**Response to referees**

We thank the two anonymous referees their careful reviews. This document contains responses to the reviews and details how the manuscript has been altered to address the comments. A summary of the main concerns raised during the review were

1. Missing chemical composition information.
2. Attribution of the diel $\kappa$-cycle to changes in chemical composition alone.
3. Interpretation of the volatility measurements.
4. Questions regarding the validation of the instrument performance and analysis techniques.

To address these concerns we have added chemical composition data from PILS-IC and PILS-WSOM to the main manuscript (collaboration with H. Guo and R. Weber and who will be added as co-authors in the revised paper). We also added a supplement that contains comparisons of the SMPS volume and TEOM mass concentrations, analysis without resorting to log-normal fits, and a simplified closure model using measured chemical composition and the thermodynamic E-AIM model.

The remainder of this document is structured as follows.

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|---|---|
| Referee #1 (anonymous) | pg. 2-10 |
| Referee #2 (anonymous) | pg. 11-24 |
| Added References | pg. 24-25 |

We have identified the key issues raised in each comment and sequentially number them Issue #1 – Issue #n for each set of comments. Editorial comments are sequentially numbered as Comment #1 – Comment #n. Original comments are in *italic font*, our response is in roman font, and changes made to the manuscript are in **bold font**. We also provide a manuscript version with tracked changes that will be uploaded to the Copernicus manuscript system.

**Response to Anonymous Referee #1:**

*This paper is a single study to present a methodology to try and resolve the potential effects of semi-volatile loss/gain in deriving instrument based measured hygroscopicity. As the authors are aware, this area is fraught with difficulties, not least forced by the measurement techniques used and the complexity of ambient aerosol and single particle processes. Much work is needed in the area before the effects are truly resolved. The authors provide a valid point in that actual concentrations of aerosol water are not routinely measured. This study presents a methodology to rectify this. Whilst I feel the paper is appropriate for ACP, there are a number of general points that need to be addressed before publication that will affect the tone of the delivered conclusions. Presently, the results are interesting as a proof of concept study, but obviously require caution in further extrapolation. In addition, there are a number of highly qualitative discussions that would benefit from some clarity, including an appropriate testing ground for the proposed methodology.*

Response: We thank the referee for the careful review of our manuscript. We agree that the volatility part should be seen as a proof-of-concept study and furthermore that the results should be seen only as a test if the used preconditioning inlet leads to loss particle volume. The uncertainties are too large to extrapolate the results to a quantification of semi-volatile material and we have removed the few places where it might have appeared that we made that claim. In response to the comments we quantified outstanding issues as outlined in the detailed responses below.

*R1 Issue #1: General introduction. There is obviously still debate as to the role of water in SOA partitioning. I would suggest providing a few more succinct up to dates more wider references to discussions had on this in your introduction: the potential impact of LLE, the mass and molar based absorptive partitioning frameworks.*

Response: We now include the following paragraph to address this concern.

**Revisions: The role of water in SOA formation in a particular environment is complex. In addition to the availability and relative abundance of particle phase liquid water, SOA enhancement depends on the amount of semi-volatile and water-soluble gas-phase material (Carlton and Turpin, 2013). For absorptive partitioning, SOA formation is dependent of the activity coefficient of the organic in the solution (Pankow et al., 2001, Barley et al., 2009). The presence of inorganic material mixed with hydrophobic organic compounds may lead to liquid-liquid phase separation (Bertram et al., 2011) and the presence of liquid-liquid equilibria may influence partitioning (Prisle et al., 2010). Partitioning of water-soluble material is also influenced by the presence of inorganic material through salting effects (Lim et al., 2010; Knote et al., 2014). Semi-volatiles and dissolved gases that are associated with the aqueous phase may be lost by particle drying, which could hamper measurement and predictions of cloud condensation nuclei from dried aerosol streams (Topping and McFiggans, 2012).**

*R1 Issue #2: Page 7476: Line 4:'Presumably some semi-volatile substances were irreversibly removed inside the chilled copper tube. We expect that warming of the sample flow after the copper tube would result in re-equilibration of the semi-volatile compounds, similarly to what is observed with water. Thus this configuration was intended to measure the particle size distribution with minimal perturbation to sample temperature and RH after removal of some fraction of semi-volatiles.' - This is very qualitative. I appreciate the difficulties in quantifying this effect but it would help the reader to know how these qualitative hypotheses might be untangled. If the authors feel that discussion exists, then please better reference different parts of the manuscript. See my comment below re testing using proxy systems.*

Response: First, in accordance with our initial text, it should be understood that the proposed technique is not well enough characterized to permit full quantification of the amount of semi-volatile material in the sample. Indeed a set of carefully designed laboratory studies testing proxy systems resulting in quantifiable range of vapor pressures removed by the inlet would be needed. Such studies are beyond the scope of this manuscript. We agree with the referee that the label "semi-volatile DMA" is misleading. A more appropriate statement would be that we test the hypothesis whether differences in drying/preconditioning resulted in measurable differences of water uptake and/or loss of semi-volatile material. No measurable differences were observed.

