Anonymous Referee #2

We would like to thank Referee #2 for reviewing our manuscript and providing helpful comments. Hereafter, Referee's comments are written in black and our responses are detailed in blue.

Authors have provided a comprehensive response to the issues addressed by the Referees in the first round. The revised manuscript has been clearly improved, grammatical way and scientific wise, and it has strong potential to be published eventually in ACP. Regardless of the improvements there are couple of issues for that is debatable whether the statements and interpretations are true. The main issues are:

1. *Control experiment to retrieve O:C from XPS and AMS*

O:C of surface layer (10nm) differs from O:C of the total particle (d=100-200nm). O:C values are derived based on different method (XPS and AMS) and the methods are not compared with well known species. If any calibration is not performed, the results of the differences in O:C between bulk and surface should be moved to discussion.

Response: As requested by Referee #2 and the Editor, we performed a control experiment to verify the ability of XPS and AMS to retrieve O:C values on homogeneous particles containing a standard compound. For that purpose, we generated homogeneous pinic acid particles and analyzed them with the XPS and the AMS) under the same instrument conditions as in our experiments. We observed that the obtained values were in good agreement (O:C$_{AMS}$ = 0.34 ($\pm$ 0.10) and O:C$_{XPS}$ = 0.37 ($\pm$0.08)). In addition, both methods reproduced (within experimental uncertainties) the known O:C = 0.44 of pinic acid. Therefore, we are confident to apply these methods for determining O:C of both the bulk and the surface composition of SOA.

These results have been added in section 2.4. as follows: "To exclude biases in the comparison of the surface and bulk O:C ratios by different experimental methods, a control experiment was performed on pinic acid which is pure homogeneous compound containing multiple carbon-oxygen bonds and which is representative of α-pinene-O$_3$ SOA (theoretical value O:C value of 0.44). An aqueous solution containing 0.003 M of pinic acid solution (Santai Labs, purity by ^{1}HNMR of >95%) was atomized using a constant output atomizer (TSI, model 3076) and then passed through a Nafion tube, which reduced the RH below 35%. Particles were analyzed with the AMS and simultaneously collected on PTFE filters for XPS analysis. The O:C values obtained experimentally by AMS and XPS analysis were 0.34 ($\pm$ 0.10) and 0.37 ($\pm$0.08), respectively, as expected for particles homogeneous composition. In addition, both methods reproduced the expected molecular O:C of pinic acid within the uncertainty range. This control experiment sets the reference case for the joint use of XPS and AMS instruments to resolve compositional differences in non-homogenous SOA particles."

2. *GF definition*

GF values measured with H-TDMA at ~20%RH are ~1.14. It is not ruled out that some possible issues (explained by Mikhailov et al. (2009) and Dublissy et al. (2009)) in experimental setup would not affect these results. Moreover GFs in this manuscript denote d(RH)/d(40), not *Hygroscopic growth* (Petters & Kreidenweis (2007)). GF of ~1.14 at 20%RH do not represent

hygroscopicity because d(40) has been used as a reference. Hence, the "odd" behaviour in H-TDMA need to be explained more comprehensively than just citing studies about glassy phase state of SOA particles or then hygroscopicity need to be replaced by "particle growth" and GFs need to be replaced by d(RH)/d(40).

Response: To clarify that GF and f(RH) were calculated by considering 40% RH to be dry conditions, we added the definition of GF and f(RH) as follows: GF=Dp,m(RH)/Dp,m(40%RH) and f(RH)=σscat(RH)/σscat(40%RH). We also included these definitions in Figures 4 and 6.

3. *Change of O:C as a function of distance from the core*

In the manuscript, size range of SOA particles varied in a range of ~100-200nm (electrical mobility diameter). Initial O:C measured with AMS was 0.68 which then decreased to 0.55 with time whereas surface O:Cs from XPS were 0.33 and 0.46. O:C values calculated from AMS measurements represent average O:C of the entire SOA particle, meaning the bulk AND the surface. XPS is sensitive to measure surface O:C with the thickness less than 10nm [...]. Hence, it is incoherent and misleading to argue that this effect is negligible. In fact these calculations question the whole comparison of XPS and AMS measurements if any comprehensive calibration is not included to the study. The idea that on the surface O:C would be 0.33 and then in the core it would be 1.02 is unlike but instead O:C could decrease gradually as a function of the radius of the particle. Nevertheless this scenario would increase the difference between the bulk and the surface composition even further (this could be calculated assuming linear change of O:C as a function of distance from the core…so called O:C-profile).

Response: We thank the Referee for this comment, for taking time to clarify the calculation of O:C and we apologize for the wrong calculation reported in our first answer. As indicated in the manuscript, XPS measures O:C of the particle surface to a depth up to 10 nm. However, from this technique, we are not able to provide more precisely the thickness of the surface analyzed and it is possible that the obtained O:C values corresponds to a thinner layer.

