Response to the referees' comments acp-2011-712

The authors want to thank the referees and the editor for their useful comments that helped to improve the manuscript. In the following to each referee comment will be answered and changes to the manuscript will be highlighted.

Anonymous Referee #1:

1.) *From the current manuscript it is not clear if blank filters have been analyzed. Background contamination certainly exists and has to be subtracted properly. Fig 10 reveals that many peaks with more than 9 carbon atoms (i.e. the carbon number of TMB) have been detected in the filter measurements. Does this signal really come from collected SOA? I suspect that these peaks are due to background contamination and should not be accounted for in the analysis. Similarly, all other analyzes done with filter measurements could be significantly biased if no proper background correction has been applied.*

Indeed Teflon filters can be a source for impurities. Therefore all analyzed filters were pretreated the same way: they were mounted into the filter housing, constantly flushed with 5 l/min pure N_2 and heated up to 140°C prior to the experiment. Figure R1 displays a comparison of a pretreated blank Teflon filter with the aerosol sample filter, both analyzed at 120°C. After pretreatment, only a small BG is visible at lower m/z, no higher m/z peaks appear (except of constant intensity internal calibration peaks around m/z 300). Therefore we assume that the peaks with more than 9 carbon atoms indeed originate from the collected SOA filter sample.

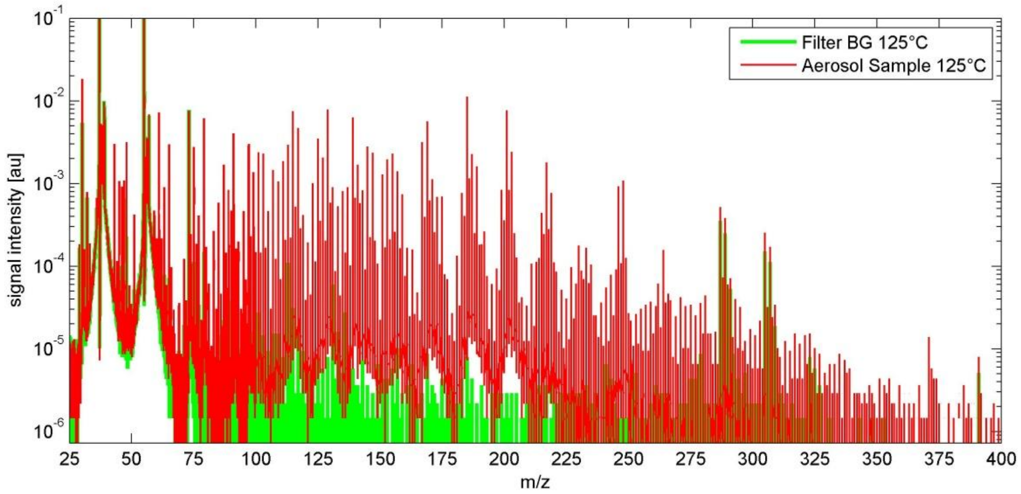

Figure R1. Mass spectrum measured at 125°C desorption temperature for a BG filter sample and the aerosol filter sample.

For clarity the following was added to the manuscript (p25879, l2):

"**To eliminate filter impurities from the aerosol sample, Teflon filters were pretreated by flushing with 5 l/min of pure N_2 at 140°C for 90 min. In addition blank filter spectra were subtracted from the aerosol filter spectra for each desorption temperature.**"

2.) *The authors do not provide a quantitative analysis of the detected SOA species. The total SOA mass can be estimated - for example from SMPS data. The fraction of SOA detected with the PTR-TOF should be constrained and reported. If the authors can provide the requested analysis the SOA part can be a valuable addition. Otherwise I suggest to remove the SOA related part and to concentrate on the interpretation of the gas phase.*

During the complete desorption process a total of 14.8 µg/m³ was analyzed by PTR-TOF. During the sampling period the SMPS measured an average of 23.01 µg/m³, applying an aerosol density of 1.4 g/cm³ (Alfarra et al., 2006). This corresponds to a measured aerosol fraction of 64.3%.

