

Determining the link between hygroscopicity and composition for semi-volatile aerosol species

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Abstract. Internally and externally mixed aerosols present significant challenges in assessing the hygroscopicity of each aerosol component. This study presents a new sampling technique which uses differences in volatility to separate mixtures and directly examine their respective composition and hygroscopic contribution. A shared thermodenuder and unheated bypass line are continuously cycled between an aerosol mass spectrometer and a volatility and hygroscopicity tandem differential mobility analyser, allowing real-time comparative analysis of heated and unheated aerosol properties. Measurements have been taken of both chamber-generated secondary organic aerosol and coastal marine aerosol at Cape Grim, Australia, to investigate system performance under diverse conditions. Despite rapidly changing aerosol properties and the need to restrict analysis to a narrow size-range, the former experiment separated the hygroscopic influences of ammonium sulfate and two distinct organic components with similar oxygen to carbon ratios but different volatilities. Analysis of the marine aerosol revealed an external mixture of non-sea salt sulfates and sea spray aerosol, both of which likely shared similar volatile fractions composed of sulfuric acid and a non-hygroscopic organic component.

1 Introduction

20 Atmospheric aerosols have important roles in air quality and the climate. These roles are strongly affected by their hygroscopicity, which represents the capacity of aerosol to adsorb water vapour from the surrounding air. Amongst other effects, this water uptake promotes aqueous chemistry and can lead to the formation of cloud droplets (Seinfeld and Pandis, 2016).

Organic aerosol (OA) compounds make a large contribution to global aerosol mass (Jimenez et al., 2009), and they include a huge range of compounds with varying chemical and hygroscopic properties. ~~Furthermore, many are volatile. Since many are semi-volatile, their relative partitioning between the particle and gas phase can be sensitive to concentration changes and local atmospheric conditions transitioning between the particle and gas phase in response to changes in their gas phase concentration and local atmospheric conditions~~ (Seinfeld and Pankow, 2003; Donahue et al., 2012). ~~Furthermore, as their partitioning changes, they can become exposed to different phase-dependent chemical reactions. These volatile compounds are often more reactive, subject to oxidative and oligomeric processes, and their~~ These dynamic changes dynamic nature complicates predictions of bulk aerosol properties.

Extensive lab-based and atmospheric studies of organic species have reported a wide range of organic hygroscopicities. For example, secondary organic aerosols (SOA) condensed from the oxidation products of α -pinene have demonstrated hygroscopic growth factors ranging from 1.01 to 1.4 (Prenni et al., 2007; Duplissy et al., 2008). This range is due to the mixture of oxidation products generated by varying concentrations of precursors, oxidisers, environmental conditions, aging processes and experiment duration.

Volatility-based methods can directly separate aerosol components and have been used to investigate their independent hygroscopic contributions. Most commonly, this is achieved by passing the aerosol sample through a heated thermodenuder (TD), causing a volatile component to desorb, and examining the resulting change in properties. Until recently, this

technique has been separately applied to either measurements of composition or hygroscopicity (Hong et al., 2014; Johnson et al., 2004; Sellegri et al., 2008; Villani et al., 2013; Huffman et al., 2008). Three recent studies have combined these measurements by splitting heated samples from a TD between an aerosol mass spectrometer (AMS) and a cloud condensation nuclei (CCN) counter (Cain and Pandis, 2017; Cerully et al., 2015; Hildebrandt Ruiz et al., 2015).

- 5 Cain and Pandis (2017) and Hildebrandt Ruiz et al. (2015) examined chamber-generated SOA from α -pinene and toluene respectively, while Cerully et al. (2015) performed atmospheric measurements of rural aerosol from the south-eastern United States. Across these three cases, a clear relationship between hygroscopicity and oxidation level (often measured as an oxygen to carbon ratio, O:C) could not be established. In addition, the least volatile organic compounds were shown to have the lowest hygroscopicity, which contrasts with many previous studies. Cain and Pandis (2017) found that low volatility compounds had typically high O:C ratios, while Hildebrandt Ruiz et al. (2015) observed conflicting trends. Cerully et al. (2015) did not report either trend for O:C ratio but found correlation between low volatility and high average carbon oxidation state (\overline{OS}_C), an alternate measure of oxidation level (Kroll et al., 2011). In short, each study highlighted the complexity of organic hygroscopicity and the importance of volatility-based methods in distinguishing their competing contributions.
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- 15 The above techniques for measuring bulk aerosol properties are convenient to implement, however generally they do not examine size-dependent variations in hygroscopicity or the presence of external mixing. Although water uptake is typically more strongly influenced by particle size than by composition (Dusek et al., 2006), the role of composition becomes highly significant near the critical diameter for cloud droplet activation and a large proportion of the aerosol number concentration is often centred there (Wex et al., 2010). The critical diameter is sensitive to changes in aerosol hygroscopicity, so the composition of aerosol at or near the critical diameter can significantly affect the number concentration of available CCN (Andreae and Rosenfeld, 2008; Mallet et al., 2017). Similarly, bulk analysis of externally mixed aerosol can be confounded by the competing hygroscopic influences of aerosol from different sources. Measurement techniques which separate these mixtures can assist with source apportionment and investigation of each aerosol type.
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- In this article, we describe a novel real-time sampling system which couples an AMS to a volatility and hygroscopicity tandem differential mobility analyser (VH-TDMA), and discuss how this combined approach provides valuable insight into the properties of the semi-volatile component.
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2 Methodology

2.1 Sampling system design

- The AMS provides real-time non-refractory chemical speciation and, while it is most commonly used to sample bulk (total) aerosol composition, it is also capable of size-dependent measurements derived from the particle time of flight (PTOF). A full explanation of its design is given by Drewnick et al. (2005). For this study, a compact Time of Flight AMS has been used which generates spectra with unit mass resolution and offers maximum sensitivity for aerosol with vacuum aerodynamic diameters (d_{va}) between 100 – 600 nm (Liu et al., 2007; Takegawa et al., 2009). Detection limits for each species are calculated as three times the standard deviation of their background concentration, observed when sampling particle-free air through a high-efficiency particle filter (DeCarlo et al., 2006). This accounts for the instrument's background signal from stray ions and electronic noise. Uncertainties are given as the larger value of either the detection limit or the species-dependent measurement accuracy of the AMS. These accuracy estimates encompass uncertainties in the ionisation efficiencies, particle collection efficiencies and the inlet flow rate and is commonly estimated as $\pm 37\%$ for organics, $\pm 35\%$ for SO_4 and Chl, and $\pm 33\%$ for NO_3 and NH_4 (Bahreini et al., 2008).
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- 40 The VH-TDMA measures aerosol volatility and hygroscopicity under sub-saturated conditions. The function of our instrument has been explained in other papers (Johnson et al., 2005; Fletcher et al., 2007). In short, aerosol of a pre-selected

narrow size range is heated in a compact TD with maximum temperature of 500 °C and residence time of 3 s. The sample then passes to two scanning mobility particle sizers (labelled: V-SMPS and H-SMPS, respectively), with a humidified stage preceding the H-SMPS. These measure the mobility diameter (d_m) change due to loss of volatile material and subsequent hygroscopic growth, respectively. Particle hygroscopicity is reported as a hygroscopic growth factor (HGF), representing the relative increase in particle diameter after humidification compared to the dry diameter.

To obtain simultaneous hygroscopic and compositional measurements, the two instruments (AMS and VH-TDMA) have been coupled together through a combined flow system, shown in Fig. 1. After passing through a shared inlet, the aerosol is dried to a relative humidity (RH) of approximately 30 % using a membrane dryer (Nafion MD-700) or a silica gel diffusion dryer. ~~If additional drying is required, a silica gel diffusion dryer is also added.~~ To assist electrical mobility-based measurements in the VH-TDMA, a well-defined charge distribution is applied to the sample with a Kr-85 neutraliser (TSI Model 3012A). The RH and temperature of this dried aerosol flow is measured with a humidity probe (Rotronic HC2-WIN-USB) which is recessed in a sealed T-junction to avoid disrupting the sample flow. Since air exchange in the recessed region is diffusion limited, the probe provides an estimate of mean inlet RH, rather than precise time-resolved measurements.

The flow is then evenly split between the TD and an unheated bypass line ~~(labelled: Line A and Line B, respectively)~~. A series of fast-acting solenoid valves are used to direct these two sampling flows so that one instrument measures heated aerosol while the other receives the unheated sample. Under normal sampling conditions, the flow paths are switched between the instruments every three minutes, allowing them both to perform a continual series of consecutive heated and unheated measurements. Changes in HGF, composition and particle diameter between these alternating samples can be attributed to the removal of the semi-volatile species. The switching process is automated using control software developed in LabView. This software also manages the VH-TDMA pre-selected aerosol diameter, TD temperature and humidifier settings. These can be progressively stepped through a range of set values to investigate size dependencies, volatility distributions or to reveal any deliquescence or efflorescence transitions between dry and aqueous particle phases.

The two instruments sample at different flowrates. To avoid flowrate-dependent variations in transmission efficiencies and temperature fluctuations in the TD, flowrates of 1 L min⁻¹ are maintained in both sampling lines. Since this is lower than the combined flowrate required for the V- and H-SMPS, mass flow controllers provide supplementary filtered air to these components and their measured particle concentrations are corrected for this dilution. Likewise, since the AMS requires only 0.1 L min⁻¹ sample flow, the additional 0.9 L min⁻¹ is maintained by a mass flow controller and vacuum supply connected near the AMS inlet. With the exception of a few short flexible connections using conductive silicon, stainless steel tubing has been used throughout the sampling system, to avoid siloxane-based contamination of the hygroscopic and compositional measurements (Timko et al., 2009).