Second, we revised the paragraph to clarify the mechanism by which we believe semi-volatile compounds are removed.

**Revisions: (1) All statements referring to the SV-DMA technique have been removed. The hypothesis regarding the removal of material during drying has been clearly stated in the introduction.**

**(2) Revised paragraph**

**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 re-equilibration of the semi-volatile compounds may result in net loss of organic mass from the particle. We note that compounds having high vapor pressure and low saturation ratios (e.g. glyoxal) will not be affected by this mechanism and may re-equilibrate with the aqueous phase. This configuration was designed to test if the drying procedure resulted in net removal of particle volume.**

*R1 Issue #3: Page 7479: Equation 6. So the authors are presuming no semi-volatiles re-equilibrate on re-humidifying as might be expected if a gaseous component were to re-equilibrate according to Raoults law? This is confusing in relation to the statement made : 'We expect that warming of the sample flow after the copper tube would result in re-equilibration of the semi-volatile compounds, similarly to what is observed with water.*

Response: Please see our revisions in response to R1 Issue #2.

*R1 Issue #4: Page 7479: Equation 6, according to the other equations this should be Vw,lv and not total water shouldn't it? So equation 6 just gives you water associated with your definition of low volatility compounds?*

Response: Correct.

**Revisions: Consequently aerosol water volume associated with low volatile material is**

$$V_{w,lv} = V_{dry-humidified} - V_{dry} \qquad \mathbf{(6)}$$

*R1 Issue #5: Page 7480: 'Non-hygroscopic materials lost during drying': So these compounds evaporate due to the temperature increase? What volatility range of compounds would you expect to lose from this effect based on a simple C* calculation with a fixed typical enthalpy of vaporisation? What about timescales used in the instrument, do these reflect typical conditions used in other studies of hygroscopicity?*

Response: In response to the first question: 'Non-hygroscopic materials lost during drying': So these compounds evaporate due to the temperature increase?

In the context this statement simply refers to a thought experiment. If semi-volatile material lost upon drying is also hygroscopic, then its loss will also imply loss of water. The operational definition used in Eq. (7) (which correctly should have read $V_{\mathrm{sv,instrument}} = V_{\mathrm{unperturbed}} - V_{\mathrm{dry,humidified}}$) will erroneously interpret this as a loss of semi-volatile bound water. For the special case where the semi-volatile compounds are also non-hygroscopic the operational definition will coincide with the loss of actual semi-volatile material. Our Eq. (8) quantifies the effect. We clarified the text to better explain this behavior.

In response to the two remaining questions: 'What volatility range of compounds would you expect to lose from this effect based on a simple C* calculation with a fixed typical enthalpy of vaporisation? What about timescales used in the instrument, do these reflect typical conditions used in other studies of hygroscopicity?'

We revised the description of the dry-humidfied to clarify this point. Providing a C* value is difficult since it will depend on the enthalpy of vaporization and the saturation ratio of the compound in the atmosphere. The time-scales are comparable to other studies of hygroscopicity.

**Revisions: (1) Non-hygroscopic material during drying:**

**Eq. (8) demonstrates that if $\kappa_{sv} = 0$ (corresponding to a hypothetical non-hygroscopic material that is lost during drying)**

**(2) Residence time:**

**The residence of sample at the measurement RH is comparable to those used in other studies of hygroscopicity (cf. Table 1, Duplissy et al., 2009).**

**(3) Revision of dry-humidified state:**

**Please see our response to R1 Issue #2**

*R1 Issue #6: Section 2.4 How much is 'slightly lower'?*

Response: We now quantify this effect.

**Revisions: Since $RH_{\text{unperturbed}}$ 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 $(RH_{\text{met}}-RH_{\text{shed}})/RH_{\text{met}}$, was 15%.**

*R1 Issue #7: Isn't there any supporting aerosol composition information? It is very hard to try joining all pieces of information without this data. There is a brief discussion as to the potential effects in section 4 which is interesting. Similarly, isn't one crucial piece of information at least some idea as to the 'expected' volatility of the aerosol you are sampling. Is it heavily aged SOA for which the proposed effect would be minimal anyway? One interesting hypothesis comes to mind is the following. The partitioning of compounds, if we are to believe absorptive partitioning playing a dominant role, is dependent on the available absorptive mass. That is, in the atmosphere, the re-partitioning of available semi-volatile material is sensitive to particle size distributions and number concentrations. I presume the authors do not feel the instrument samples gaseous components in the inlet that would prevent the evaporation of compounds from mono-disperse particles (very small mass relative to available mass in the gas phase perhaps)?*

Response: (1) We now include supporting aerosol composition information in support of the water content measurements.
(2) We added the ideas articulated by the referee to the discussion in Section 4. An excerpt of the revised section is provided below

