Response to Anonymous Referee #2:

This document contains responses to the reviews and details how the manuscript has been altered to address the comments. Original comments are in *italic font*, our response is in roman font, and changes made to the manuscript are in **bold font with red highlighting to illustrate recent changes**.

Comment #1: *The authors have addressed main points of the previous reviews. Addition of chemical composition data is certainly a significant improvement relative to the previous version. There are a few relatively minor points remaining, which are listed below with a reference to the author numbering of their replies.*

Response: We thank the referee for the second review. The remaining minor points are addressed below

Comment #2: *R1 Issue #2 "(2) Revised paragraph": I doubt that an example of glyoxal is a good one in this case. It is water-soluble; a large fraction of it could be lost from the gas to the wet walls in the cooling section. This is a minor question, since particle re-equilibration of semi-volatile material is hardly possible anyway (see below). The purpose of the example of high vapor pressure and low saturation ratio compounds is also not clear. Most of such compounds are in the gas phase anyway and probably will remain there even upon cooling.*

Response: The point we are highlighting is that there is a distinct difference between two types of organic gases that may affect water uptake: water soluble gases and semi-volatile organic compounds. Water-soluble gases may dissolve into growing aqueous drop and provide dissolved solute that drives additional water uptake (e. g. Kulmala et al., 1993 using nitric acid as example). Water-soluble gases are typically present at high vapor pressure and low saturation ratio. The cold trap should not remove these gases unless some of them a scrubbed by the water condensed on the walls (a point we admit that we did not consider). We further revised the paragraph in question. We also specifically point out there that the equilibration time scale may be very slow.

Revisions: **The dry-humidified state is similar to the unperturbed state (Fig. 1, panel 3). The difference is that the sample aerosol was dried using the same method as the dry instrument state. A temperature reduction of 30°C is expected to drop the saturation vapor pressure of typical semi-volatile organic compounds by 1-2 orders of magnitude (Booth et al., 2010). Compounds that become supersaturated will condense onto the wall or on the particles. Warming of the sample flow to the original temperature results in lower saturation ratio of gas-phase organic species. Subsequent evaporation of now strongly**

subsaturated semi-volatile compounds may result in net loss of organic mass from the particle. **Note that equilibration time for semi-volatile compounds is longer than the transit time through the equipment (~ 11 s between inlet loop and DMA entrance). For examples, the time required to evaporate to a diameter that is within 10% of the equilibrium size after a 30K warming varies between 30 and 1000 s for α-pinene SOA and aged SOA (cf. Figure 2, Riipinen et al., 2010).** We note that **water soluble organic gases may be affected differently than semi-volatile compounds. Water soluble gases (e.g. glyoxal) have high vapor pressure and low saturation ratio. Due to their low saturation ratio they will not be removed by the cold trap by direct condensation onto the wall. However, some fraction may dissolve into water condensate that is forming due to removal of water vapor. The dry humidified state** was designed to test if the drying procedure resulted in net removal of particle volume.

Comment #3: R1 Issue #6: a 15% relative deviation from ambient RH is very far from being "slight". At 50% RH it translates to a 7.5% RH deviation. For hygroscopic growth, this is a very significant difference and, actually, could translate to "huge" underestimation of water content, especially at RH > 80%. The authors should state upfront that their measurements represent a low estimate of the actual ambient water content.

Response: We added qualification to the abstract and the text to be more upfront. We also provide a mechanism to correct for mismatch in the instrument RH and ambient RH.

Revisions: Throughout the SOAS campaign, median water mass concentrations at the RH encountered in the instrument typically ranged from 1 to 5 µg m^{-3}, but were as high as 73 µg m^{-3}.

This work contains a description and analysis of the instrument design, data reduction methods, and field measurement results based on measured RH, explores influences on ambient water content, and provides a method to estimate water content at different RH conditions.

For these calculations, we assume a_w is equivalent to RH measured by the instrument, and the implications of this assumption are discussed later on in Section 2.4.

Since $RH_{unperturbed}$ was slightly lower than that measured at the meteorological station due to slight heating of the shed, the reported water contents represent a lower estimate. The relative difference between the two RH sensors, computed as (RH_{met}-RH_{shed})/RH_{met}, was 15%. Eq. (11) can be used to

estimate the corrected water content at conditions deviating from instrument conditions.

A campaign-based statistical summary of selected parameters encountered in the instrument is summarized in Tables 1 and 2.

Figure 4 summarizes trends of particle phase liquid water (V_w) throughout the campaign at the RH encountered in the instrument.

Temperatures measured by the instrument typically fluctuated between ~24 °C during nighttime and ~30 °C during daytime.

