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) 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. Authors do claim that surface mass fraction is negligible for AMS analysis, but they have made mistakes in the calculations and thus, this has to be taken into account again.
2) 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).

Comments to the responses:

(Colors: Orginal referee comment, Authors response, Revised referee comment)

Referee #2, Comment 2: The other main result in the manuscript is the different O:C at the surface of SOA particles. This should be highlighted more since it has not been reported before. The explanation of the XPS analysis should be more comprehensive. It is conceivable that the particles evaporate within the XPS preparation and analysis which could change the O:C remarkably. Moreover a controller measurements of O:C of totally homogeneous SOA particles with the instruments (AMS & XPS) would make the O:C surface/bulk analysis much more reliable. The question about the offset between the analysis methods remains open.

Author Response: It is possible that some volatile compounds evaporate during the XPS analysis due to the low pressure in the instrument. However, we observed in our companion paper (Denjean et al., 2014b), an increase of the O:C after heating by the evaporation of semi-volatile components of SOA. This indicates that the O:C at the surface at the SOA reported in the present study would be an overestimation of the real values and strengthen the clear different O:C at the surface and the bulk SOA particles.
This point has been added in the new manuscript as follows: "Some volatile compounds could evaporate during the XPS analysis due to the low pressure in the instrument. In our companion paper (Denjean et al., 2014b), an increase of the O:C has been observed after heating by the evaporation of semi-volatile components of SOA. Therefore, the O:C at the surface of the SOA was certainly overestimated in the present study." (P16 L18)

Performing new measurements with homogeneous particles is clearly a control that should be pursued in future work. However, for the comparison, we considered an uncertainty of ±30% on the O:C of the bulk SOA, which may be largely overestimated compared to the experimental variability. In addition, as discussed above, the O:C of the surface of SOA was certainly an overestimation of the real value, which suggests a clear difference of O:C between the surface and the bulk SOA.

…

Referee #2, Comment P16L10-16: So bulk O:C is decreasing and surface O:C is increasing but after hours they are ~equal (within errorbars). So it also means that bulk O:C inside the particles is decreasing effectively even more than 0.68 => 0.55. Have you calculated how much should it be in the core of particle if the surface O:C is 0.33 versus 0.46?

Author Response: The XPS allows the measurement of the O:C of the particles to a depth less than 10nm. This means that, for a particle of Dp=200 nm, the O:C at the surface contributes at 43π.10343π.1003. 100=0.1 % *of the O:C of the bulk, which is negligible.*

Referee Response:

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. Thus mass fraction of surface layer is equal to O:C ratios as

$$\frac{m_{surf}}{m_{tot}} = \frac{(O{:}C)_{surf}}{(O{:}C)_{tot}}$$

Now, we want to see, what is the actual BULK/CORE O:C if the results shown in the manuscript are reliable. Total mass of the particles consists of mass fraction of surface and a mass fraction of bulk as

$$\frac{m_{surf}}{m_{tot}} + \frac{m_{bulk}}{m_{tot}} = 1$$

Total O:C can be calculated if we know the mass fractions and the O:Cs in the surface and in the bulk

$$\frac{m_{surf}}{m_{tot}}(O{:}C)_{surf} + \frac{m_{bulk}}{m_{tot}}(O{:}C)_{bulk} = (O{:}C)_{tot}$$

where by assuming spherical particles we can derive

$$\frac{m_{surf}}{m_{tot}} = \frac{\frac{4}{3}\pi(r_{tot}^3 - r_{core}^3)\rho_{surf}}{\frac{4}{3}\pi r_{tot}^3 \rho_{tot}}$$

and

$$\frac{m_{bulk}}{m_{tot}} = 1 - \frac{m_{surf}}{m_{tot}}$$

Assuming equal densities at the surface and the total, $\rho_{surf} = \rho_{tot}$, and the sensitivity of XPS as 10nm layer we get for 200nm particles mass fraction of

$$\frac{m_{surf}}{m_{tot}} = \frac{\frac{4}{3}\pi(r_{tot}^3 - r_{core}^3)\rho_{surf}}{\frac{4}{3}\pi r_{tot}^3 \rho_{tot}} = \frac{100^3 - 90^3}{100^3} \approx 27\%$$

For 100nm particles similarly we get

$$\frac{m_{surf}}{m_{tot}} = \frac{\frac{4}{3}\pi(r_{tot}^3 - r_{core}^3)\rho_{surf}}{\frac{4}{3}\pi r_{tot}^3 \rho_{tot}} = \frac{50^3 - 40^3}{50^3} \approx 49\%$$

Thus, mass fractions of the surface layer cannot be defined as "*negligible*". For mass fractions of bulk we get 100-27 = 73% and 100-49 = 51%. Now, we can use O:C values derived based on XPS and AMS analysis. In the initial state ($(O{:}C)_{tot} = 0.68$ & $(O{:}C)_{surf} = 0.33$) for 200nm particles we get the core/bulk O:C as

$$(O{:}C)_{bulk} = \frac{(O{:}C)_{tot} - \frac{m_{surf}}{m_{tot}}(O{:}C)_{surf}}{\frac{m_{bulk}}{m_{tot}}} = \frac{0.68 - 0.27 \cdot 0.33}{0.73} \approx 0.81$$

and for 100nm particles we get

$$(O{:}C)_{bulk} = \frac{(O{:}C)_{tot} - \frac{m_{surf}}{m_{tot}}(O{:}C)_{surf}}{\frac{m_{bulk}}{m_{tot}}} = \frac{0.68 - 0.49 \cdot 0.33}{0.51} \approx 1.02$$