The following was added to the manuscript (p25886, l12):

"Integrating the aerosol signal over the whole desorption experiment results in a total SOA concentration of 14.8 µg/m³. With a scanning mobility particle sizer 23.01 µg/m³ (aerosol density = 1.4 g/cm³, Alfarra et al., 2006) were measured. This results in an aerosol fraction of 64.3% that was detected by PTR-TOF."

3.) Specific comments:

- P25876
    - *19: give the corresponding pulse time for m/z 600*

The TOF Pulse time for m/z 600 measurements corresponds to **44 µs** (added to manuscript).

-
    - *23-24: the sentence 'Co-addition : : :' is not clear and understandable.*

The m/z axis of TOF-MS is not very stable due to temperature effects to the TOF metal housing and changes in TOF voltages. Therefore the m/z axis slightly moves within tens of minutes even under lab conditions. The addition of spectra measured within 30 min will definitely result in a smearing out of the peaks. Therefore, according to the methods described in Müller et al. (2010), all spectra were m/z calibrated and afterwards these congruent spectra were co-added. This resulted in no loss of resolution within the 30 min of integration time. For clarity the sentence was changed to: **"With this method the spectra could be integrated over 30 min periods without any loss of mass resolution."**

- *27-28: what do you mean by 'duty cycle correction'? More explanation needed.*

Like every mass spectrometer, TOF-MS have an instrumental duty cycle. In case of an orthogonal acceleration TOF-MS as used for the PTR-TOF, this mass duty cycle is caused by a lower density of lower m/z ions in the pulser region. This behavior is very well described by Graus et al. (2010) and Müller et al. (2010). As these publications are cited several times throughout the text, no further explanation was added.

- P25877
  - *4: typo 'o'*

The nitrogen numbers are indexed with an "o" (N_o). Therefore "o" is not a typo.

- *Section 2.1.2: within the accuracy of 20 ppm it is hard to imagine that the attribution of an empirical formula was always unequivocally (for example in Atmos. Chem. Phys.,10, 10111-10128, 2010 the authors found up to four possible identifications for mass peaks obtained with a similar instrument). This needs discussion!*

Graus et al. (2010, Supplementary Information) very well showed the performance needed to distinguish between individual elemental compositions. For a simple system containing only C, H and O atoms, 20 ppm are enough to distinguish any compositions up to *m/z* 260. Indeed, for identification we allowed an additional nitrogen atom to be present. Therefore the elemental compositions calculated were sometimes not unique and all compositions had to be manually checked for chemical meaning. For ambient measurements a higher accuracy is needed. Current models of the PTR-TOF combined with state of the art data reduction software (Müller et al., 2012, paper in preparation) results in mass accuracies less than 5 ppm. With addition of the isotopic information, most ambient compounds can be identified.

- *Section 2.2.1. add date and time of the experiments.*

The authors think the addition of date and time of the experiments to section 2.2.1. would decrease the readability of the section. **Instead, the experiment duration was added to table 1.**

- *Section 2.2.3: see major comments above.*

See responses above.

- P25878
    - *17: give the size of the PTFE filter.*

    The filter diameter was 47 mm. (**added to the mansucript**)

    - *21: give the size of the aliquot that was inserted into the oven.*

    The complete filter was inserted into the oven.

- P25879
    - *1-2: the statement is misplaced and should be moved to section 2.1.1 or to the supplement.*

    Indeed this statement is misplaced and therefore moved to 3.3.

    - *18-21: I was not able to follow this discussion.*

    This is the definition of the Carbon Oxidation State as shown in equation (1).