**Revisions: (1) Revised discussion**

**Correlations between ambient temperature, relative humidity, and particle phase liquid water can potentially obfuscate the attribution of semi-volatile partitioning into the condensed phase to either the presence of water due to increased RH or reduced vapor pressure due to reduced temperature. Although this conceptual distinction is important, it is irrelevant for this study because loss of semi-volatile volumes $V_{\text{sv}}$ during our drying procedure was not statistically discernible (Fig. 9). 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. Improved methodology will be needed to further reduce the uncertainty to resolve removal of less than 0.5 μg m$^{-3}$ amounts, establish volatility limits that**

**can be detected using proxy system, lengthen residence time between the exit of the cold trap and SMPS to ensure full equilibration, and test whether the conclusion is valid when single particle sizes are considered.**

**(2) New Figure 10. Methods regarding PILS-IC and PILS-WSOM have been added to the text.**

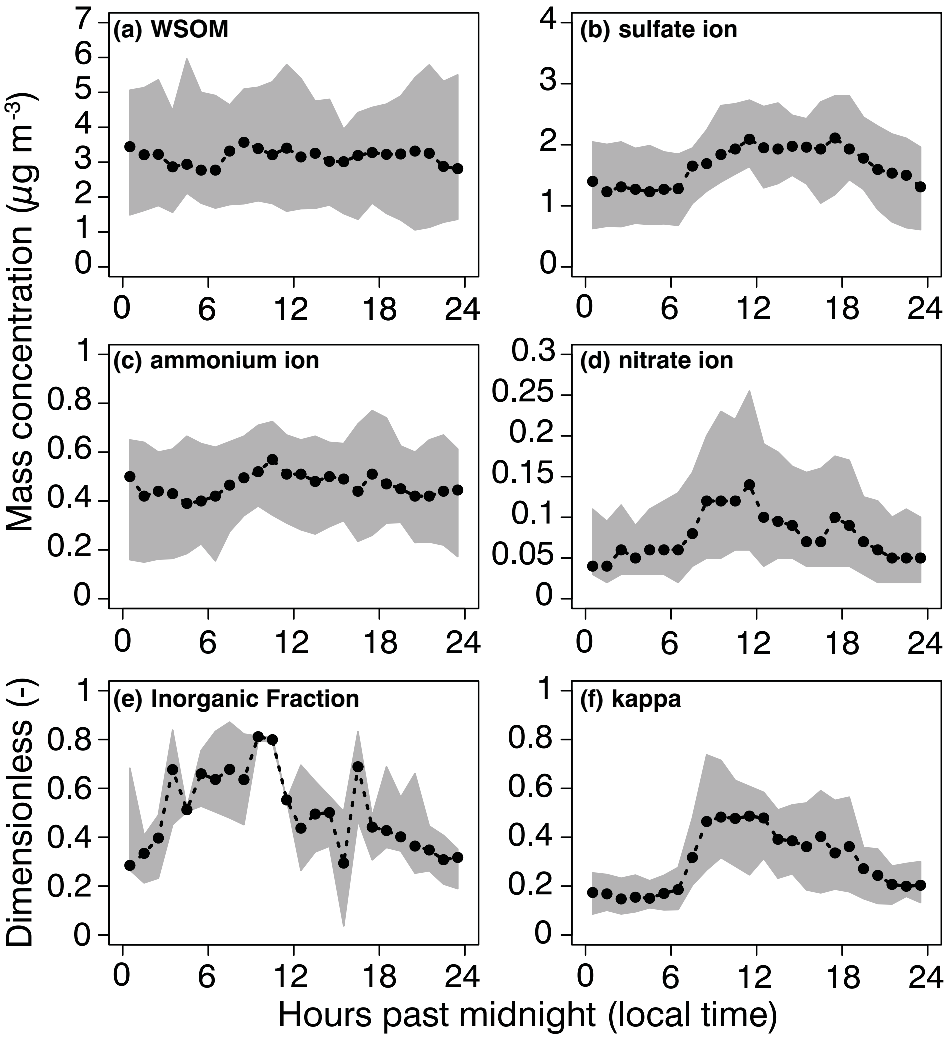

*Fig. 10. Diurnal trend of select aerosol chemical species measured by PILS-IC and WSOM calculated from PILS-WSOC. The central black line shows the median of the measurements. The shaded area indicates the interquartile range. Panel (e) shows the ratio of ∑(b)+(c)+(d) over ∑(a)+(b)+(c)+(d). Panel (f) is identical to Fig. 8.*

*R1 Issue #8: On this note, as the paper is presenting a new technique, I'm surprised to not find any tests on proxy systems for which you could confidently extract the myriad of processes effecting these measurements: Individual component volatility, non-ideal effects, phase separation effects, diffusion effects. Would the authors not feel it appropriate to study at least a few, say, ternary or quaternary proxy mixtures before moving to complex ambient aerosol?*

Response: We agree with the referee that proxy studies are needed to quantify the loss of semi-volatile material in the inlet. As stated in response to R1 Issue #2, it is more appropriate to view our experiments as a test to determine if our particular method of particle drying resulted in detectable loss of semi-volatile opposed to attempting to quantify the amount of semi-volatile material contributing to particle mass.