For the aged particles ($(O{:}C)_{tot} = 0.55$ & $(O{:}C)_{surf} = 0.46$) we get

$$(O{:}C)_{bulk} = \frac{(O{:}C)_{tot} - \frac{m_{surf}}{m_{tot}}(O{:}C)_{surf}}{\frac{m_{bulk}}{m_{tot}}} = \frac{0.55 - 0.27 \cdot 0.46}{0.73} \approx 0.58$$

and for 100nm particles we get

$$(O\!:\!C)_{bulk} = \frac{(O\!:\!C)_{tot} - \frac{m_{surf}}{m_{tot}}(O\!:\!C)_{surf}}{\frac{m_{bulk}}{m_{tot}}} = \frac{0.55 - 0.49 \cdot 0.46}{0.51} \approx 0.64$$

All the O:C values are listed in Table below:

SOA type, d_p	**$(O:C)_{surf}$ (XPS)**	**$(O:C)_{tot}$ (AMS)**	**$(O:C)_{core}$ (calculated)**
α-pinene, 200nm	0.33	0.68	***0.81***
α -pinene, 100nm	0.33	0.68	***1.02***
α -pinene, 200nm	0.46	0.55	***0.58***
α -pinene, 100nm	0.46	0.55	***0.64***

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).

Referee #2, Comment P18L20: "The variation of GF due to the chemical composition change may not be detected due to sensitivity of the H-TDMA." Indeed, but WHY are you then analyzing hygroscopicity at all? In my point of view, lot more of data with different O:C, VOC concentrations, different precursors and wider GF range would be required.

Response: The aim of the paper is not only to find relations between hygroscopic properties and chemical composition of SOA, but also to see if these properties evolve during the aging of α-pinene-O_3 SOA. As stated in the introduction, previous studies show disagreements on the evolution of the hygroscopicity of α-pinene-O_3 SOA and here we provide new data under different experimental conditions. It is also important to note that none of the previous studies have provided the O:C of α-pinene-O_3 SOA together with the GF. We modified the sentence as follows: "The variation of GF due to the chemical composition change is smaller than the sensitivity of the H-TDMA"

Referee Response:

Authors write that "*It is also important to note that none of the previous studies have provided the O:C of α-pinene-O3 SOA together with the GF*." This is already widely studied previously by many groups (e.g. Dublissy et al. (2011), Massoli et al. (2010)) and they are saying it on the paper as well (P5L4).

Referee #2, Comment P35L1: Table 3 & P42L1: Figure 6: Where is the point 175nm/190nm? If the residence time in the Table 3 is not listed the table is misleading.

Response: The GF(90%) has been calculated with Dp,m(RHdry) at 40 % RH. Below 40% RH, if the physical state of particles change (discussed in section 4.2.), the particles may appear at a higher mobility size. Using mobile diameter below 40% RH to calculate GF would underestimate the GF and overestimate the amount of solute in the droplets. As no information is available on how high the real GF should be at RH<40%, we used Dp,m(RHdry) at 40 % RH to avoid GF less than 1.
The following sentences have been added to Figure 6 as follows: "For the calculations of f(RH) and GF, we used σscat(RHdry) and Dp,m(RHdry) at 40 % RH."

Referee Response:

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 H-TDMA 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 H-TDMA measurements, what is the time difference between measurements at ~20%RH and ~90%RH?

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.

References:

Duplissy, J.; DeCarlo, P. F.; Dommen, J.; Alfarra, M. R.; Metzger, A.; Barmpadimos, I.; Prevot, A. S. H.; Weingartner, E.; Tritscher, T.; Gysel, M.; Aiken, A. C.; Jimenez, J. L.; Canagaratna, M. R.; Worsnop, D.

R.; Collins, D. R.; Tomlinson, J. & Baltensperger, U. Relating hygroscopicity and composition of organic aerosol particulate matter, *Atmospheric Chemistry and Physics*, 2011, 11, 1155-1165

Massoli, P.; Lambe, A. T.; Ahern, A. T.; Williams, L. R.; Ehn, M.; Mikkilä, J.; Canagaratna, M. R.; Brune, W. H.; Onasch, T. B.; Jayne, J. T.; Petäjä, T.; Kulmala, M.; Laaksonen, A.; Kolb, C. E.; Davidovits, P. & Worsnop, D. R. Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, *Geophysical Research Letters*, 2010, 37

Mikhailov, E., et al.,Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, *Atmospheric Chemistry and Physics*, 2009, 9.24, 9491-9522.

Vaden, T. D.; Imre, D.; Beránek, J.; Shrivastava, M. & Zelenyuk, A., Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proceedings of the National Academy of Sciences, National Acad Sciences, 2011, 108, 2190-2195

Shiraiwa, M.; Ammann, M.; Koop, T. & Pöschl, U., Gas uptake and chemical aging of semisolid organic aerosol particles, Proceedings of the National Academy of Sciences, 2011, 108, 11003-11008