre-existing seed aerosol concentrations (~9 μg/m³), I would expect that there is significant nucleation and new particle formation during toluene photooxidation. As a result, polydispersed aerosols are likely generated, e.g., a larger particle mode comprised of inorganic-organic mixed particles and a smaller particle model primarily with pure SOA particles. If this is the case, how would it affect the phase partitioning behaviors of organic compounds as well as the irreversible uptake of small species such as methylglyoxal.

Typically monodisperse seeds were injected ranging from 113 to 169 nm (mobility diameter). This information has been introduced in table S1 and introduced in the text (page 4). As a function of the experimental conditions more or less condensed organics were formed in the particle phase. The bottom plots show SMPS size distribution before and during photooxidation of toluene. Yes, some nucleation is observed at the beginning of the oxidation, after few minutes as the surface condensation increases nucleation is suppressed at least under our experimental conditions. See below the size distribution (SMPS) for seeds and during toluene photooxidation. Partitioning has been calculated during stable periods in absence of nucleation events.

> *Line 287: These parameters are expected to significantly impact the gas-phase oxidation chemistry, phase partitioning, and/or particle-phase chemistry (e.g, irreversible uptake of methylglyoxal), but it is found in the present study that they have little impact on the overall speciation of the oxidation products. The authors only present the data obtained at different temperatures in the manuscript. I suggest also providing the data obtained for other parameters in the SI.*

Speciation measurements were mainly carried out during experiments at different temperatures. Text was modified to highlight the focus put on temperature impact and speciation data were added to SI (in part 3).

We agree that RH, initial seeds, toluene and IPN (i.e. OH radical) concentrations can impact phase partitioning. Seed impact has been shown in the SI section (Figure S2). The figure shows as increased

sees surface favors SOA formation. But it also clearly suggests that experimental temperature has a stronger impact on SOA mass loading with respect to seed concentration. Therefore, temperature variation has been considered a key parameter. Other parameters have not been extensively investigated in this work. Under our experimental conditions, however, we did not observe a significant impact on gaseous chemistry and therefore overall speciation (i.e. in both phases). This is reflected in the identification of the same m/z (with different intensities), whatever the experimental conditions.

The core of the modeling work was to reproduce the global speciation of secondary compounds before reproducing and analyzing their partitioning. As particle-phase chemistry was not represented, this work consisted in developing new chemical mechanisms for gaseous oxidation, on which RH and the initial concentrations of toluene, seeds and IPN had no impact. Only experiments at two different temperatures were therefore reproduced.

The most debatable choice is probably not to reproduce experiments at two different RHs, but as the RH range covered during the experimental campaign was restricted (from 24 to 40%) and the artifacts generated by its variations in the tube little analyzed (e.g. RH-dependent wall condensation), this choice was made. Regarding the impact of RH on methylglyoxal partitioning, as mentioned in the article, the parameterization is very simplified. It is based mainly on field data where temperature and RH are dependent, and leads to potential discrepancies by not integrating either temperature or OH concentrations in its calculation. In this respect, the test is mainly exploratory.

Now that an oxidation mechanism has been proposed, an analysis based on a new campaign of experiments focusing on the partitioning of compounds as a function of conditions should be envisaged, in particular to reduce the uncertainties associated with the processes considered.

> Line 356: In addition to losing a H2O molecule, how likely do the toluene oxidation products fragment via C-C scission during PTR-MS measurements? How would it affect the discrimination between parent and fragment ions?

Yes, it has been shown in the literature (Gkatzelis et al., 2018; Leglise et al., 2019) have shown that at the conditions used in this study (E/N = 105 Td) scission of the C-C bond may occur. Part of the low C compounds found in the particle phase may thus be measurement artifacts. This comment has been added to the text (page 17).

> Line 401-402: Please clarify what type of heterogeneous reactions on the reactor wall can produce these small molecules.

Typical reaction occurring on the wall of OFR or chamber give rise to HONO, HCHO, HCOOH formation. In general adsorbed molecules on the chamber or OFR tube can undergo chemical reaction and produce such small molecules (Doussin et al., 2023). This sentence has been introduced in the section 3.2 (page 17).