Daily fluctuations for RH within the instrument were typically within 60% to 77%. Periods of heavy rainfall included 5 – 7 June, 18 June, and 3 – 6 July.

First, our results show that at minimum 7% of the aerosol volume is composed of water at the measured RH

Aqueous phase liquid water was always present, comprising at minimum 7% of aerosol volume at the measured RH. Water mass concentrations at the RH encountered in the instrument typically ranged from 1 to 5 µg m^{-3}.

Comment #4: *R1 Issue #7, "(1) Revised discussion": The text starting with "The absence of this effect needs to (be) interpreted…" and any discussion related to semi-volatiles in other parts of the text should be thoroughly revised. As I have mentioned in my original review, it is not feasible to achieve gas/particle equilibrium at time scales of the measurements (a few minutes). The characteristic time, i.e., e-folding time, to achieve equilibrium at ambient concentrations (~1000 1/cm3 during SOAS) and the mean particle size of 100 nm is about 30 min (for example, see eq. 12.133 in Seinfeld and Pandis, 2nd edition). If the aerosol is solid or if the accommodation coefficient is less than 1, this time will be even longer. It is a well-established fact that it is impossible to reach equilibrium in thermodenuders (residence times up to 1 min) at ambient conditions (see, for example, Cappa and Jimenez, ACP 2010, 5409-5424). Any discussion about the effect of compound activity, physical state, C*, calibration with different model compounds, etc., is absolutely irrelevant, because it is hardly possible, even when working with an ideal liquid aerosol, to "extend the residence time between the cold trap and the SMPS" to at least one hour (remember, 30 min is the e-folding time, still quite far from equilibrium). I recommend the authors remove any discussion that suggests that something could be done to quantify semi-volatiles using this method or that the observed results could be due to one or the other factor that affects aerosol volatility. The relatively long equilibration time is the main reason why no noticeable evaporation of semi-volatile material was observed. Actually, this is a good thing for the method because the interference of semi-volatile material in water determination is*

fundamentally limited.

Response: We removed the following discussion about particle phase effects: "The absence of this effect needs to interpreted in light of the experimental limitations discussed in Section 2.4 (particle phase/viscosity/diffusion and non-ideal solution effects) as well as in context of the organic mass concentration, whether partitioning should follow Raoult's law, the mass of pre-existing non-volatile and dissolved material, and the expected amounts of semi-volatile compounds (Barley et al., 2009). For heavily aged SOA loss of semi-volatile compounds would be minimal. Small differences in mass may be more difficult to detect if overall aerosol mass loadings are large."

We added the fundamental limitation about residence time as suggested by the referee.

Revisions: The absence of this effect is likely due to the mismatch of residence time (~ 11s) and slow equilibration time of the organic phase with after a perturbation in of the gas-phase saturation ratio, which is system dependent and may exceed 60 min (Riipinen et al., 2010, Cappa and Jimenez et al., 2010). Improved methodology will need to lengthen residence time, reduce the uncertainty to resolve removal of less than 0.5 µg m^{-3} amounts, and establish volatility limits that can be detected using proxy system.

Comment #5: As a side note, a question about the effect of removing most particle mass when selecting particles of a single size is quite misinformed too. As long as the gas chemical composition remains the same, removal or addition of particles of the same composition does not affect equilibrium. This follows from $C_{g,i} = C_{sat,i}$ $C_{a,i}/C_{a,tot}$ (the basic equation of absorptive partitioning for an ideal solution, uniform molar mass and other usual assumptions), in which $C_{g,i}$, $C_{a,i}$ and $C_{sat,i}$ are gas, particle and saturation concentrations of compound i, respectively, and $C_{a,tot}$ is the total particle concentration. If $C_{a,i}/C_{a,tot}$ remains constant, as is the case when one removes some particles from the aerosol, $C_{g,i}$ will remain constant too. In other words, the aerosol remains in equilibrium. The misunderstanding of Reviewer 1, which the authors have apparently followed, comes from confusing the effect of pre-existing particle mass with the (non)effect of removing or adding particles of the same composition.

Response: The statement this comment refers to has been removed from the discussion.

Comment #6: R1 Issue #8 and #9. As was discussed above, all of this discussion is irrelevant. Characteristic equilibration times for ambient aerosols, including those observed at SOAS, are of the order of one hour or longer, even if one assumes no kinetic limitations. I would also respectfully advise the authors to avoid citing the infamous Vaden et al., 2011 paper. There is much better evidence for existence of solid aerosols. This particular paper, however, is full of errors and misinterpretation (a discussion of its numerous problems can be found in the interactive discussion of a rejected ACPD paper by that group http://www.atmos-chem-phys-discuss.net/11/20107/2011/acpd-11-20107-2011-discussion.html).