    - *Section 2.4: there is no information on how N-containing compounds (PAN!) were treated.*

    Paper Kroll et al. (2011) broadly discussed the influence of nitrogen to the average carbon oxidation state. Accordingly, due to the low typical N/C ratios only a low impact in the OS_C can be expected. In case of experiment 1 the MCMv3.1 predicts a N/C ratio of 0.07 after 7h of reaction time.

    "As the nitrogen content is expected to be low compared to the carbon content of the system (N/C < 0.07, MCMv3.1 prediction) only a low deviation due to nitrogen can be expected." was added to the manuscript.

    - *Section 3.1: The title is not appropriate. The section largely discusses the observed VMRs. Comparison with PTR-MS is a minor aspect.*

    The title actually refers to the comparison of the two PTR-TOF mode measurements and an additional comparison with a PTR-MS. Therefore it is a comparison of PTR-TOF_{400}, PTR-TOF_{600} and PTR-MS. To clarify, the title was changed to "**Comparison of PTR-TOF_{400}, PTR-TOF_{600} and conventional PTR-MS results**".

- P25881
    - *12 and 14: $C_9H_{13}O^+$ should actually be $C_2H_5O_3^+$, shouldn't it?*

    $C_9H_{13}O^+$ was changed to $C_2H_5O_3^+$.

  - *Section 3.3: Another reason for declining O/C with temperature could be charring*.

  We do not believe that there is charring at these relative modest temperatures. However, as pointed out by reviewer 2 there might be compounds splitting off H2O and CO2, which would also decrease the O:C ratio. We added this sentence at page 25885, line 28: **"It is also possible that from some species H2O and CO2 is split off at the highest temperature which would lead to a further underestimation of the O:C ratio."**

- P25886
  - *10-11: ': : : somewhat less oxidized : : :' is not correct. Fig 8b shows that the number of atoms is actually increasing with higher temperature. I suggest ': : : somewhat lower oxidation state: : :'*

    Indeed, "somewhat less oxidized" is changed to **"somewhat lower oxidation state".**

  - *Section 3.4: I find the discussion of the van Krevelen diagram rather weak. What do we learn from this analysis?*

    As shown in section 2.3, Van Krevelen Diagrams have recently been used as a diagnostic tool for the analysis of organic aerosols. Heald et al. (2010) found that for all analyzed organic aerosol a typical slope of -1 can be found, starting form an H:C ratio of typically 2 (at O:C = 0). The Teflon filter SOA samples of analyzed in this work show a similar position in the Van Krevelen diagram. In our discussion we emphasize, that the gas phase precursors show a different behavior, resulting in a slope of about 0.

- P25887
  - *14-15: I guess that the authors refer to Fig 9.*

    Figure 6 was changed to figure 7.

  - *14-15: Fig 9 does not show a higher O:C of exp 2 as compared to exp 1!*

    Figure 9 is not a good presentation in respect to see the O:C ratios of the experiments. Figure 7 directly shows the O:C ratios for all 4 experiments.

- *Table 1: add a column giving start date and duration of all experiments*

An additional column has been added, indicating the duration of the experiments.

- *Table 2: it is impossible to understand the meaning of numbers 1134 and 324 in the last column.*

In this table typesetting mixed up the original layout by removing separation lines between the different C_n groups. Respectively, 1134 ppbC is the sum of all C6 compounds and 324 ppbC is the sum of all C9 compounds as modeled by the MCM.

- *Table 3: improve layout. It is not always clear to which species the numbers in the last two columns refer to.*

Similar to table 2, the layout of table 3 will be optimized prior to final publication.

- *Figure 1: This scheme is not necessary and can be omitted. It is only used to show the 3 initial reaction pathways. These pathways are explained in the text anyway. Together with Table 2 this provides sufficient information*.

The authors agree that this scheme is not necessarily needed. Nevertheless we decided to insert it into the manuscript to give a quick overview into the TMB degradation chemistry.

- Figure 4a: *what is the bold black line*.

As written in the figures legend, the bold black line refers to reacted carbon (see text for more information).