2.2 Thermal volatility measurements

Desorption rates within a TD are kinetically limited, particularly at high concentrations, and aerosol may not reach thermodynamic equilibrium within the TD (Riipinen et al., 2010). This can lead to under-representations of particle volatility (An et al., 2007) and requires considerable analysis to determine effective saturation concentrations. Future studies may extend this approach to quantify the volatility of each desorbed component; however, in this study, the TD has been operated at a single temperature (120 °C) and used simply for component separation. In line with this, the fraction desorbed within the TD has been referred to as the semi-volatile component, while the remainder has been termed the less-volatile component. This scheme implicitly assumes complete separation of the two components. The TD used in this study had a short residence time and no cooling stage, therefore it is possible that some residual proportion of the semi-volatile component have remained (or recondensed) in the particle phase. As a further complication, several studies have suggested that heating the aerosol may promote chemical change, leading to either formation (Huffman et al., 2009; Denkenberger et al., 2007) or decomposition of oligomers (Hall and Johnston, 2012). So any change in aerosol properties after heating may be due to

removal of a semi-volatile component, heat-dependent chemical change of the less volatile component, or both factors. This is an inherent limitation of most thermal sampling processes, including the AMS, and requires consideration when examining the influence of desorbed species.

2.2.3 Size-resolved composition

- 5 The AMS is commonly used to assess the bulk composition of non-refractory aerosol smaller than 1 μm . However, when sampling aerosol with size-dependent composition, this bulk analysis becomes dominated by aerosol with larger diameter and mass. This study primarily focused on ~~In this study, all measurements were performed on~~ aerosol with $d_m = 100\text{ nm}$, as this is both sufficiently small for composition to have a significant influence on CCN-forming potential and large enough to be within the peak sensitivity range of the AMS. ~~Therefore, for samples with strongly size-dependent composition, PTOF AMS measurements were integrated over a range of d_{va} which best represented aerosol at the preselected d_m used by the VH-TDMA. If the aerosol is strongly size-dependent, the focus on ultrafine aerosol inhibits meaningful conclusions from bulk compositional analysis. In that case, more representative analysis can be obtained using PTOF size resolved measurements, given with respect to d_{va} . This range was affected by particle density (ρ_p) and the Jayne shape factor (S), as given by the following calculation (DeCarlo et al., 2004): The conversion to d_{va} from d_m , using particle density (ρ_p), unit density (ρ_0) and the Jayne shape factor (S), can be calculated as follows (DeCarlo et al., 2004):~~

$$d_{va} = \frac{\rho_p}{\rho_0} S \times d_m \quad (1)$$

- ~~where ρ_0 is the unit density. Since ρ_p and S are composition-dependent, PTOF mass concentrations are integrated over a d_{va} range which best represents aerosol at the preselected d_m used by the VH-TDMA. For heated measurements, this PTOF d_{va} range is was shifted downwards in proportion to the d_m reduction observed with the VH-TDMA. AMS particle transmission efficiency decreases for diameters below $d_{va} = 100\text{ nm}$, reaching approximately 0 % transmission at 40 nm. Since the chamber-based measurements, discussed in Section 3.1, required Where PTOF data are required from this reduced sensitivity diameter range, a linear correction factor is was applied to account for transmission losses (Knote et al., 2011).~~

- While this use of PTOF data provides composition that is more directly relevant to the VH-TDMA measurements, it encompasses a reduced fraction of the overall aerosol mass concentration and does not benefit from as much signal averaging as is available for bulk analysis. This is particularly exacerbated when high time resolution is required, or during periods of low mass loading, and can result in a highly variable timeseries. In this study, we present two scenarios in which these challenges have been addressed by using nonparametric regression to smooth the dataset (Section 3.1) or by significantly reducing the time resolution of the analysis (Section 3.2).

2.4.3 Hygroscopic analysis

- 30 The hygroscopicity of small particles is reduced by the Kelvin effect, which causes water activity (a_w) at the droplet/air interface to increase with particle curvature. To account for this, the measured HGFs can be re-expressed in terms of the hygroscopicity parameter (κ), using κ -Köhler theory (Petters and Kreidenweis, 2007):

$$\frac{RH/100}{\exp\left(\frac{4\sigma M_w}{RT\rho_w D_d HGF}\right)} = \frac{HGF^3 - 1}{HGF^3 - (1 - \kappa)} \quad (2)$$

- where RH is the relative humidity set in the H-SMPS, σ is the droplet surface tension (assumed to be equivalent to pure water, $\sigma_w = 0.072\text{ J m}^{-2}$), M_w is the molecular weight of water, R is the universal gas constant, T is the temperature, ρ_w is the density of water and D_d is the dry particle diameter. The κ values can then be reverted to Kelvin-corrected HGFs (HGF_{corr}) by setting a_w equal to RH/100:

$$\frac{1}{a_w} = 1 + \frac{\kappa}{HGF_{corr}^3} \quad (3)$$

After excluding the effect of droplet curvature, the compositional influence on hygroscopicity can be investigated in detail. The hygroscopicity of internally mixed aerosol is commonly estimated using the following volume-weighted model (Stokes and Robinson, 1966):

$$HGF_{total}^3 = \sum_i \varepsilon_i HGF_i^3, \quad (4)$$

where ε_i and HGF_i are the volume fraction and independent HGF contribution of each component. If the components have substantially different volatilities, these parameters can be directly determined from VH-TDMA measurements. Otherwise assumed HGF contributions are used and ε_i is derived from the corresponding mass concentrations (m_i) and densities (ρ_i) of each component:

$$\varepsilon_i = \frac{m_i/\rho_i}{\sum_i m_i/\rho_i} \quad (5)$$

2.54 Aerosol transmission efficiencies

The two sampling lines offer different transmission efficiencies due to variations in tubing geometry, an additional solenoid valve on the ~~TD line~~Line A, and losses associated with the TD itself. Diffusional losses in the TD have been reduced by omitting the cooling section. When sampling at high aerosol loading, this may cause recondensation of volatile species onto the aerosol as it cools at the outlet, however negligible recondensation is expected for most atmospheric samples (Saleh et al., 2011). The remaining differences in transmission efficiency have been quantified by examining size- and temperature-dependent changes in aerosol concentration between the two flow paths.

Ammonium sulfate (AS) aerosol was generated with a nebuliser (Mesa Labs, 6-jet Collison). The aerosol was dried, neutralised and sampled at three preselected sizes: $d_m = 50, 150$ and 300 nm. The humidifier and H-SMPS were replaced with a condensation particle counter (CPC; TSI Model 3772) and a suitable bypass flow to maintain normal sampling flowrates throughout the system. From each sampling line, measurements were made with the TD at room temperature, to examine differences in tubing and solenoid valves. The TD temperature was then progressively increased in 5°C increments up to the volatilisation point of AS (180°C at 50 nm in this system), to quantify thermophoretic losses.

Figure 2 displays the relative transmission efficiency of ~~the TD line~~Line A compared to ~~the unheated line~~Line B. For diameters of 150 nm and above, path-dependent losses of less than 5% were observed at room temperature. This increased to over 12% at 50 nm. In addition, transmission efficiency decreased linearly with increasing temperature, for all sizes. Based on these results, a constant correction factor has been applied to all size-resolved AMS mass concentrations in this study, assuming a mean 85% relative transmission efficiency for aerosol of $d_m \leq 100$ nm at 120°C . This reduces bias between the two sampling lines and isolates the compositional changes caused by removal of volatile species.

2.65 Smog chamber sampling

A system test was conducted under controlled conditions to examine correlation between the two instruments and ensure that meaningful conclusions could be drawn. Measurements were performed using AS-seeded secondary organic aerosol (SOA), generated in a temperature-controlled, 8 m^3 Teflon[®] smog chamber. To minimise wall losses, this chamber has not been fitted with any mixing fans. During all chamber preparations, purified air was generated with a zero air generator (Aadco, Model 737-13). Type 2 laboratory-grade deionised water was used in all solutions and in humidifying the chamber. The chamber was cleaned by first flushing it with a 1 ppm concentration of O_3 in purified air until particle number concentrations fell below 100 cm^{-3} . The UV lights were turned on for 10 minutes to promote particle formation, and the chamber was again flushed with ozone-free purified air until particle numbers decreased below 100 cm^{-3} . The chamber was then prepared by successively passing water vapour, gaseous nitrous acid (HONO), N-butanol and α -pinene into the chamber

using a 15 L min^{-1} carrier flow of purified air. Water vapour was flushed into the chamber from a heated glass flask of deionised water until a relative humidity of 50 % was achieved. The HONO was generated by adding a 0.15 M aqueous solution of NaNO_2 (Sigma-Aldrich) to 1.1 M sulfuric acid (Thermo Fisher Scientific) and was introduced over a 20 minute period. $1 \mu\text{L}$ of N-butanol (D9, 98 %, Sigma-Aldrich) and α -pinene (Sigma-Aldrich) were each vaporised in separate heated glass bulbs. The former acted as a tracer, allowing OH concentrations to be monitored with a Chemical Ionisation Time-of-Flight Mass Spectrometer (Barnett et al., 2012). A polydisperse distribution of AS seed particles were generated by nebulising an 0.07 M aqueous AS solution, using laboratory compressed air filtered through a high-efficiency particulate air filter. These were injected into the chamber until particle number concentrations reached 10^4 cm^{-3} with a geometric mean diameter of 94 nm. The chamber was then irradiated by twenty 160 W UV lamps and sampling was conducted over a four-hour period.

VH-TDMA measurements were performed on 100 nm aerosol with a 6-minute time resolution (3 minutes per sampling path). The TD was set to 120°C , to ~~target-desorb~~ organic compounds with higher volatility than AS. ~~A nafion dryer was used to maintain the~~ The inlet RH ~~was maintained~~ at $32.6 \pm 0.3 \%$ throughout the experiment and ~~the~~ H-SMPS ~~was humidified~~ ~~humidifier was set to~~ $90\text{--}88\% \text{RH}$. ~~Initial gas-phase concentrations within the chamber were 35 ppb α -pinene, 0.042 ppm NO_x and approximately $1.5 \times 10^7 \text{ molecules cm}^{-3}$ of OH, at a relative humidity of 56 %. However, due to time constraints, UV irradiation and sampling commenced immediately after aerosol injection was completed, so initially the chamber may not have been uniformly mixed. Figure 3 gives an example of the direct measurements obtained from both instruments, from the first 2.5 hours of alternating heated and unheated measurements.~~

2.76 Remote coastal measurements

To investigate the suitability of the combined system for atmospheric sampling, it was deployed to the Cape Grim Baseline Air Pollution Station for a two-week measurement campaign in March 2015. This remote site on the northwest coast of Tasmania, Australia, frequently receives strong westerly winds carrying marine aerosol with negligible terrestrial or anthropogenic influences. From 22:00 on 2nd March, these baseline conditions were observed for an 8-hour period, with mean particle number concentrations of $400 \pm 60 \text{ cm}^{-3}$ for aerosol diameters above 10 nm. This period was accompanied by significantly increased sulfate-related mass concentration and a pronounced bimodal particle number size distribution (Fig. 34), consistent with cloud-processed marine aerosol (Hoppel et al., 1986). The final two hours of baseline sampling was accompanied by a pronounced decrease in sulfate- and ammonium-related signal and a decrease in particle number concentration, suggesting a change in the air mass and associated aerosol properties. For this reason, analysis has been focused on the initial 6 hours which exhibited the most consistent properties.