**Revisions: The numerous uncertainties regarding resolving total amounts are discussed in the manuscript. A specific statement has been added to clarify that this concept study does not quantitate all semi-volatile material in the sample. All statements that refer to semi-volatile amounts have been clarified to refer to "semi-volatile materials lost during our drying procedure".**

**Revised Section 2.4: "Although losses of semi-volatile compounds during drying are expected, the total amount lost unlikely corresponds to what would be expected from thermodynamic equilibrium. Several reasons are listed here. First, fast kinetics for aerosol dissolution are required. However, this may not be the case if the initial *RH* is low, as the aerosol becomes viscous and formation of a homogenous liquid phase may be slow (Vaden et al., 2011; Renbaum-Wolff et al., 2013). Second, evaporation rates must be fast enough to remove semi-volatiles in the inlet even though evaporation rates may be slow (Bilde et al., 2003). Succinic acid, for example, has been measured to have an evaporation rate of 2.76 nm $s^{-1}$ at 299.8 K and 64.1% *RH* (Koponen et al., 2007). The residence time of the preconditioning inlet may not be adequate to capture full evaporation of succinic acid. Third, the phase state of the particles after drying is uncertain. Sub-cooled liquid vapor pressure may be up to three orders of magnitude higher than solid vapor pressure (Booth et al., 2010). Since partitioning between gas and particle phase is dependent on the saturation vapor pressure of the organic compound in the liquid state (Pankow, 1994), semi-volatile content may be underestimated if particles are in the solid state after drying. However, water in the organic phase could reduce organic equilibrium partial pressure according to Raoult's law (Pankow and Chang, 2008), though this effect did not play a strong role on $\alpha$-pinene SOA formation (Prisle et al., 2010). Detailed studies with proxy systems are needed to quantify the amount removed as a function of compound volatility in the context of particle phase/viscosity/diffusion and non-ideal solution effects. Therefore, the tests with the preconditioning inlet only test whether the selected drying procedure lead to loss of material"**

*R1 Issue #9: Do you think the conditions and time scales from which you are extracting impacts are appropriate for atmospheric timescales and conditions. If, for example, the aerosol was in a viscous state with equilibrium timescales approaching 10's of minutes, then what difficulties arise in using these measurement techniques to prescribe wider impacts?*

Response: As discussed in the original manuscript (also see revised paragraph to previous comment regarding viscosity effects), the time scales required for equilibration may be longer than the residence time in the inlet. Lengthening the residence time in the conditioning system would be possible in principle, but may also worsen artifacts arising from wall effects.

**Revisions: The limitation is discussed in the manuscript. All statements that refer to semi-volatile amounts have been clarified to refer to "semi-volatile materials lost during our drying procedure".**

**Response to Anonymous Referee #2:**

*The manuscript describes measurements of aerosol water content using semi-volatile differential mobility analysis (SVDMA) during the Southern Oxidant and Aerosol Study (SOAS). This is an important topic and is appropriate for ACP. The manuscript, however, is under-developed and needs significant improvement prior to publication. One of the major omissions is a comparison with chemical composition data, without which the conclusions drawn by the authors appear to be mostly speculative. There are also issues related to data processing and interpretation that need to be addressed.*

Response: We thank the referee for the careful review of our manuscript. We have addressed the issues related to data processing raised by the referee (log-normal fitting, particle drying, and volume measurement) by considering the points and implementing the suggested changes. None of these significantly changed our reported results.

*R2 Issue #1: I doubt that SVDMA can reliably measure semi-volatile material. The authors are correct in their assessment that SVDMA measures only "some" of semi-volatile material. A few seconds that air spends in the instrument is hardly enough to equilibrate the sampled particles at the fairly low ambient concentrations that were observed during the SOAS. The residence time will allow only a small fraction of semi-volatile material to evaporate. It is, thus, not surprising that very little semi-volatile material was observed in the instrument. A larger problem is that the fraction of evaporated material depends on the aerosol loading (condensational sink). This means that the evaporated fraction will change as the aerosol concentration changes. One can use a numerical model to derive the actual semi-volatile fraction, but this approach is still quite problematic as it requires accounting for wall effects and de-convoluting hygroscopicity of the semi-volatile and non-volatile material that are not known a priori. SVDMA, thus, does not provide a reliable measure of semi-volatiles, but only a measure of aerosol water content that is biased high by (hopefully) a small amount. Thus, I would suggest removing "semi-volatile" from the name of the method.*

Response: We follow the referee's suggestion and remove the “semi-volatile” from the name of the method. As we made clear in the draft manuscript we cannot quantify the entire semi-volatile fraction in a meaningful way. A more appropriate way to frame our measurement is that we test whether a measurable amount of semi-volatile material is lost upon particle drying. We revised the manuscript accordingly.