- Figure 6b: *I am not sure this presentation really makes the point. Furthermore it contradicts the statement made in the text: e.g. O/C 0.5-0.55 peaks after 4 hours while O/C 0.65-0.7 already peaks after 2.5 hours.*

This presentation has been chosen to illustrate that many species really contribute to the total O:C ratio, not only primary reaction products like methylglyoxal. Indeed the statement made in the text **"Reaction products with a higher O:C ratio start to rise later than products with a lower ratio" is inaccurate and was removed**.

- Figure 10: *CO is displayed in the plot. This is not a common PTR-MS compound. How was it measured? For the filter measurements detection of CO could be another indication of charring*

The CO^+ ion is commonly observed in PTR-TOF mass spectra. The origin of this ion is not yet clear but it may be produced in fragmentation reactions in the extraction region of the drift tube. As such it is not formed from neutral CO and the labeling is indeed misleading. **The CO label has been removed**.

Anonymous Referee #2:

1.) Major comment:

> *- Central to much of this work is the quantitative measurement of absolute concentrations of individual organic species. Such measurements require an accurate calibration of all mass spectrometric signal; however there is little discussion of the absolute accuracy of such measurements, and the description of the calibration approach (in the Supplement) is quite confusing. Some questions/concerns about this quantification: - A brief description of calculations of proton-transfer rate constants is provided, but then it is stated that "Calculated rates of the expected products were linked to experimental calibration results." What exactly does this mean? In other words, how do the use of rate constants and the use of acetone sensitivities relate?*

The authors agree that quantification is a very important part of the manuscript. Most accurate results can be achieved by direct calibration of each individual organic species. As this is not possible, the second accurate possibility is the calculation of reaction rate constants for all uncalibrated signals. These reaction rate constants are very much depending on the structure of the molecule. In this work we calculated the reaction rate constants of the most prominent m/z peaks according to MCM model predictions. These calculated reaction rate constants are consequently compared to the reaction rate constant of a well calibrated compound, i.e. acetone. For example, acetone reaction rate constants are calculated to be 3.0E-9 cm²s^-1 (see e.g. Zhao et al., 2004). Therefore for example methyl maleic anhydride with a calculated reaction rate of 3.37E-9 cm²s^-1 has a 12% higher sensitivity compared to acetone. Sticking to this example, we decided to group methyl maleic anhydride to a group with acetone sensitivity.

> *- A stated error of 30% for generic products is given – what data is this value based upon?*

Calibrated acetone sensitivities have an expected error of 10%, composed of the error of two flow controllers and the error of the gas calibration gas cylinder. We assumed that the calculated reaction rate constants also have an error of at least 10%. In addition the ions grouped as acetone-like sensitivity showed a deviation up to 15% to the acetone reaction rate constant (table S2). This results in an overall error of about 25%. To be on the save side, the authors decided to round it up to 30% error for uncalibrated and unknown signals.

> *- Based on Table S1, acetone seems to be detected more sensitively than nearly any other compound – meaning use of acetone as a calibration standard is likely to lead to an overestimate of most species' concentration (which would in turn lead to an overestimate of carbon balance).*

As mentioned above, the acetone reaction rate of 3.0E-9 cm²s^-1 is within 15% of the reaction rate of the calculated acetone-like compounds shown in table S2. In addition, a higher sensitivity would actually lead to an underestimation of the volume mixing ratios.

> *- All the species in Table S1 are monofunctional; how do the response factors change for multifunctional species (e.g., diols, diketones, etc)?*

To study this, quantum chemical calculations for the most prominent expected products have been performed (table S2) and corresponding reaction rate constants were calculated. By comparison of these reaction rates with the reaction rate constant of acetone, corresponding sensitivities can be calculated. Some of the compounds shown in table S2 do have multifunctional groups (e.g. methylglyoxal and 2- methyl-4-oxo-2-pentenal). Nevertheless, according to the very limited set of data, no general assumption how the sensitivity changes for multifunctional species can be given.