To account for the low aerosol concentrations, ~~aerosol properties were averaged over this 6 hour period and the resulting mean values were used for all further analysis~~ ~~all measurements have been averaged over this period, rather than examining trends over a higher time resolution~~. Likewise, uncertainties have been determined from standard deviations in the means. The sampling inlet RH was consistently dried ~~with a diffusion dryer~~ to below 30 % ~~and the humidifier was maintained at 90 %RH. and sampling~~ Sampling was conducted using the same pre-selected diameter ~~and~~ TD temperature ~~and humidifier RH~~ as in the chamber-based experiment (i.e. 100 nm , 120°C , ~~90 %~~ respectively).

3 Results and validation

3.1 Chamber-generated aerosol

~~A characteristic example of the alternating heated and unheated measurements obtained from both instruments is given in Fig. 4, showing the impact of an increasing SOA component on bulk aerosol composition, volatility and water uptake during the smog chamber experiment. Measurements commenced immediately after injecting the AS seeds and there was no active~~

mixing mechanism within the chamber. In light of this, the initial rapid decrease in SO_4 concentrations suggest that the chamber was not initially well mixed during the first 40 minutes of sampling. After this point, the total mass loading, and mode diameter of the number size distributions, progressively increased in response to SOA formation (Figs S1 and S2).

Compositional measurements of the seeded SOA indicated a strong size dependence, with the AS mass distributed around a mean d_{va} of approximately 500 nm, while the SOA component progressively dominated at 100-200 nm (Fig. 5a). Since the size-distribution of each species did not change substantially over time, further compositional analysis was restricted to diameters in the range: $130 < d_{va} < 180$ nm. These diameter limits were selected to reflect varying proportions of internally mixed SOA and AS with densities of 1.3 and 1.78 g cm^{-3} , respectively (Chen and Hopke, 2009).

While these size limits ensured that the compositional analysis was directly relevant to the d_m used by the VH-TDMA, it reduced the sensitivity of the AMS measurements in two ways. Firstly, this diameter range represented a comparatively low proportion of the total particle mass, decreasing the signal to noise ratio of the measurements. Secondly, by using only a subset of PTOF measurements rather than the bulk aerosol measurements, less signal averaging was applied to each sample, increasing the variability of the measurements. To account for this, the size-resolved composition was averaged to a 12 minute time resolution and the resulting time series has been provided in the supplement (Fig. S3). This resolution was sufficiently fast to observe the SOA fraction progressively growing to dominate the mass composition at 100 nm, while offering enough averaging time to ensure measurements were sufficiently stable to be useful for hygroscopic predictions.

At this time resolution, the estimated detection limits were 0.123, 0.012, 0.023, 0.245 and 0.023 $\mu\text{g m}^{-3}$ for organics, NO_3 , SO_4 , NH_4 and Chl respectively. While these values are elevated compared the sensitivity that can be achieved when measuring bulk aerosol, a large proportion of the PTOF measurements remained above these limits, with two notable exceptions. Chl concentrations were consistently negligible and since there was no source of this species, it has been disregarded in the subsequent analysis. In addition, the NH_4 background signal increased by an order of magnitude when averaged over the narrow PTOF range. NH_4 often exhibits higher variability than most other species. Also, some residual AS may have remained in the instrument during the filtered background measurements since these were performed shortly before the experiment commenced and the AMS had been sampling from the chamber during injection of the AS seeds. Ultimately the cause of this variable signal has not been established. In any case, NH_4 represented a significant fraction of the injected AS aerosol mass and therefore it was not feasible to exclude its contribution. Instead, the NH_4 mass concentrations were approximated with a linear fit to the NH_4 PTOF measurements.

Detection limits for each species were calculated as three times the standard deviation of their background concentration, observed when sampling through a high efficiency particle filter. Estimated detection limits were quite high due to the use of high time resolution samples, a narrow range of PTOF diameters, and the strongly time dependent nature of the sample. Likewise, the observed signal was quite unstable, especially for heated measurements, often falling below the detection limit. For this reason, data below the detection limit was not removed as it would have excluded a large proportion of the data.

As expected, the SO_4 and NH_4 signals correlated strongly and were combined to give the total mass concentration of AS throughout the experiment. Similarly, a strong correlation was observed between the organic and NO_3 signals indicating the secondary formation of organonitrates or nitric acid from NO_x -based reactions. To simplify analysis, these species were summed to give the mass concentration of OA. Likewise, the SO_4 and fitted NH_4 concentrations were combined to give size-resolved AS concentrations throughout the experiment. Since there was no source of chloride in this experiment, and this species was constantly below the detection limit, it has not been included in the analysis. In these cases, a locally weighted smoothing method (LOESS) can be used to discern qualitative trends within the PTOF data.

As shown in Fig. 5b, during the first 100 minutes of the experiment, a semi-volatile organic component rapidly formed, increasing particle volatility and reducing the HGF of the unheated aerosol from 1.5 to <1.1 (Fig. 43c). After this point, there was no significant change to HGFs and volatility gradually decreased. Figure 5b also shows that the heated aerosol composition revealed an increasing proportion of less volatile organic compounds which did not desorb at 120 °C. For

convenience, these two semi-volatile and less-volatile organic components are labelled as SVOA and LVOA, respectively. ~~This can be attributed to dark reactions that occurred during the preceding 30 minutes while AS seed particles were being generated, after the injection of α -pinene, as supported by a progressive decrease in α -pinene concentrations during this time.~~ The unit mass resolution parameterisation given by Canagaratna et al. (2015) was used to calculate elemental ratios of oxygen to carbon (O:C), averaged across all diameters with the assumption that these ratios would be size-invariant. The OA concentrations were most stable and well-resolved during the final 30 minutes of the experiment. Based on this period, both the LVOA and SVOA components exhibited similar O:C ratios of 0.43 ± 0.16 and 0.45 ± 0.16 , respectively. ~~It should be noted that there was a non-negligible concentration of organics at the beginning of the UV irradiation period.~~

To confirm the predictive power of this combined sampling approach, the measured HGFs of the heated sample were compared against the composition-based model defined in Eq. (4). Assumed densities of 1.3 g cm^{-3} (Duplissy et al., 2008) and 1.78 g cm^{-3} were used for α -pinene SOA and AS, respectively. AS calibration measurements indicated that the HGF of AS at ~~90-88~~ %RH was 1.58 ± 0.03 , after correcting for residual water in the particle phase during pre-selection. The hygroscopic contribution of the low-volatility SOA component was determined using the O:C parameterisation proposed by Massoli (2010), giving an HGF_{LVOA} of 1.1 ± 0.2 . This value agrees well with a range of α -pinene HGFs reported in other studies (Varutbangkul et al., 2006; Virkkula et al., 1999; Prenni et al., 2007; Cocker Iii et al., 2001). Applying these AS and LVOA parameters to the composition-based model produced HGFs which closely matched the direct VH-TDMA measurements of the heated sample, as seen in Fig. 6.

Having established agreement between the instruments, Eq (4) was adapted to determine the hygroscopic contribution of the SVOA using measurements of particle diameter (d) and HGF:

$$HGF_0^3 = \left(\frac{d_0^3 - d_{TD}^3}{d_0^3} \right) HGF_{SVOA}^3 + \left(\frac{d_{TD}}{d_0} \right)^3 HGF_{TD}^3, \quad (6)$$

where the subscripts 0 and TD refer to the unheated and heated samples, respectively. This use of direct VH-TDMA measurements avoided any dependence on an assumed SVOA density. The first 20 minutes of the experiment was excluded due to low SVOA concentrations which caused unreliable HGF estimates. The remaining data support a stable mean HGF_{SVOA} of 1.02 ± 0.02 (Fig. 6). This low value mirrors other studies of semi-volatile organics (Meyer et al., 2009; Raatikainen et al., 2010), and is within the range of α -pinene HGFs observed by Prenni et al. (2007) and Denjean et al. (2015).

In the preceding steps of this analysis, the HGF contributions and volume fractions for all three components (AS, SVOA and LVOA) were established. Using these parameters and the same additive model, the hygroscopicity of the unheated aerosol was calculated. The results closely agreed with the observed HGFs (Fig. 7), confirming that the derived parameters accurately describe the aerosol properties throughout the experiment.

3.2 Remote coastal measurements

During the initial 6 hours of sampling under baseline conditions at Cape Grim, mass concentrations were very low and there was little evidence of size-dependent composition. ~~Therefore, To to provide better statistics, bulk aerosol composition has been used in this analysis the composition has been averaged across the full size range of the AMS.~~ The non-refractory aerosol mass was dominated by sulfate (65.8 %), ammonium (12.9 %) and organic compounds (20.7 %) (Fig. 8), while the nitrate- and chloride-related signals were consistently below their respective detection limits. ~~49.5% of this non-refractory mass was desorbed at 120 °C, including the entire non-refractory organic fraction Comparison between the heated and unheated samples indicated that the organic fraction was entirely desorbed at 120 °C.~~ This organic volatility was reflected in the O:C ratio of 0.24, which is consistent with semi-volatile oxygenated OA observed in other AMS studies (Jimenez et al., 2009; Raatikainen et al., 2010). 42 % of the sulfates were desorbed, despite being well below the volatilisation temperature of ammonium sulfate. In contrast, the ammonium signal showed minimal volatility, indicating that a significant proportion

of the sulfate was in the form of sulfuric acid and ammonium bisulfate. This is further supported by an ammonium to sulfate molar ratio of 1.03 ± 0.04 in the unheated aerosol.