> Line 405: Although the authors are able to determine the gas-particle partitioning coefficients (Kp) of the toluene oxidation products, they did not present such data in the manuscript. As the Kp can offer additional insights into the phase partitioning behaviors of the oxidation products, I suggest the authors add an analysis of those data as well as their measurement-model comparisons in the manuscript.

The experimentally derived Kp are now in table S3.

Concerning modeled Kp, we chose not to detail or represent their comparison with experimental data for several reasons: the uncertainty of partitioning according to the processes considered, and the impossibility of calculating a Kp for (1) many major compounds of the modeled SOA due to their total

transfer in the condensed phase, or (2) compounds whose Kp is measured experimentally but present only in the gas phase in the simulations (i.e. light compounds). A bubbles plot comparison figure would have compared different species that do not necessarily represent the major part of the secondary mass produced.

> Line 413: It seems that some content is missing before the sentence "Other 20 ions were detected…". Please check.

Nothing is missing but the sentence was not clear, text was modified.

> Line 425: Figure 3 does not include any pie charts described in the figure caption. Also, there are no descriptions/discussions regarding the comparisons between organic compounds measured by CHARON PTR-MS and the SOA mass measured by AMS in the text. Please double check.

The mention to pie charts was removed. The authors added in table S1 the SOA measured by CHARON/PTR-ToF-MS and added a plot of SOA comparison for the two instruments in SI section (now Fig. S5). SOA composition is only investigated with CHARON/PTR-ToF-MS since HR-ToF-AMS presents heavy fragmentation. The HR-ToF-AMS is used here to evaluate the total SOA mass only.

An additional text has been added at page 16-17: "The particle phase mass loading recovered by CHARON/PTR-ToF-MS accounts for approximately 77 % of the mass measured by the HR-ToF-AMS (Fig. S5.a) when considering all the 24 experiments (Table S1). Part of this discrepancy can be explained by the loss of water occurring in the PTR-ToF-MS technique (see Table S2) but also from the different size cut-off of the two instruments inlets. This hypothesis is confirmed in Fig. S5.b, where CHARON/PTR-ToF-MS mass recovering decreases to 55% of that observed by HR-ToF-AMS when only particles below 150 nm (mobility diameter) are considered"

> Line 430-431: The volatility is affected not only by the oxidation state, but also by the molecular size. Therefore, a trend for OSc versus C* may be observed if the data are further discriminated by the carbon number. In addition, Fig. S6 should be Fig. S5.

The numbering error was corrected. We tried to make additional plots considering the C number but we do not observe any interesting trend.

> Line 608: Why does the inclusion of the wall loss parameterization lead to the reduction of the concentration of all m/z values in the particle phase but only the heavier compounds in the gas phase?

Wall losses of compounds depend on their volatility, whatever their m/z. It's therefore logical to see compounds in the particulate phase (i.e. the least volatile) all impacted to a greater or lesser extent. Text was modified to mention that. The term "homogeneously" in the text appears to be incorrect and unclear and was removed.

Here, the impact on the gas phase is minimal in all cases. It is concentrated on two types of compounds: (1) those of low volatility, which are present in both phases (the decrease in particulate concentration goes hand in hand with the decrease in gas concentration) and (2) compounds formed after several oxidation steps, whose parent species have seen their concentrations decrease due to wall losses (these compounds are potentially the heaviest due to the successive addition of functions). This does not mean that there is no effect on other gaseous compounds, but it is negligible.

> In addition, the following language errors should be corrected.
Line 91: produced -> produce
Line 249: wall losses -> wall loss effects

Line 273: Delete "controlled".
Line 287: as -> as well as
Line 298: as -> such as
Line 346: by -> followed by
Line 407: cercles -> circles
Line 442: that -> than
Line 443: Delete either of "only".

The text was modified.

References:

Doussin, J.-F., Fuchs, H., Kiendler-Scharr, A., Seakins, P., and Wenger, J. (Eds.): A Practical Guide to Atmospheric Simulation Chambers, Springer International Publishing, Cham, https://doi.org/10.1007/978-3-031-22277-1, 2023

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