*R2 Issue #2: There is a potential bias in the data processing that involves fitting bi-modal lognormal distributions to size distribution data. I understand that this procedure reduces noise in individual size distributions, but I do not see the need for this when working with such a large dataset. Ambient aerosol distributions can and often do deviate from a lognormal shape. Further, even if a dry aerosol is lognormal, the distribution shape could be distorted upon growth due to differences in chemical composition at different particle sizes and the Kelvin effect. Using mean sizes for each mode and total volume concentrations (corrected for arcing artifacts, if needed) instead of fitted parameters should provide the necessary information without (potentially) biasing the results.*

Response: We originally perform the analysis both ways, based on data only and based on log-normal fits, but only reported the results obtained using the fitting procedure. Although two modes were often needed to obtain good fits, the modes often blend into each other, making it difficult to devise an objective procedure separating the modes without resorting to curve-fitting. We now include tabulated results using total volume concentrations and note that they are very similar to the derived $gf_{\mathrm{vol}}$ from the procedure reported in the original manuscript.

**Revisions: (1) Added a Table to the supplementary information that summarizes our analysis similar to what the referee suggests.**

**(2) Clarified issues about potential bias in retrieved mode diameter (see R2 Comment #5)**

**(3) Provided detailed statistics regarding the differences between fit-derived and data-derived number and volume concentrations (see R2 Comment #6).**

*R2 Issue #3: The instrument characterization is not entirely convincing, since it is based on particle count inter-comparison, while the measurements were concerned with a mass-based property (aerosol water concentration). Number concentration is mostly determined by small particles, while volume concentration – by larger ones. If particle losses are size-dependent, which they often are, a number concentration comparison will not accurately represent inter-comparability of volume concentration measurements.*

Response: Three points.

First, we now provide direct comparisons between dry aerosol volume derived by the SMPS and dry aerosol mass measured by a TEOM that was co-located with the SMPS. These are presented in the supplement of the manuscript. To the extent that these two techniques can be compared (uncertainties include differences in dry RH, particle shape effects, and particle density), the comparison indicates that derived SMPS volumes are reasonable.

Second, we not only checked total number concentrations against that of the CPC but also characterized instrument transfer and sizing of monodisperse particles between 20 and 600 nm. We found (1) no losses in the DMA at 50 nm < $D$ < 600 nm and (2) a gradually declining performance toward smaller sizes. These are taken into account in the inversion and we do obtain good count comparisons with the co-located condensation particle counter most of the time.

Third, we selected to work with a single SMPS system operating sequentially in the unperturbed, dry, and dry-humidified states to ensure that even if biases in the total volume were present they would almost exactly cancel. The largest observed diameter growth factors were 1.3 (for $gf_{\mathrm{vol}} > 2$, see Figure 7 in original manuscript) with the volume mean diameter varying between 200 and 300 nm. It is unlikely that a shift in the spectrum by a factor of 1.3 will result in a biased volume estimate due to size-dependent particle losses.

**Revisions: Measured volume concentrations were correlated with mass concentrations from a co-located tapered element oscillating microbalance (Patashnick and Rupprecht, 1991, see supplementary information). The offset between these measurements is broadly consistent with an aerosol density of 1.5 g cm$^{-3}$, a value that is reasonable for the measured aerosol chemical composition.**

*R2 Issue #4: There is an error in Eq. 7. V dry should be V dry−humidified . I assume that the correct formula was used to interpret the data and that this is just a typo.*

Response: We thank the referee for pointing out the mistake that occurred when we changed nomenclature in our internal revisions. The calculations were indeed performed as implied by the referee.

**Revisions: The semi-volatile volume is**

$$\mathrm{V}_{\text{sv,instrument}} = \mathrm{V}_{\text{unperturbed}} - \mathrm{V}_{\text{dry-humidified}} \tag{7}$$

*R2 Issue #5: Calculation of aerosol water content used in this paper implicitly assumes that there is no particle-bound water at "dry" conditions. This is questionable. The presented measurements show that the ambient aerosol was in the meta-stable state. There is, thus, a good chance that the aerosol can retain some water even at "dry" conditions. The equations need to be edited to account for this possibility and its implications for the calculated κ values, etc., should be discussed.*

Response: This is indeed a possibility that we ought to have mentioned in the list of uncertainties. We added an estimate of the error due to this effect to Section 2.4.

**Revisions: Some compounds do not effloresce and thus may retain water at low RH. In that case the measured $V_{\mathrm{dry}}$ will be overestimated and the instrumented-inferred $gf_{\mathrm{vol}}$ and $\kappa_{\mathrm{vol}}$ will be biased low. The dry instrument state corresponds to RH = 12.5% ± 2.3%, where 2.3% denotes the variability of the RH in absolute units at the dry state throughout the campaign. Eq. (1) can be used to estimate the magnitude of particle-bound water at $a_{\mathrm{w}}$ = 0.12, assuming that $\kappa$ is invariant with $a_{\mathrm{w}}$. The relative error in the inferred $\kappa_{\mathrm{vol}}$ is $\kappa = (\kappa_{\mathrm{vol,dry}} - \kappa_{\mathrm{vol,0.12}})/\kappa_{\mathrm{vol,dry}}$, where $\kappa_{\mathrm{vol,dry}}$ is the true hygroscopicity, and $\kappa_{\mathrm{vol,0.12}}$ is the hygroscopicity one would calculate if particle-bound water was present at $a_{\mathrm{w}}$=0.12. The estimated error is independent of $a_{\mathrm{w}}$ and scales with $\kappa_{\mathrm{vol,dry}}$. For $\kappa_{\mathrm{vol,dry}}$ = 0.01 and $\kappa_{\mathrm{vol,dry}}$ = 0.6 the error is $e$=-0.1% and $e$=-7.6%, respectively.**