Humidification of the 100 nm pre-selected aerosol frequently produced a bimodal particle size distribution, indicating that the aerosol was externally mixed. The dominant proportion exhibited a mean HGF of 1.57 ± 0.01 , while a second aerosol type had a mean HGF of 1.90 ± 0.04 . These growth factors are characteristic for non-sea salt (nss) sulfate-dominated particles and sea spray aerosol (SSA), respectively (Sellegrì et al., 2008; Villani et al., 2013). In further support of this subdivision, the SSA aerosol comprised $7 \pm 2\%$ of the observed number concentration of 100 nm particles, which is consistent with the total proportion of SSA reported by Quinn et al. (2017) at similar latitudes. There was no apparent difference in volatility at 120 °C, with a universal $12 \pm 2\%$ reduction in particle volume; however, this increased their HGFs to 1.61 ± 0.02 and 2.01 ± 0.05 , respectively (Table 2). The difference between the volume and mass fractions which remained after heating imply the presence of a substantial volume of refractory material (such as SSA) which could not be efficiently detected by the AMS.

The hygroscopic contribution of the semi-volatile component was estimated from its mean composition using Eq. (4), assuming a simple mixture of sulfuric acid and OA. The corresponding parameters are listed in Table 1, where the OA HGF has been determined from an O:C – HGF parameterisation (Massoli et al., 2010). This compositional model gave a semi-volatile HGF of 1.13 ± 0.05 . Applying the same model to direct VH-TDMA measurements of the nss sulfate aerosol yielded, a semi-volatile HGF of 1.2 ± 0.3 , in agreement with the composition-based estimate.

Since both the SSA and nss sulfate aerosol shared similar volatilities, their semi-volatile components may have likewise shared similar composition and hygroscopic contributions. Based on the VH-TDMA measurements of heated SSA HGF and the above semi-volatile HGF, the model predicted an unheated SSA HGF of 1.94 ± 0.05 . This is in line with the observed value and strongly suggests that both aerosol types had accumulated similar semi-volatile sulfates and OA during their atmospheric lifetimes.

4 Conclusions

A new sampling system has been developed which pairs a VH-TDMA and an AMS to obtain simultaneous measurements of hygroscopicity, volatility and composition. By cycling both instruments between heated and unheated sampling lines, properties of the semi-volatile fraction can be directly measured in near real-time, over a range of pre-selected diameters, TD temperatures and humidities. Size- and temperature-dependent transmission efficiencies have been characterised for the two sampling lines and relative losses of up to 15 % are observed in the ~~heated-TD~~ line at 120 °C (50 nm, AS).

Two ~~diverse~~-measurement campaigns have been discussed which presented distinctly different and challenging sampling conditions. The capacity of both instruments to perform size-resolved measurements allowed size-dependencies to be identified and targeted in the analysis of the chamber-based campaign. However this requirement for size-dependent composition restricted analysis to a small subset of the total aerosol mass. In addition, the rapid SOA formation required a reasonably high time resolution to capture the progressive impact on composition and hygroscopicity. Although these constraints led to limited signal averaging and elevated detection limits, the independent composition-based HGF estimates demonstrated consistent agreement with direct VH-TDMA measurements. The O:C ratio of the LVOA offered a reasonable estimate of its hygroscopic contribution. However, direct VH-TDMA measurements indicated that the HGF contribution of the SVOA component was markedly lower, despite having a very similar O:C ratio to LVOA. This may further support the conclusion that these parameters are not well correlated, as reported by Hildebrandt Ruiz et al. (2015), and demonstrates the benefit of the complementary analysis offered by the combined sampling system.

In contrast to the chamber experiment, aerosol number and mass concentrations were very low during the marine atmospheric measurements, but by averaging across the full 6-hour period and using bulk compositional measurements, the

two instruments obtained meaningful measurements consistent with characteristic marine aerosol properties. The distribution of HGFs in the marine aerosol revealed an external mixture of nss sulfates and SSA. From these, an internally mixed semi-volatile fraction was separated and attributed to sulfuric acid and an OA component with a low degree of oxidation ($O:C = 0.24$). Finally, hygroscopic modelling supported the assumption that this semi-volatile component was common to both aerosol types.

presented in which the system demonstrated consistent agreement between the instruments and reliable composition-based predictions of hygroscopicity, despite distinctly different and challenging sampling conditions. represent highly cases presented significant challenges demonstrated consistent agreement between the instruments, despite, leading to reliable composition-based predictions of hygroscopicity. The chamber based measurements involved rapidly changing aerosol and compositional analysis of a narrow range of aerosol diameters, while particle concentrations remained very low throughout the marine campaign. As a result, low counting statistics introduced large uncertainties and inhibited more detailed compositional analysis. This may have influenced the poor agreement between hygroscopicity and $O:C$ ratio, observed for the SVOA component of α pinene SOA. Alternatively, it may reflect that these parameters are not well correlated, as reported by Hildebrandt Ruiz et al. (2015).

The capacity of both instruments to perform size resolved measurements allowed size dependencies to be identified and targeted in the analysis of the chamber based campaign. Furthermore, this combined system is well suited to analysing complex mixed aerosols. The distribution of HGFs in the marine aerosol revealed an external mixture of nss sulfates and SSA. From these, an internally mixed semi-volatile fraction was separated and attributed to sulfuric acid and an OA component with a low degree of oxidation ($O:C = 0.24$). Finally, hygroscopic modelling supported the assumption that this semi-volatile component was common to both aerosol types.

In summary, these findings demonstrate that the combined system is well suited to analysing complex mixed aerosols and directly linking the composition of volatility-separated components to their hygroscopic contribution. If suitable sampling parameters and analytical methods are carefully chosen, the approach is resilient to low concentrations, size-dependent compositions or rapidly evolving aerosol properties. the value of pairing both instruments through a shared TD to directly link the composition of volatility separated components to their hygroscopic contribution. It is hoped that future measurements using this method will help improve models of aerosol-cloud interactions, particularly in regions subject to high levels of volatile organic emissions or mixed aerosols from diverse sources.

5 Data availability

The underlying research data can be accessed upon request to the corresponding author (Zoran Ristovski; z.ristovski@qut.edu.au).

6 Author contribution

Joel Alroe operated the instrumentation, analysed and interpreted the data and prepared the manuscript. Luke Cravigan assisted with operation of the VH-TDMA, and contributed to data analysis and interpretation. Marc Mallet assisted with operation of the VH-TDMA and AMS, and contributed to data interpretation and writing. Zoran Ristovski contributed to campaign organization, data interpretation, writing and supervised the work of Joel Alroe. Branka Miljevic contributed to campaign organization, data interpretation, writing and supervised the work of Joel Alroe. Chiomeriwo Osuagwu assisted with operating the smog chamber and contributed to data analysis. Graham Johnson contributed to data interpretation, writing and supervised the work of Joel Alroe.

7 Acknowledgements

This work was funded by an Australian Government Research Training Program Scholarship and an ARC Discovery grant (DP150101649). The authors would like to acknowledge and thank the Cape Grim Baseline Air Pollution Station staff for providing on-site support and meteorological data, and Alastair Williams from the Australian Nuclear Science and Technology Organisation for associated radon-222 measurements.

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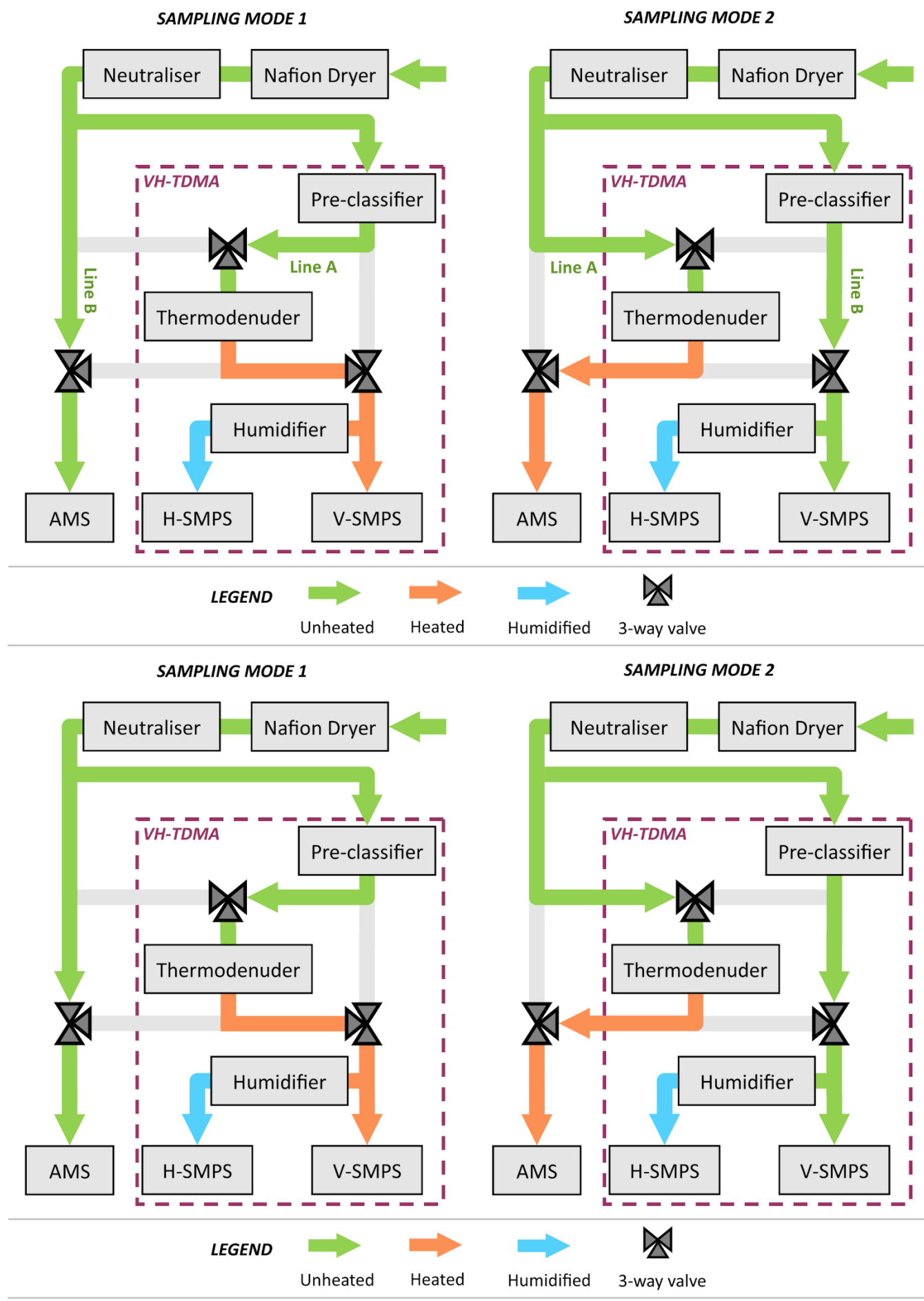


Figure 1: Schematics of the VH-TDMA / AMS sampling system, demonstrating the alternating flow paths used for consecutive samples.