We examined the effect of different possible thicknesses of the SOA surface analyzed by XPS on the bulk O:C, using the equations proposed by the Referee (Figure A). From these calculations, we observed that bulk O:C ranges from 0.68 (±0.20) to 1.01 (±0.40) for fresh SOA and from 0.55 (±0.17) to 0.58 (±0.23) for aged SOA. Based on the elemental composition of identified compounds of α-pinene-O₃ SOA, highly oxygenated compounds were found in the literature. For example, peroxypinic acid is a product of α-pinene ozonolysis proposed by Docherty et al. (2005) with O:C=0.56. Although this compound might represent an upper limit of O:C of α-pinene-O₃ SOA, it indicates the plausibility of the results.
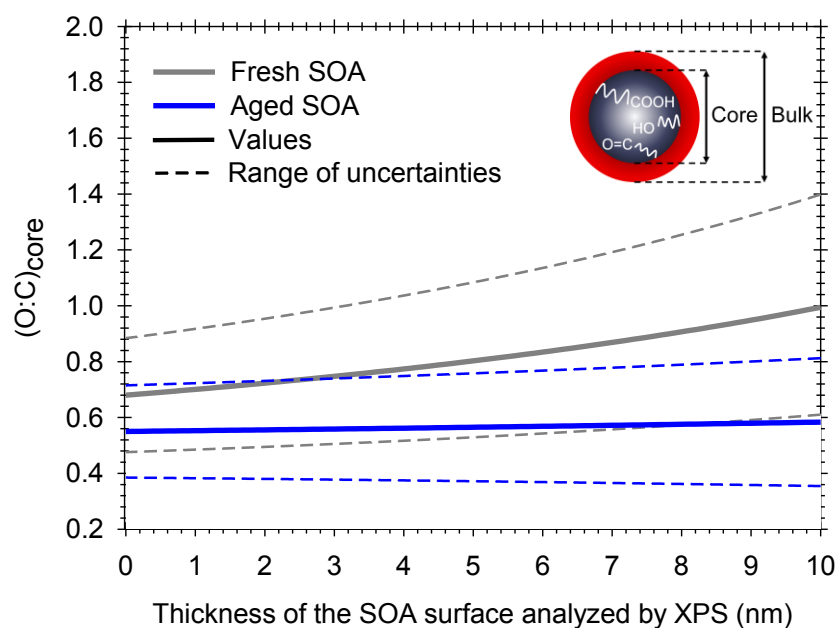
Figure A. Effect of the thickness of the SOA surface on the core O:C ratio. Values are calculated for SOA after 1 hour of reaction (grey) and after 14 hours of reaction and aged SOA (blue).

We added these calculations and the Figure in the manuscript as follows:

"We examined the sensitivity of the SOA chemical composition on the surface O:C by calculating the O:C of the core. For simplicity, we assumed that the O:C of the core SOA is constant and independent on the distance from the center of the particle. O:C of the core can be expressed as a function of the O:C of the bulk from AMS measurements, the O:C at the surface from XPS and the mass fraction of surface and core in the particle:

$$(O{:}C)_{core} = \frac{(O{:}C)_{bulk} - \frac{m_{surf}}{m_{bulk}}(O{:}C)_{surf}}{\frac{m_{core}}{m_{bulk}}} \qquad (6)$$

XPS quantifies the O:C of the SOA surface to a depth less than 10 nm. However, this technique cannot provide the precise thickness of the surface analyzed and it is possible that the O:C corresponds to a thinner layer. Therefore, O:C of the core SOA was calculated for different possible thicknesses of the analyzed surface O:C. Figure 8 shows the O:C of the core for fresh and aged SOA. From these calculations, we observed that bulk O:C ranges from 0.68 (±0.20) to 1.01 (±0.40) for fresh SOA and from 0.55 (±0.17) to 0.58 (±0.23) for aged SOA. Based on the elemental composition of identified compounds of α-pinene-O₃ SOA, highly oxygenated compounds were found in the literature. For example, peroxypinic acid is a product of α-pinene ozonolysis proposed by Docherty et al. (2005) with O:C=0.56. This simple calculation highlights the importance of monitoring the surface chemical composition separately from the bulk."

4. *Artefacts in H-TDMA measurements*

3) GF values measured with H-TDMA at ~20%RH are ~1.14. It is not ruled out that the experimental setup would not affect these results. GFs at dry conditions were measured the first meaning that inside the HTDMA tubings, the gas-phase were "cleaner", whereas in the CESAM gas-phase was in equilibrium with walls and particle phase. Thus, when you start the scanning with H-TDMA, closed loop system start to "eat" particle phase but it is possible that in the initial state of the scan (meaning lowest RH level) the particles had not time to evaporate (Mikhailov et al. (2009)). At the same time the CESAM is filled with pure air (assumption) so it is possible that the equilibrium there is also shifted since the gas-phase is diluting. This drives particles to evaporate. The question to ask: Would authors get the same GF value (~1.14) for 20%RH at the end of the all H-TDMA measurements and/or did the authors measure GFs at 20%RH for longer time, e.g. 1-2 hours to rule this out? What was the total sampling time used in HTDMA measurements, what is the time difference between measurements at ~20%RH and ~90%RH?

Response: GF was determined for a minimum time of 30 minutes, as can be seen in Figure 4. GF at 20% RH was measured at the beginning and the end of each series of H-TDMA measurements. The total sampling line used for HTDMA measurements ranged between 10 and 20 cm. Therefore, we are confident that the gas-phase within the H-TDMA was close to the one in CESAM and that the system was at equilibrium. In addition, the time difference between measurements at 20% RH and 90% RH was ~1h30, but GF at 20% RH at the end of the humidogram was the same as at the beginning of the measurement.

These information have been added in the manuscript in section 2.3.

This is important to mention that you are not using an actual dry diameter in growth factor calculations. Thus, data points below 40%RH do not represent hygroscopic growth of particles and the data on the RH range of 0-40%RH should be removed. Another option is to replace GF with d(RH)/d(40) like it is used in evaporation studies (e.g. Vaden et al. (2010), Shiraiwa et al. (2010)). To publish GF (if it denotes *Hygroscopic Growth*) of ~1.14 for a-pinene-derived SOA measured at 20%RH is somewhat questionable.

Response: As reported in our response to point 2, we clarified the definition of GF used in this study.