> *- Were fragments (e.g., M+1-H2O) and clusters (e.g., M+1+H2O) included in the total ion signal when calculating concentrations?*

Indeed, as stated in the Supplementary Information, fragments und water clusters were identified using the 400 V and 600 V drift tube voltage measurements. These signals are then included into calibration calculations for the corresponding compound.

> *- All these concerns should be addressed in the manuscript (and not just the Supplementary Information), since they relate directly to most of the results/conclusions of the work.*

The authors agree that quantification is a very important part of this work. Nevertheless the authors decided prior to publishing to move the quantification information that is only interesting for PTR-MS experts, to the Supplement of the manuscript to increase the overall reading fluency of the paper.

2.) Specific comments:

- *Section 3.1: The title of this section does not relate very well to the content – this section is mostly about comparing measurements of individual species (as determined with HR-PTR-MS) to MCM results.*

The title actually refers to the comparison of the two PTR-TOF mode measurements and an additional comparison with a PTR-MS. Therefore it is a comparison of PTR-TOF$_{400}$, PTR-TOF$_{600}$ and

PTR-MS data. To clarify, the title was changed to "**Comparison of PTR-TOF$_{400}$, PTR-TOF$_{600}$ data and conventional PTR-MS results**".

- *Sections 3.1-3.2: Throughout these sections, experimental results are compared to MCM data. The similarities/differences are noted, but rarely commented upon. I think it's important to at least acknowledge explicitly that the discrepancies could arise not just from experimental problems (e.g., fragmentation or clustering in the MS) but also because of shortcomings of the MCM scheme. As a first test of how well MCM describes the observed chemistry, agreement between simple modeled and measured chemical parameters - TMB, NOx, O3 – should be discussed.*

A comparison of the chamber data and the applied MCMv3.1 model was examined for the TMB mechanism in detail by Metzger et al. (2008). The authors demonstrated that great accuracy of TMB, NOx and O3 could be achieved. Therefore we decided, as it is already published and well cited in the manuscript, not to include a comparison of those compounds.

"**The excellent agreement between MCMv3.1 predictions and measured TMB, O3, NOx is presented for various initial conditions by Metzger et al. (2008)**." was added to section 2.2.2.

- *25876, line 7 (also last sentence of the Supplement): it is mentioned that the different voltages allow for examination of clustering, but this is never discussed in the paper. (It might explain the very small differences in O:C in Figure 6a.)*

Clustering and fragmentation was examined and corrected for using different PTR drift tube voltages.

- *Section 2.2: How were blank runs carried out? It is highly likely that NOx + light +"clean chamber air" would lead to some formation of secondary organics. A discussion of the role of these organics, and the subtraction from all PTR-MS data reported, is needed.*

The blank runs were carried out by irradiation of the clean chamber without addition of any species (NOx, HONO). These experiments produced between 0.2 - 0.5 µg/m^3 SOA which is only about 1-3% of the sampled SOA. Typical VOC species observed in blank runs include acetic acid, formic acid, propionic acid, acetone, acetaldehyde and methanol. Levels were significant only in the case of acetic acid and this finding has been described in the text.

- *25878, line 4: It is stated that the MCM simulations are limited to 1st generation products only; how is this consistent with the decrease in some modeled concentrations(i.e., Fig 5b)? If the simulations are limited to 1 generation only, this seems like a major possible source of* *model-measurement discrepancy. Oxidation products of aromatic hydrocarbons tend to react with OH substantially faster than the parent hydrocarbons(due to the addition of OH and other activating groups to the aromatic ring), so the formation of 2nd- (and later-) generation products is more or less unavoidable. Moreover, the data (e.g., Figs. 2, 3, 5, 6b and 25885 lines 2-4) show clear evidence for multigenerational chemistry. Ignoring such chemistry is therefore a serious limitation of the model; this either needs to be corrected, or discussed in some detail.*

This is a misunderstanding of the reviewer. Figure 1 shows only the first generation products. The simulation was done with the full MCM scheme which is a complete mechanism. We changed the wording to:

A schematic representation of the OH initiated oxidation of TMB (first-generation oxidation products) as implemented in the MCMv3.1 (Bloss et al., 2005a, b; Metzger et al., 2008) is depicted in Fig. 1.