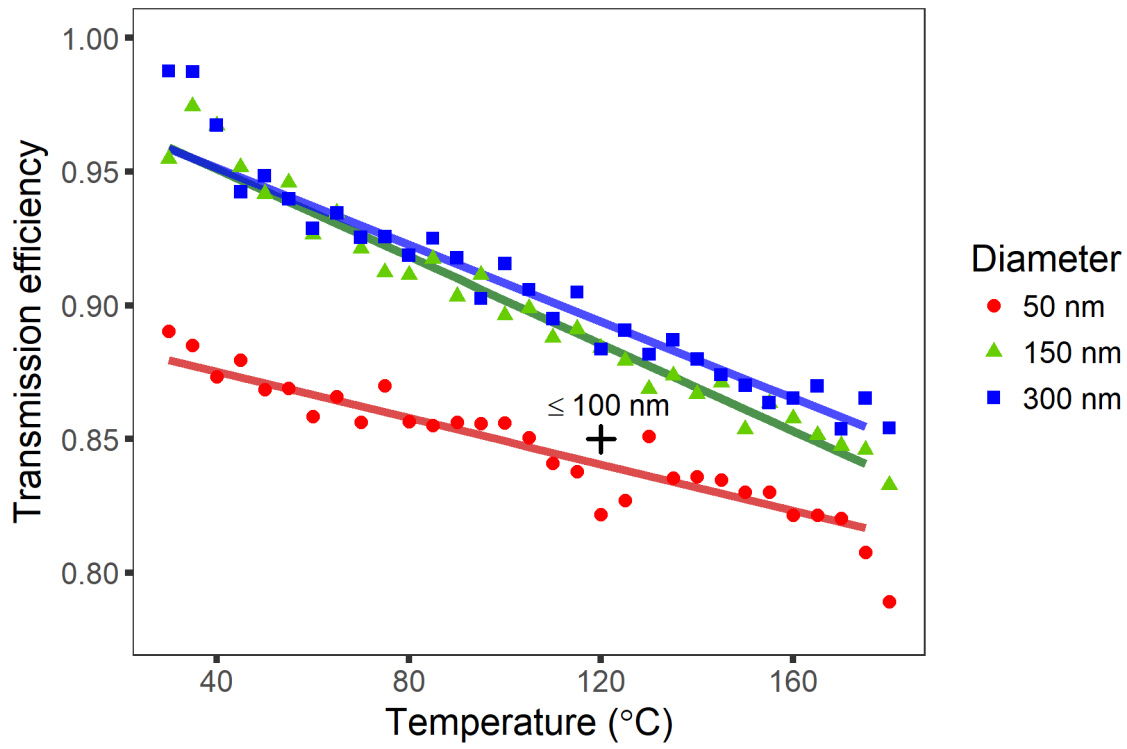


Figure 2: Size- and temperature-dependent aerosol transmission rates of the ~~heated-TD~~ sampling line compared to the unheated line, for AS aerosol. The value used in this study for aerosol ≤ 100 nm has been marked for comparison.

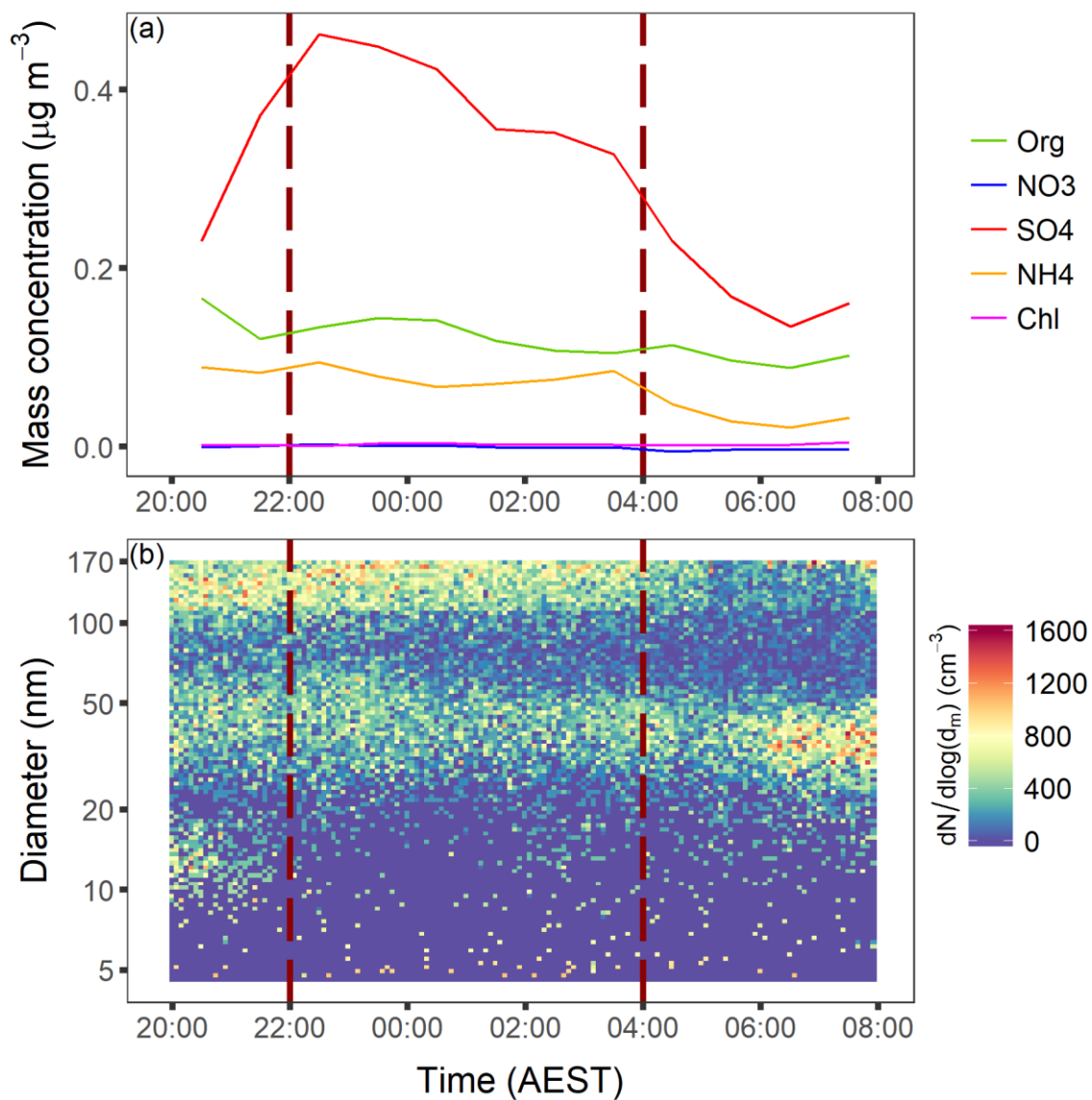
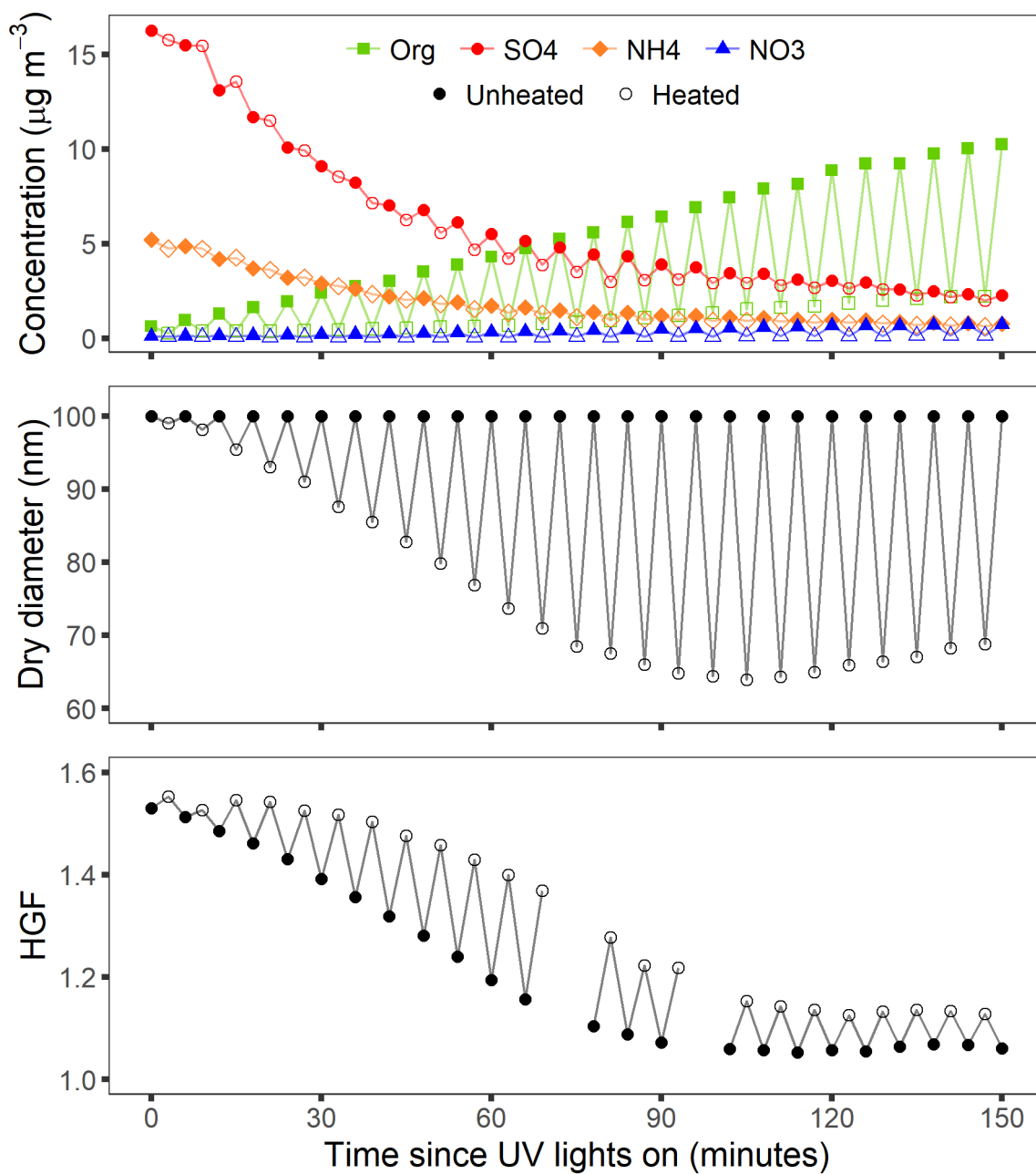


