Title: Relating hygroscopicity and optical properties to chemical composition and structure of secondary organic aerosol particles generated from the ozonolysis of α-pinene

General comments:

In general, the topic of the manuscript is crucial for the restriction of uncertainties of aerosol direct effect in climate models. There are still lots of open questions in this field, related to the hydroscopicity and scattering effect of SOA particles. The manuscript has potential results for the publication in ACP but in my point of view, drastic revisions would be demanded to the manuscript before acceptance. The title is a bit misleading since the main focus of the manuscript is to investigate the effect of residence time on hygroscopicity and optical properties of SOA particles. Hygroscopicity and optical properties of pure α-pinene derived SOA have already reported widely in previous studies (cited in the manuscript). If the present title is not rephrased, strengthening of the relation between hygroscopicity and optical properties is needed (interpretation, figures etc.).

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.

Indeed, there is high interest related to the core-shell chemical structure and more detailed analysis of mass spectrums from the two methods could improve the paper significantly. Nevertheless, this is not related to the optical properties in the manuscript at all, so, what is the main purpose of the surface/bulk –composition analysis in this manuscript?

Additional proof reading is required throughout the manuscript.

Comments in more detail (also some minor comments included)**:**

P1L9: Affiliation information incomplete
P1L22: “Physical, hygroscopic, optical and chemical properties of …” Hygroscopic and optical properties ARE physical properties
P1L25: “under various relevant atmospheric conditions, including relative humidity (RH)” In terms of variability, RH was the only variable in the system and mainly it was kept <30%RH which doesn’t make it so atmospheric relevant.
P1L27-28: “…the dependence to RH of the particle size (*GF*)…” This is misleading, it would rather be: “…the dependence of RH on the hygroscopic growth factor (HGF) of particles…”

P2L10: “adsorption” should be absorption since the O:C wouldn’t decrease adsorption / hydrophilicity.
P2L12-13: “We postulate that this change could be due to a change in viscosity of the SOA from a more glassy state to a more liquid state” For this postulation I do not find any data to make an interpretation like this.
P2L29: “…the mixtures found in the atmosphere..”, I would replace atmosphere with “atmospheric SOA” since the atmospheric gas phase compounds are not making the large uncertainties directly.

P3L1: “residence time in the atmosphere” …lifetime?
P3L4: “atmosphere” …atmospheric SOA?
P3L12-13: “Some models…” incomplete sentence
P3L19-21: “α-pinene ozonolysis is one…and its ozonolysis is…” Ozonolysis and its ozonolysis
P3L22: α-pinene-O_3 has to be defined here.

P4L1-3: What are the reasons for the simultaneous measurements?
P4L2&L9 Word “their” refers to SOA particles or physical properties or aging?
P4L15: I assume you can control more than RH, also T, p, gas phase concentrations etc.
P4L20 + all the other acronyms in the text: Acronyms with multiple capital letters should not be written *italic*.
P4L27: σ should be defined here.

P5L12: “over more..”
P5L18: Accuracy of Vaisala RH sensor is typically +/-3% over the whole RH range which should be mentioned.

P5L28: "…at flow rates 3/0.3 Lpm" The aerosol flow in TSI-CPC3010 is 1 Lpm (+/-10%), not 0.3 Lpm. Moreover, the response time of CPC3010 is ~1-5 sec., has it taken into account in SMPS scans (i.e. what was the scanning time)?
P5L30: PSL is not defined in the text

P7L20: replace *-signs with dots in the equation

P8L1: Equation (3): Why there are sum and differential in a same equation? The sum could be an integral or then differentials could be increment deltas (Δ). The same equation is used in previous paper, Denjean *et* al. (2014).
P8L18: H-TDMA is defined already at P8L13.
P8L21: I would not use a manner of representation: $D_{p,m}(dry)$, whereas I would prefer to use $D_{\mathrm{p,m}}(\mathrm{RH}_{\mathrm{dry}})$ or something similar. "dry" is not a variable, RH is. (Note: Compare also the style between these representations)

P9L1: There is accuracy for RH of +/-1%. Accuracy of the sensor is 3% and then in P15L1 you show accuracy of 4.2% for humidity. This is not totally logical.