R2 Issue #6: *The authors use diurnal variation of water content and the associated κ values to justify their conclusion that chemical composition changes on time scales of a few hours. While this could be true, the argument and data presented in the paper are not sufficient to prove it. κ is a measure of aerosol hygroscopicity, but not a strict one. For a single component aerosol it is equal to the ratio of the molecular weight of solute to that of water and multiplied by the maximum number of ions the solute can produce upon dissociation (the van't Hoff factor). As the authors admit, κ changes with relative humidity (due to higher solute concentrations at low RH values, the degree of dissociation, or solute activity, changes). Since RH changes during the day, κ values will change too. Thus, observing diurnal variability of κ does not provide enough information on aerosol chemical composition. This variation needs to be analyzed in the context of the RH dependence of κ.*

Response: To address the referee's concern we have (1) added chemical composition data to the manuscript and (2) performed calculations using the E-AIM model and the available data. These have been added to the manuscript in form of a supplement. We point out that the model calculations are illustrative since many key parameters needed for full chemical closure are not available for SOAS (yet). These include black carbon and dust, time-resolved speciation of the organic phase and compelling estimates of aerosol density. Nonetheless, the model can be used to estimate the magnitude of the RH effect on $\kappa$. We revised the discussion to include the mentioned effect.

**Revisions: (1) Added chemical composition data:**
**The diel evolution of the hygroscopic species sulfate, nitrate, ammonia, and WSOM is shown in Fig. 10. Ammonia and WSOM are approximately constant while sulfate and nitrate show a diel cycle with a daytime maximum. We note that these speciated compounds only represent a subsection of the total aerosol since dust and elemental carbon are not included. However, 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.**

**(2) Added supplement detailing E-AIM model closure based on available chemical data and stating required assumptions (please see revised manuscript)**

**(2) Revised the discussion based on new data and model calculations:**
**Finally, the diel cycle of aerosol hygroscopicity suggests that significant changes in aerosol composition may occur on the time scale of a few hours. This is supported by changes in the inorganic aerosol fraction derived from the PILS measurements shown in Fig. 10e. Variation range from 20% to 80% for the inorganic fraction and the diel cycle in organic fraction mimics that of $\kappa$ (Fig. 10 f). However, the actual relationship between chemical composition and $\kappa$ is complex since $\kappa$ may strongly vary with water content (or RH) for concentrated solutions (Kreidenweis et al., 2008). Assuming that the PILS measured chemical composition captures most of the species responsible for water uptake and**

**assuming a representative composition for the WSOM fraction we estimated the RH dependence using the E-AIM model (Clegg et al., 1998). These calculations show that the reduction of RH from 90% to 40% may cause a 60% increase in $\kappa$ (see supplemental information). The diel fluctuation in $\kappa_{vol}$ is from 0.14 to 0.46. Notably, the aerosol is most hygroscopic when the fractional water content is larger, which is consistent with the modeled RH dependency of $\kappa$. The magnitude of the RH dependence, however, is insufficient to explain the full diel $\kappa$-cycle which is driven by a combination of the two effects. We note that deconvolution of the two effects will require closure calculations between time-resolved chemical composition and $\kappa$ that are contingent upon complete speciation of the aerosol (including black carbon and dust), detailed information about the composition of WSOM, and estimation of aerosol solubility and density (see supplemental information).**

*R2 Issue #7: The observed κ values need to be compared to chemical composition data to check whether the observed values can be explained by changes in aerosol chemical composition and whether these values are realistic. For example, are the estimated κ values for the organic fraction realistic? Or, if one assumes κ for organics, does it lead to the organic mass fraction or the WSOC mass fraction that have been measured during the SOAS?*

Response: We added chemical composition information. The discussion this comment refers to is obsolete.

**Revisions: Please see response to R2 Issue #6**

*General and Minor Comments*

*R2 Comment #1: p.7471, l.13-14. The direct aerosol effect is also affected by hygroscopic growth.*

Response: We added this to the list.

**Revisions: Particle phase liquid water and its interactions with aerosol chemical composition is associated with many aerosol health and welfare effects: acid deposition (Calvert et al., 1985), impaired visibility through light scattering (e.g. Malm et al., 1994; Park et al., 2004; Pitchford et al., 2007), climate through effects on aerosol optical depth (Pilinis et al., 1995, Leibensperger et al., 2012), and cloud condensation and ice nuclei (e.g. Cruz and Pandis, 1997; Pöschl, 2005).**

*R2 Comment #2: p.7473, l. 22. The temperature stability needs to be quantified.*

Response: We quantified the information and also provide statistics on the dry RH.