Figure 3: (a) Mass concentrations of major compositional species and (b) size distributions of particle number concentration observed at the Cape Grim site on 2-3 March 2015. Dashed lines delimit a 6-hour period of relatively stable baseline sampling conditions.



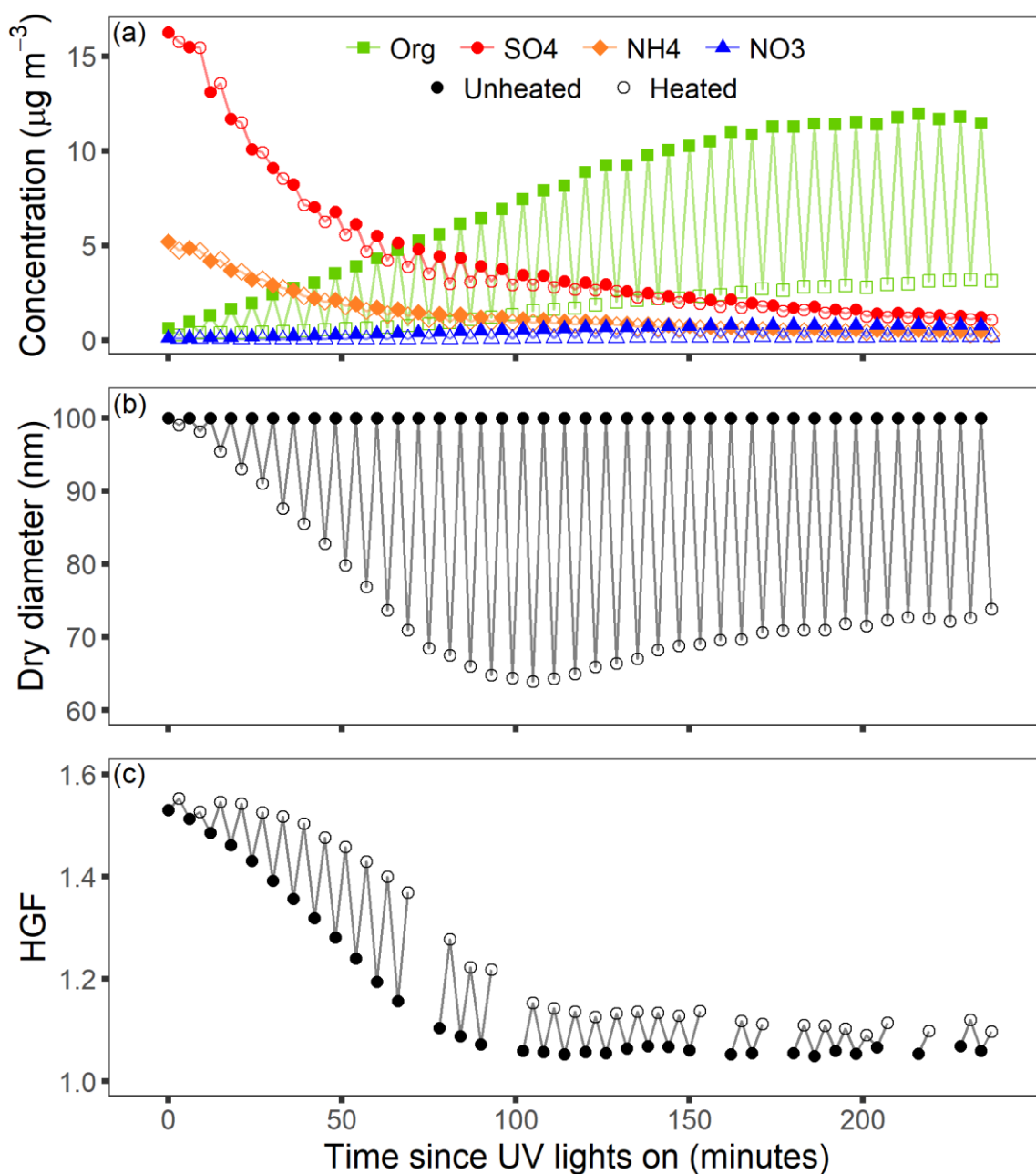


Figure 34: Alternating direct measurements of unheated and heated aerosol properties during four hours of α -pinene SOA formation on AS seed particles, demonstrating decreases in (a) bulk non-refractory mass concentration and (b) dry particle diameter, and (c) the corresponding increases in HGF after removal of a semi-volatile fraction at 120°C. ~~Consecutive measurements of unheated and heated aerosol properties during the first 2.5 hours of α -pinene SOA formation on AS seed particles.~~ Gaps in the HGF data are due to faulty H-SMPS measurements which have been discarded.