Response: We prefer to not take sides in the arguments about the (mis)interpretation of the Vaden et al. (2011) results. They did provide experimental data of evaporation kinetics and thus are relevant to the discussion. We also do not agree that our discussion is irrelevant. In fact we summarize some of the evidence why equilibration time is long and the issues that arise. Although we agree – and make clear in the manuscript – that our residence times are inadequate to quantify semi-volatile amounts we also believe that question whether aerosol drying leads to loss of organic material is a valid question to address. It is gratifying to know, both theoretically and experimentally, that evaporation may not be an issue in sampling.

Comment #7: R2 Issue #3: Please confirm that the losses discussed here are not limited to the DMA, but to the complete system, including its inlet.

Response: The size dependent loss test is limited to the DMA. However, losses of the complete system were accounted for as was discussed in the instrument section:

To account for differential transmission between the different states, the unperturbed, dry-humidified, and dry states are multiplied by a constant factor 1, 1.2, and 1.12 respectively to match the concentrations of a co-located CPC that was available prior to the start of the campaign (27–29 May) as well as 3–15 July.

The evaluation against the TEOM was performed after those complete system corrections were applied.

Comment #8: R2 Issue #5: The effect of residual water should be mentioned before the relevant equations. The equation for relative error in k should use a different symbol (epsilon_k or something like that), otherwise the symbol overlaps with k definition itself. It would be also useful to provide a more detailed explanation of how the values were obtained.

Response: We have restructured the paragraph so that the statements precede the relevant equations. We also changed the symbol that represents the relative error in κ, and provided a more detailed explanation of how the values were obtained.

Revisions: **Some compounds do not effloresce and thus may retain water at low RH. In that case the measured V_{dry} will be overestimated and the instrumented-inferred gf_{vol} and κ_{vol} will be biased low. The relative error in the inferred κ_{vol} at a_w=0.12, for example, is $e_\kappa = (\kappa_{vol,dry} - \kappa_{vol,0.12})/\kappa_{vol,dry}$, where $\kappa_{vol,dry}$ is the true hygroscopicity, and $\kappa_{vol,0.12}$ is the hygroscopicity one would calculate if particle-bound water was present at a_w=0.12. Eq. (1) can be used to estimate the magnitude of the particle-bound water at $a_w = 0.12$, assuming that κ is invariant with a_w. From that the total particle volume $(V_w + V_d)$ can be computed. If the total volume is mistakenly assumed to equal the dry volume, a $\kappa_{vol,0.12}$ can be computed. The estimated error is independent of a_w and scales with $\kappa_{vol,dry}$. For $\kappa_{vol,dry} = 0.01$ and $\kappa_{vol,dry} = 0.6$, the error is e_κ=-0.1% and e_κ=-7.6%, respectively. We also note that the dry instrument state corresponds to $RH = 12.5\% \pm 2.3\%$, where 2.3% denotes the variability of the RH in absolute units at the dry state throughout the campaign.**

Comment #9: R2 Issue #6 (1) and (3): I am not sure why the authors mention elemental carbon in this context. It is hydrophobic and does not affect water volume. Crustal material also has only a limited effect on water absorption.

Response: The referee is correct that elemental carbon and dust are not hygroscopic and thus will not affect total water mass concentrations. Since kappa scales the water content relative to the dry aerosol volume, the presence of elemental carbon and dust will affect the derived kappa value based on chemical composition. We did reword the section pertaining to R2 Issue #6 (1) to clarify this point.

Revisions: **We note that these speciated compounds only represent a subsection of the total aerosol since dust and elemental carbon are not included. Dust and elemental carbon are non-hygroscopic and therefore will not affect total water mass. Their presence will, however, lower the derived net κ value of the aerosol. Overall, the sum of the median mass concentrations for sulfate (1.7 µg m-3), nitrate (0.07 µg m-3), ammonia (0.47 µg m-3), and WSOM (3.15 µg m-3) is 5.39 µg m-3 and these species likely played an important role in governing aerosol water uptake during SOAS.**

Added References:

Cappa, C. D., and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, Atmos. Chem. Phys., 10, 5409-5424, doi: 10.5194/Acp-10-5409-2010, 2010.

Riipinen, I., Pierce, J. R., Donahue, N. M., and Pandis, S. N.: Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics, Atmos. Environ., 44, 597-607, doi: 10.1016/J.Atmosenv.2009.11.022, 2010.