P9EQ(4): incorrect font and design (*italic* etc.)
P9L10: "A the end…" …At?
P9L19: "H-TMDA" should be H-TDMA
P9L19-22: I do not find the result from the previous Denjean *et* al. (2014): "…which carry information on water transfer dynamics…etc."

P10L27-29: Reformulation of this sentence is needed.
P10L33 L min^{-1} is used instead of Lpm. The same unit has to be used everywhere in the text.

P11L1: Why didn't you collect the samples at different times, for example an initial sample and after 16 hours?

P12L1: The first sentence is not needed here. In this part of the text it is too general.

P13L7: …but up to 2 times lower compared to other studies" This sentence needs citations.

P14L27: "A" should be "The"
P14L27: The message of the first sentence is not clear to me. Is this a general overview or did you do also humidograms in this study?

P14:L27 H-TDMA

P15L2: “SOA remained hydrophobic…” This is NOT true. GF values are higher than 1 which indicates that indeed, they are hydrophilic! Nevertheless you cannot say if the water is on the surface of the particles (adsorption) or inside the particles (absorption). Restriction in water uptake of SOA particles doesn’t mean that they are automatically hydrophobic.
P15L31: Error estimations of O:Cs are straight from the Aiken *et* al. (2007), no any statistical part?

P16L1-8: This is not enough to explain the decrease of O:C over aging time.
P16L10-16: So bulk O:C is decreasing and surface O:C is increasing but after 16 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?

P16L19: The section 3.4.2 does not give any new aspects or answers to the reader. It could be shortened and combined with 3.4.1.

P18L10: The following could have an important role in this case:

> Alfarra, M.R., *et* al. Water uptake is independent of the inferred composition of secondary organic aerosols derived from multiple biogenic VOSs, ACP, 13, 11769-11789, 2013.

P18L14: “out” should be our?, “Gf” should be GF.
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 you are 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.

P18L22: You cannot say “less hydrophilic”, also solubility can play a role, not only hydrophobicity.
P18L23: I would remove the word “significantly”.
P18L25: adsorption should be absorption?

P19L6-18: You could calculate the effective change of the shape factor of SOA particles which would explain “the shrinking effect”.

P19L15: I would replace “merge into single spheres” with “coalescence as it is in Pajunoja *et* al. (2014).
P19L16-19: The residence time for α-pinene SOA in Pajunoja et al. (2014) seems to be up to two months so the particles may be agglomerates with shorter residence times (the time they are not coalescenced yet).

P19L20-P20L22: For me this concentrates too much on glassy state of particles since there are no results indicating highly viscous material. Evaporation of semi-volatiles and effect of wall losses in the chamber are not discussed enough and should be analyzed much more carefully! Partial vapor pressures of VOCs and other gas-phase compounds are changing which are affecting gas-to-particle equilibrium. Further more if the particles are assumed to be highly viscous they would need much more than 1 hour to equilibrate. Thus, the increase of RH at the end of the experiment could be way too fast for the viscous particles!

> Kokkola H, et al. (2014) The role of low volatile organics on secondary organic aerosol formation. ACP, 14(3), 1689–1700
>
> Zhang X., et al. (2014) Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol

P33L1: Table 1: Initial α-pinene concentrations could be added to this Table because it has an effect on O:C and hygroscopicity of SOA particles.

P35L1: Table 3: This table would need also O:C, (α-pinene concentration), and estimated time after ozonolysis. I think also that this table is not obligatory since the values are quite similar. More than this table, the table where are GFs as a function of residence time would make better sense.

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.

P43L1: Figure 7: Are the legends correct? The day numbers are different so how have you interpreted the data? Also in the Fig 7b, the relative f(RH) <1 at <30% RH but in Figure 6b the HGF is absolutely the highest. Why is so?

P44L1: Figure 8: This figure would need a plot b) where is a comparison between AMS & XPS methods for homogeneous SOA particles. Figure 8 should also be explained in the text since the decrease of O:C as a function of time is “odd”.

P44L2: “These bulk O:C ratio are…” need to be reformulated (should be plural etc.), O:C is a ratio itself so now it means “bulk ratio ratio…”.