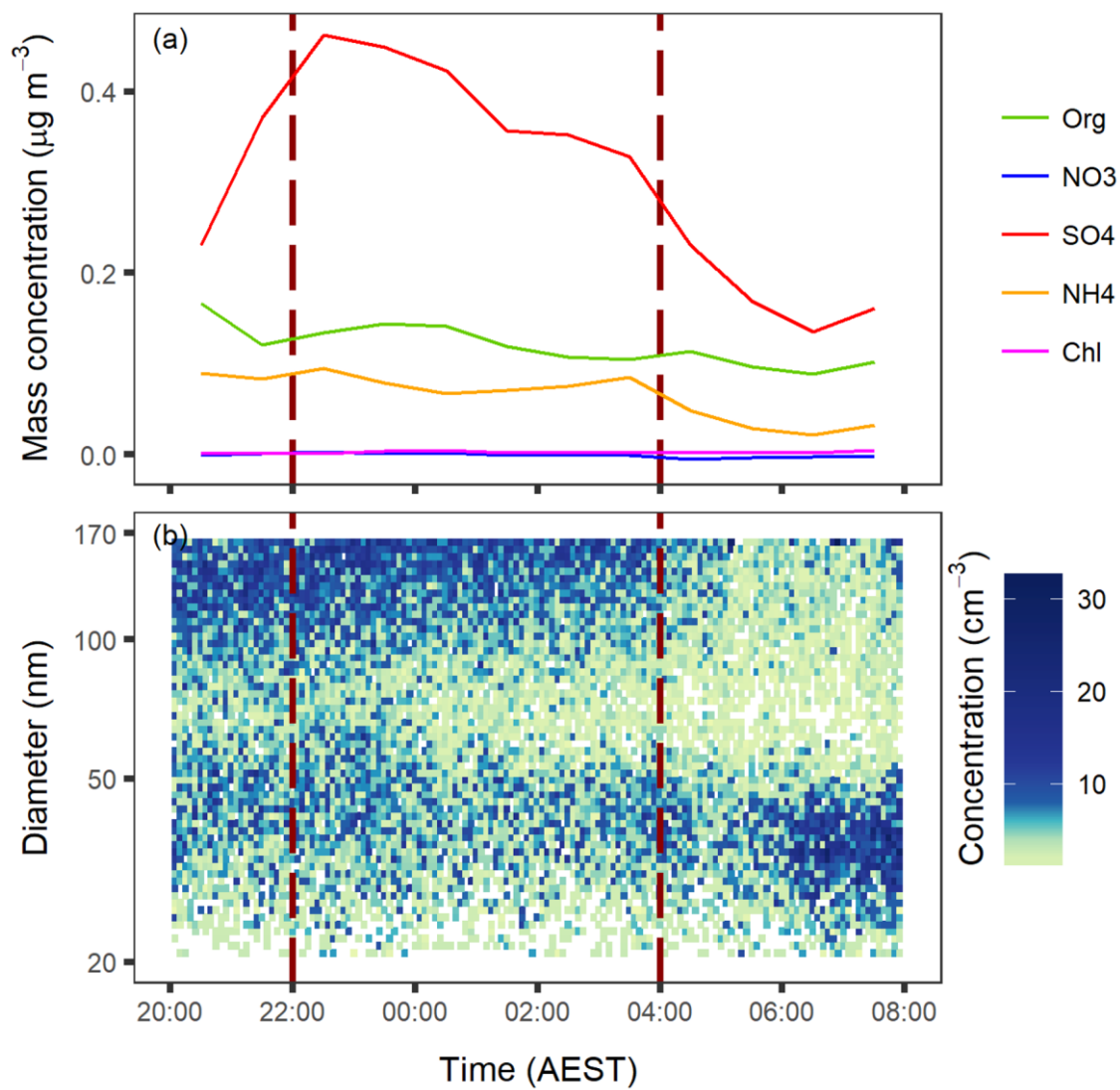
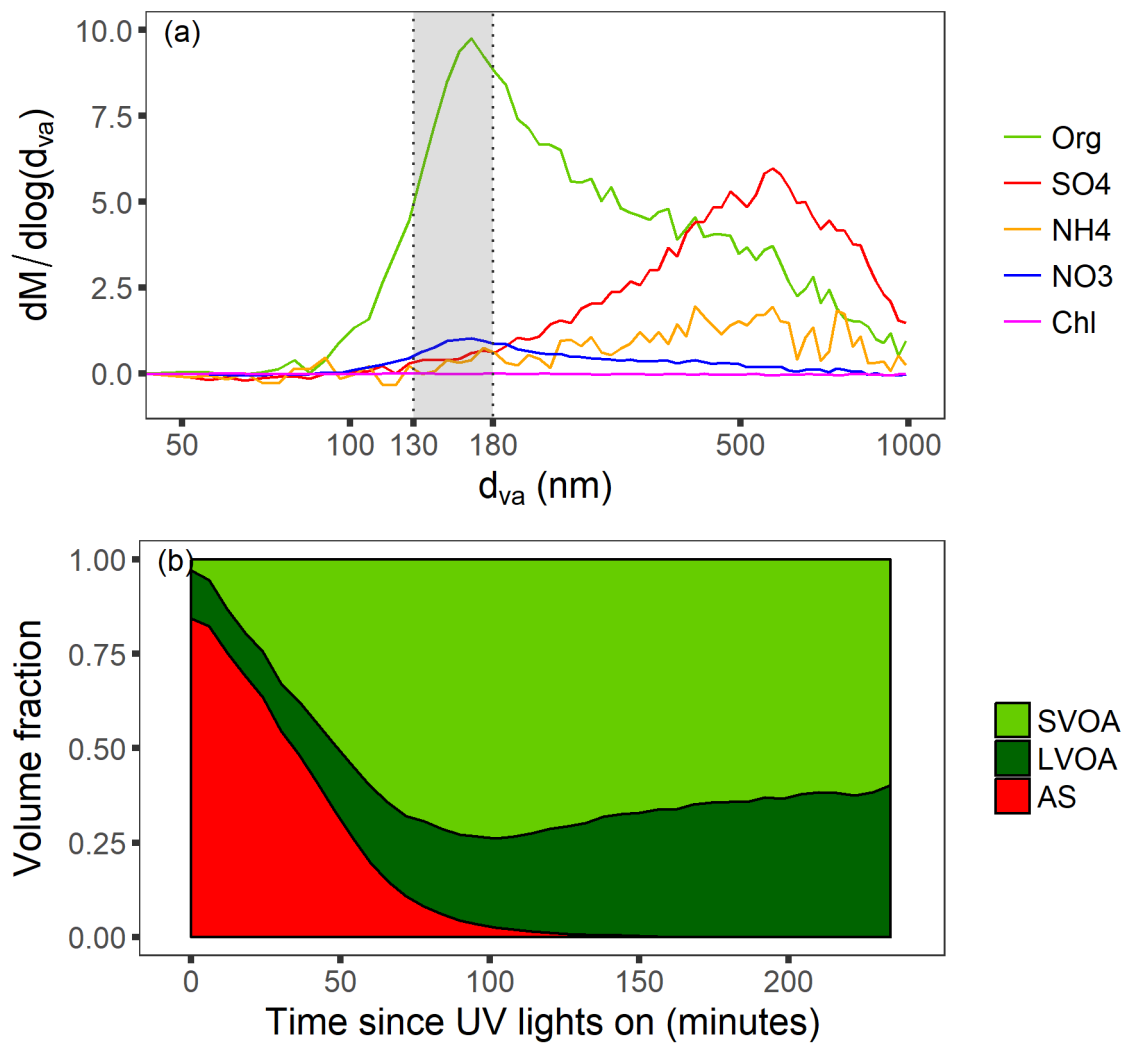


Figure 4: (a) Mass concentrations of major compositional species and (b) size distributions of particle number concentration observed at the Cape Grim site on 2-3 March 2015. Dashed lines delimit a 6-hour period of relatively stable baseline sampling conditions.



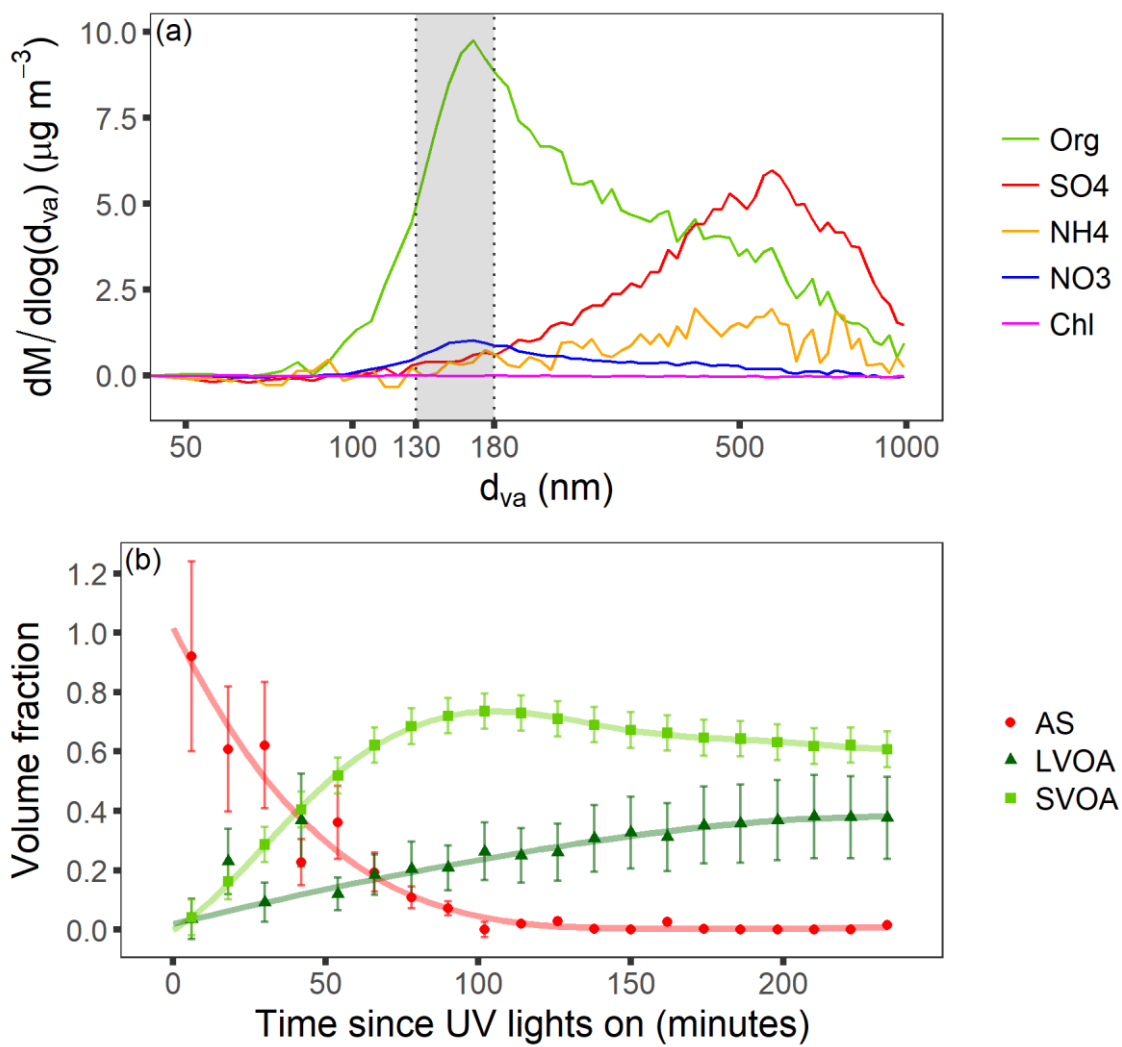


Figure 5: (a) Mean size distribution of the major compositional species measured by the AMS, observed over four hours of SOA condensation and ripening. The shaded region represents the approximate d_{va} range for particles with $d_m = 100$ nm. (b) Relative volume contributions of AS, LVOA and SVOA for aerosol in the selected d_{va} range. The curves are fitted splines to guide the eye.