The confusing sentence "**The scheme includes first-generation oxidation products only**" was deleted.

- *25881, lines 3-8: here ions are assigned to specific species, with no discussion of the reason the assignment was made. It seems that isomers or fragments of larger species could also play a role. The wording here (and in other parts of the manuscript, such as the labels of Fig 2) should be changed to reflect the fact that these are molecular assignments of measured ions, not unambiguous measurements of individual species.*

As described in this section the assignment of the ions to specific compounds was done by comparing MCM expectations to the ions measured. For each depicted signal the corresponding ion signals (protonated molecule, water cluster and fragments) are given and compared to the MCM (e.g. "…depicts the results for $C_6H_9O_2^+$ (according to MCMv3.1 dimethylfuranone and methyloxopentenal), measured on m/z 112.060 plus its hydrate on m/z 131.070."). The authors therefore expect this discussion to be clear enough.

- *25881, lines 8-11. The agreement between the data at different drift tube voltages does not necessarily mean that there is no fragmentation – it just means the amount of fragmentation is equal in both cases. An ion fragmentation channel that has a low activation energy could occur quantitatively in both cases.*

Indeed, ion fragmentation is also present for PTR-TOF$_{400}$ experiments. A good examples is PAN, as shown in figure 3/f and discussed in the Supplement, where no protonated PAN is visible either at PTR-TOF$_{400}$ and PTR-TOF$_{600}$ measurements. Nevertheless regarding to the other signals in figure 3, exactly the significant differences in fragmentation and clustering helped to identify respective intensities and therefore allowed quantification of these signals (compare to table S1).

- *25881, lines 25-26: These are the upper and lower bounds to PAN concentrations only if those are the only two (major) ions formed after protonation of the PAN. Has this been verified with an authentic standard?*

No PAN standard was used for calibration during this campaign. Therefore we relied on the findings of Hansel et al. (2000), who describe the measurement of PAN by PTR-MS.

- *25881, lines 22-27: the assignment of different ions to a single species can be constrained by comparing their temporal behavior. In the absence of matrix effects, a given molecule will produce all ions in fixed ratios – any deviations from this indicate contributions by other parent molecules. Can this sort of analysis be used to better constrain concentrations of PAN? How about for other species (as in lines 5-6)?*

Indeed, measured under stable conditions, fragmentation ratios are fixed during the whole experiment. Therefore the authors tried to further constrain the PAN concentration by looking at the temporal behavior of the expected fragments. Nevertheless, too much interference was detected to constrain the PAN concentration to a more precise value.

- *25882, lines 1-3: were these blank experiments carried out in the presence of NOx (and/or HONO)? That would seem to be the important point of comparison, not simply the irradiation of the chamber.*

The blank runs were carried out by irradiation of the clean chamber without addition of any species (NOx, HONO). It is a difficult question which would be the appropriate blank experiment. We know that there are gaseous organic impurities and there is also HONO evaporation from the chamber walls. Therefore, our blank experiment does simulate a VOC/NOx chemistry. How much NOx should one add to simulate the “real” blank? During a normal experiment the chemical regime is continuously changing. This is very difficult to simulate in a blank experiment. Addition of NOx could easily switch the chemistry in a blank experiment to a very high NOx chemistry and would also not be representative. Our blank experiments are not the “real” case but a good approximation of the back ground chemistry. Since our chamber is fairly clean and these experiments were at rather high precursor concentrations the back ground chemistry really does not matter a lot.