**Revisions: (1) Added: "The temperature of the copper tube could be stably controlled between $T_{\mathrm{inlet}}$ - 30±0.19 °C and $T_{\mathrm{inlet}}$ + 50 °C (TE Technology LC-061)."**

**(2) Added: "The dry instruments state corresponds to RH = 12.5% ± 2.3%, where 2.3% denotes the variability of the RH in absolute units at the dry state throughout the campaign."**

*R2 Comment #3: p.7473, l. 22. What is the model number of PermaPure humidifier?*

Response: The model number is PermaPure MH 110-48. The part number was added to the manuscript

**Revisions: An optional Nafion membrane water-to-gas humidifier (PermaPure MH 110-48) was used to condition the aerosol.**

*R2 Comment #4: p.7477, l. 24-25. Since the flow has changed on 3 July, has the instrument performance been characterized for this flow?*

Response: We lowered the flow rate of the CPC from 1 L $\mathrm{min}^{-1}$ to 0.5 L $\mathrm{min}^{-1}$ and added a CCN instrument pulling 0.5 L $\mathrm{min}^{-1}$. Thus the total flow through the DMA was unchanged. The regular system performance checks described in the paper were carried out also after the change and we found no instrument performance change after accounting for the reduced counting rate expected from the flow change in the CPC. We clarified the text to better describe this procedure.

**Revisions: After 3 July the CPC sample flow was reduced to 0.5 L $\mathrm{min}^{-1}$ to accommodate 0.5 L $\mathrm{min}^{-1}$ flow for a cloud condensation nuclei counter added to the setup. Thus the total flow through the DMA was unchanged. Number distribution readings from the CPC were adjusted accordingly to account for the reduced number of particles counted. The regular system performance checks were also carried out after the change. No degradation of instrument performance was observed.**

*R2 Comment #5: p.7478, l. 6-8. I agree that losses at small sizes most likely do not affect measurements of total volume concentration, but they are important for the measured parameters of the smallest of the two modes. There is a significant fraction of particles below 50 nm even in dV/dLogD (see Fig.3), which could introduce errors in the measured GMD and lognormal fit parameters.*

Response: The distribution shown in Fig. 3 exaggerates the problem. The average number and volume fraction of particles with $D < 50$ nm to smaller mode is 30.6% and 19%, respectively. The contribution of volume of the total volume for $D < 50$ nm is 3.34% (determined from the data) and 3.05% (determined from the fit). Since the contribution of $D < 50$ nm particles is less than 50% and since the potential error is likely serious only for $D < 30$ nm the instrument performance should not skew the count mode diameter. We now report these statistics and discuss the additional uncertainty for the fine mode in the text.

**Revisions: Note that the average number and volume fraction of particles with $D < 50$ nm to smaller mode is 30.6% and 19%, respectively. For those sizes, instrument performance is degraded due to diffusional losses. However, since the contribution of $D < 50$ nm particles is less than 50% and since the potential error is likely serious only for $D < 30$ nm we do not expect that diffusional losses affect the fit-determined mode diameter.**

*R2 Comment #6: p.7481, l. 1-11. The discussion of fit performance is very confusing. It refers to Fig.3, but discusses "the medians of the differences between measured values" (number count or mean diameter? what is "the data distribution"?).*

Response: We reworded the paragraph.

**Revisions: Example fits to the histograms are superimposed in Fig. 3. To test the efficacy of the fits to represent the data, the fit and data integrated moments were compared. For each distribution the relative difference between integrated number concentration from the data and the fit were 1.4±5%, where 1.4% denotes the average error and ±5% the fit-to-fit variability of the error. Similarly, the statistics for the integrated volume are 1.6%±5.3%. The variability in the data greatly exceeds any artificial error introduced by the two-mode parameterization, indicating that the two-mode parameterization is appropriate to model the size distribution**

*R2 Comment #7: p 7484 A discussion of the effect of particle state (solid vs. liquid) on evaporation rate is out of place in this paper for two reasons: (1) as discussed above, the instrument cannot provide a reliable measure of semi-volatile material, (2) the physical state of aerosol will not, most probably, affect the instrument performance, because under cooling the supersaturated material will condense mostly on the walls of the instrument, while under re-heating the particles should melt to the original liquid state.*

Response: With respect to point (1) please see our earlier response. With respect to point (2), i.e. “the physical state of aerosol will not, most probably, affect the instrument performance”, we do not agree with referee. The phase state before and after re-heating is a priori unknown. We agree with the referee that we expect that the supersaturated material will condense mostly on the walls. However, at the exit after re-heating the RH is lowered 10%. If the aerosol is crystallized or glassy it would affect the equilibration of semi-volatile fraction. We do not know if the organic phase is glassy. However, the measurements by Renbaum-Wolff et al., 2013 and others (see their Figure 2), clearly demonstrate that glassy states may exist and thus it is an uncertainty that is real and needs to be acknowledged.