- *25882, line 7: the referenced paper by Praplan et al. (2011) is not in the References section.*

Parplan et al. (2011) is still under preparation. Parplan et al. (2011) was therefore changed to **Parplan et al. (in preparation).**

- *25882, lines 17-20: The reader is referred to the Supplement for an explanation of why the data show "no significant amount of nitrates or anhydrides". However, the Supplement doesn't really address this question, other than saying that such species tend to have a neutral loss of HNO2 or HNO3. Given that, it would seem the PTRMS cannot be used to assess the importance of oxidized-nitrogen-containing organic species, since the bulk of the ion signal would show up as CxHyOz+ ions. How then are the authors confident that no nitrates or anhydrides are formed? Also, what about nitroaromatic compounds – common products of aromatic oxidation that are chemically distinct from nitrates and anhydrides?*

The reader is referred to the Supplement for an explanation of how nitrates and peroxyanhydrides are detected by means of PTR-MS. It is stated in the Supplement: "Hansel and Wisthaler (2000), D'Anna et al. (2004) and Aoki et al. (2007) found that nitrooxy-group (-ONO2) containing compounds are prone to the loss of HNO_2 and/or HNO_3 or form NO_2^+ ions losing all carbon in the neutral fragment. A small fraction of the $VOC.H^+$ ions does not dissociate, which can be used to qualitatively follow the temporal evolution of PANs and nitrates." Therefore for nitrates and anhydrides an increase of $NO2^+$ is expected. Subtracting the expected PAN contribution from the NO_2^+ signal for PTR-TOF_{400} and PTR-TOF_{600} indicates only a small extra NO_2 signal. Nevertheless, no quantitative result can be given.

- *25882, first paragraph in section 3.2, and Figure 4: Do these values (from both the experiments and the modeling) include particulate organics? What about losses of organics to the chamber walls?*

The experiments do include particulate organics while the modeling does not produce aerosols. Therefore, the model contains potential particle phase compounds in the gas phase. From the aerosol yield measurements we can conclude that only about 2 % carbon can be attributed to those compounds. Losses of organic compounds to the chamber walls are expected to be small for compounds with carbon less than 9 (Matsunaga and Zieman, 2010).

The following sentence was added page 25883 line 2**: In the model low volatility products which may partition into the particle phase are simulated as gas phase products and thus included in the carbon balance. However, from the known aerosol yield of TMB this would only contribute about 2% to the carbon balance. Wall losses of compounds may also decrease the measured amount of carbon but is expected to be small for compounds lower than C9 (Matsunaga and Zieman, 2010).**

- *25883, lines 6-7: It would seem the best comparison is between the summed PTR-MS measurements and the amount of carbon available (from the TMB reacted), rather than the modeled carbon available. Ideally the two are the same – that is, the modeled and measured TMB profiles agree. Is this the case? This agreement (which is actually very important for model-measurement comparison of product formation) should be discussed explicitly.*

As shown in Metzger el al. (2008) the applied MCMv3.1 very well follows the TMB concentration for the discussed experiments. Therefore TMB reacted corresponds to the modeled carbon available.

- *25884, lines 18-19: What concentrations of nitrogen-containing compounds does MCM predict?*

The MCMv3.1 predicts up to 540 ppbC of nitrogen containing compounds (including PAN). The maximum is reached after 470 min.

- *25884 line 26-25885 line 18, Figures 6,7,9, and elsewhere: The manuscript should make more of a distinction between the two ways to calculate O:C(gas): with and without TMB. While including TMB can be useful for describing the entire system, excluding TMB is absolutely crucial whenever discussing reaction products, since much of the changes to O:C are driven by the loss of TMB. Thus I would recommend focusing more on the O:C calculated without the TMB. For example, lines 11-12 of the Abstract – "The O:C ratio in the particle phase was about twice the O:C in the gas phase" – seems to imply to that gas phase oxidation products are less oxidized than particlephase products saying that O:C in the gas phase, when the opposite is actually true (p. 25885, line 26). Similarly, I think a version of Figure 9 that includes only products could be very interesting.*

The authors are very aware of the necessarily of a clear distinction of how the O:C is calculated (including or excluding TMB from the calculations). Therefore we addressed this explicitly in table 4. Regarding the figures: many different versions of the figures were plotted prior to submission, including TMB or excluding TMB from the O:C ratios. For clarity, we decided to plot only the complete system, including TMB.

- *P. 2885, lines 16-18: In what way is this effect "obviously small"? The general agreement between the measurements and the MCM results doesn't necessarily tell us that the PTR-MS is measuring everything correctly, only that it's measuring what the MCM predicts – it is possible there are errors in both the model and the measurements.*

Indeed, a good agreement with a model does not necessarily imply the correctness of the PTR-TOF data. To clarify this, the statement was changed to: **"In the PTR-TOF protonation may lead to loss of oxygen (e.g. via H2O loss following protonation of an –OH group or HNO_3 loss following protonation of an –ONO_2 group). The good agreement of PTR-TOF measured O:C ratios with the MCMv3.1 calculations suggests that this effect is obviously small or counterbalanced by the loss of carbon."**

- *Section 3.3: meaningful analysis of the O:C (or OSc) of the aerosol would require that all (or at least most) of the SOA components are being measured by the PTR-MS. This can be verified by comparing total PTR-MS signal (scaled to the amount of material on the filter) to the real-time measurement of the aerosol mass (by an SMPS, AMS, etc). How good is this agreement?*

As already answered in more detail above, about 64% of the overall SOA could be detected by PTR-TOF.

- *Section 3.3: it should be noted here that the higher temperatures of the desorption could promote fragmentation of the analytes (forming H2O, CO2, etc), exacerbating the underestimate of the O:C of the particulate organics. Throughout: there are seven individual references to the Supplementary Information, which is only 2 pages long! There is little reason this information needs to be in a separate document, and should be included in the main text.*

It is possible that H2O and CO2 might be lost at the highest desorption temperature although it is only 125 °C. This could lead to an underestimation of the O:C ratio. Nevertheless, our O:C ration is still somewhat higher than the one measured by HR-TOFAMS indicating that this effect might not be so large.

We added this sentence at page 25885, line 28: **It is also possible that from some species H2O and CO2 is split off at the highest temperature which would lead to a further underestimation of the O:C ratio.**

- *Figure 2: an inset showing an HR mass spectrum at m/z 113, to demonstrate the separation of ions would be helpful here.*

An inset of the mass spectrum at m/z 113 was added to Figure 2. The following was added to the legend: "**The inset illustrates the raw spectrum after 7h of reaction time between *m/z* 112.9 and *m/z* 113.2 (black squares), the fits of each detected ion (green line) and the superposition of the total ion signal (red line)**."

- *Figure 3: curves showing MCM predictions are needed here.*

MCM prediction were added to Figure 3.

- *Figure 8: the y-axis label should be changed; it's listed as intensity but is actually a fraction.*

The authors are convinced that a "relative signal intensity" is similar to a "fraction".

- *Figure 10: Sizing the markers by ion intensity (or ppbC) could be useful. Also, there is clear evidence for species with more than 9 carbons (oligomers? Background organics) in the particle phase; these should be commented upon in the text.*

Sizing the markers by intensity was tested, but no satisfying result could be achieved.

Indeed, species with more than 9 carbons have been detected in the particle phase. The following was added to the manuscript: "**Species with more than 9 carbons were detected in the particle phase indicating oligomerization reactions**."

References:

Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prévôt, A. S. H., Worsnop, D. R., Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the photooxidation of anthropogenic and biogenic precursors in a reaction chamber, Atmos. Chem. Phys., 6, 5279-5293, doi:10.5194/acp-6-5279-2006, 2006.

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