**Revisions: (1) We clearly state now that the preconditioning inlet only tests whether material is lost during drying**

**(2) We maintain the discussion regarding point 2 since it is unclear that they assume a liquid state after drying.**

*R2 Comment #8: p.7485, l. 21-22 and Table 2. I find it surprising that the aerosol surface shrinks when it is humidified. Is it an artifact of fitting lognormal distributions?*

Response: The total aerosol surface (sum of the two modes) does not shrink upon humidification. The total dry surface area is 149.4 μm$^2$ cm$^{-3}$ for the dry state, 184 μm$^2$ cm$^{-3}$ for the unperturbed state, and 181 μm$^2$ cm$^{-3}$ for the dry-humidified state. The fine mode contribution to the surface is ~36% (or 54 μm$^2$ cm$^{-3}$). As discussed in the original manuscript, the smaller mode was not often well-defined and the uncertainty regarding resolving the smaller mode is also discussed. Figure 5 shows that there is significant overlap between the two modes. The very small shrinkage in the fine mode 54.4 μm$^2$ cm$^{-3}$ vs. 54.0 μm$^2$ cm$^{-3}$ is one of 0.07%. Possible reasons are noise in the measurement and that some fraction of the particles is picked up in mode #1 for the "dry" fit and mode #2 for the humidified fit. We added discussion regarding this possibility in the manuscript.

Please also see our response to R2 Issue #2 regarding the use of log-normal distributions.

**Revisions: Surface area distributions are higher for the unperturbed and dry-humidified states than for the dry state due to the additional water uptake. For the smaller diameter mode, surface areas average at 54.0 μm$^2$ cm$^{-3}$ for both the unperturbed and dry-humidified states, and 54.4 for the dry state, while for the larger mode, the averages are 130, 127, and 95 μm$^2$ cm$^{-3}$ for the unperturbed, dry-humidified, and dry states respectively. This indicates that water uptake increases the aerosol surface area by 33.7% for the large diameter mode, while the effect for the small diameter mode is not observed, suggesting that the smaller mode is less hygroscopic. (Note that the surface area of the small mode nominally shrinks by 0.07% upon humidification. Possible reasons are noise in the measurement and that some fraction of the particles is picked up in mode #1 for the "dry" fit and mode #2 for the humidified fit.). Similarly, …**

*R2 Comment #9: p.7486, l. 27-28. This sentence is a non sequitur. Water volume is an extensive parameter, which is proportional to aerosol dry volume. If aerosol dry volume does not correlate with RH, the correlation between water content and RH will be disturbed.*

Response: The section the referee is referring to is "Water mass concentrations leveled off after the morning peak, and despite the *RH* increase after 4 p.m. LT, water mass concentrations did not experience a noticeable increase in response during that time period. The partial decorrelation of RH and water volume suggests that aerosol hygroscopicity, and thus composition, evolved during the day."

The referee correctly points out (the *not* in the original comment is a typo) that if aerosol dry volume correlates with RH the correlation with water content and RH will be obfuscated. This is elaborated extensively in the Discussion section where we report the relative sensitivity of water volume to dry volume, RH, and $\kappa_{vol}$. We do also show later in the paper that dry volume does not have a diel cycle and thus appears not to correlate with RH (Fig. 11) so we believe that the suggestion is correct. We reworded the paragraph by removing the statement to composition and adding the possible relationship to aerosol dry volume.

**Revisions: Water mass concentrations leveled off after the morning peak, and despite the *RH* increase after 4 p.m. LT, water mass concentrations did not experience a noticeable increase in response during that time period. The partial decorrelation of RH and water volume suggests that either aerosol dry volume or aerosol hygroscopicity evolved during the day**

*R2 Comment #10: p.7487 and Figure 7. Which of the calculated volume growth factors (based on the volume or size) is shown?*

Response: Figure 7 shows $gf_{vol}$ as defined in the text. We now clarify this in the caption.

**Revisions: Fig 7. Diel profile of volumetric growth factor, $gf_{vol}$, binned into hourly intervals. The central lines …**

*R2 Comment #11: Since κ changes with RH, how valid is the inference that if kappa changes during the day then it necessarily means that chemical composition is changing too?*

Response: Please see our response to R2 Issue #6 and #7.

**Revisions: Please see our revisions in response to R2 Issue #6 and #7.**

*R2 Comment #12: p.7489, line 27. This could be also due to the larger mode being more processed, i.e., more oxidized, not necessarily via aqueous pathways.*

Response: We added this possibility

**Revisions: The higher *κ* values for the larger mode suggest the presence of more hygroscopic solutes such as more oxidized or hydrolyzed organic species, sulfates or nitrates.**

*R2 Comment #12: p.7491, line 2. Remove "that"*

Response: Deleted the superfluous that from “that that”.

**Revisions: “Since dew points are relatively constant during the day at the site location (see Fig. 4), we believe that the diel ...”**

*R2 Comment #13: p.7492, line 7-9. There is nothing in this manuscript that can support this statement. The residence time used in the instrument and the aerosol concentrations during the SOAS are such that one cannot make any conclusions about kinetics or reversibility of partitioning based on the measured data.*

Response: We deleted the sentence.

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