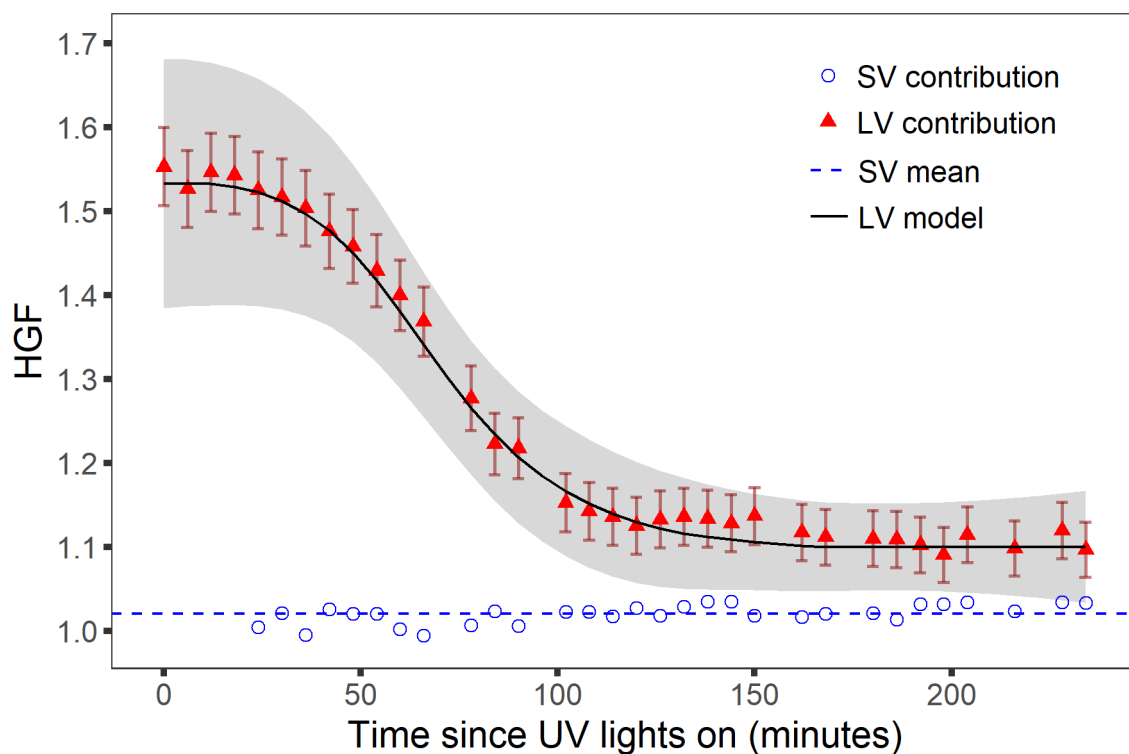
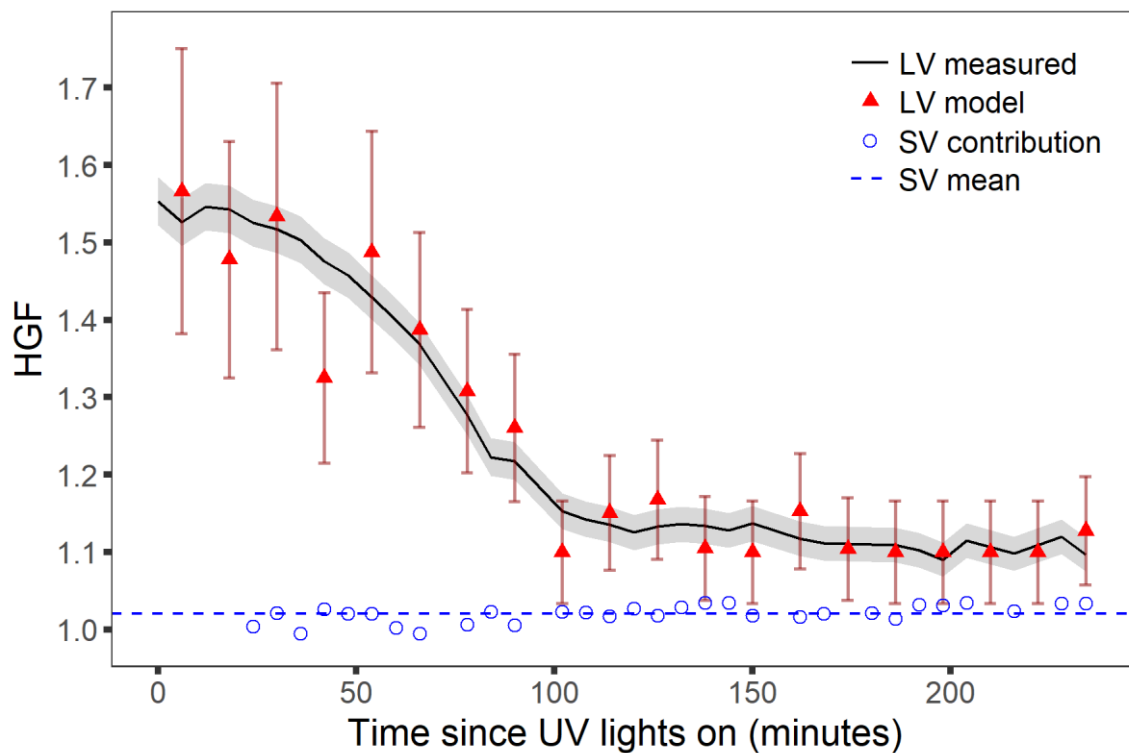


Figure 6: Comparison between measured (data points black line) and modelled (smooth curve triangles) HGFs for the lower volatility component during SOA formation. The shaded region shows Error bars represent $\pm 2\%$ uncertainty in H-SMPS measurements, while error bars the shaded region represent composition-dependent uncertainties gives a 99 % confidence interval for this model. The derived HGF of the semi-volatile component is shown for contrast.

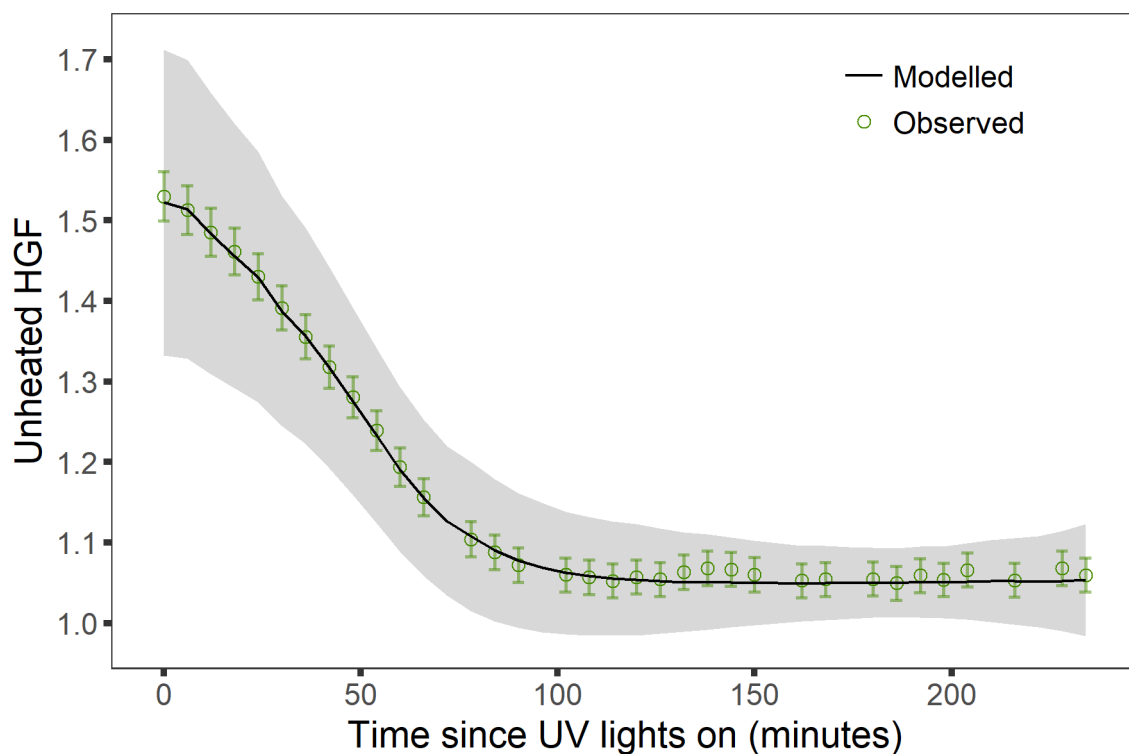
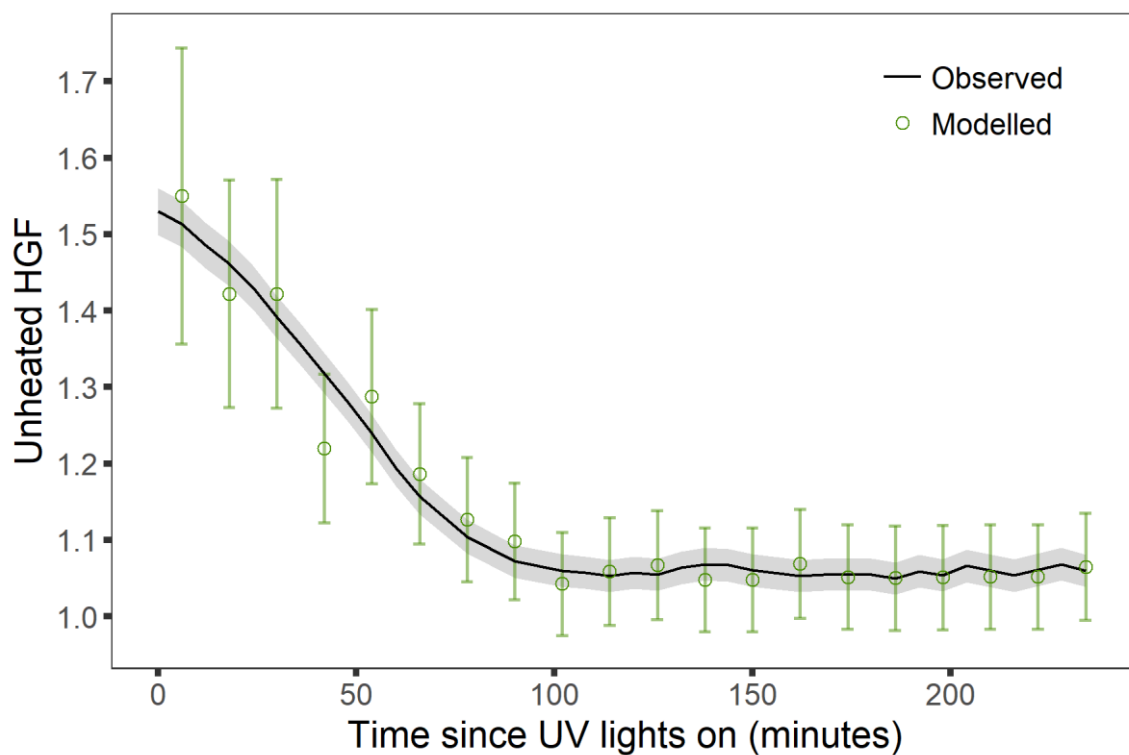


Figure 7: Observed and predicted hygroscopicity of unheated, internally mixed α -pinene SOA and AS aerosol during four hours of SOA formation. The shaded region shows $\pm 2\%$ uncertainty in H-SMPS measurements, while error bars represent composition-dependent uncertainties for this model. Error bars represent $\pm 2\%$ uncertainty in H-SMPS measurements, while the shaded region gives a 99 % confidence interval for this model.

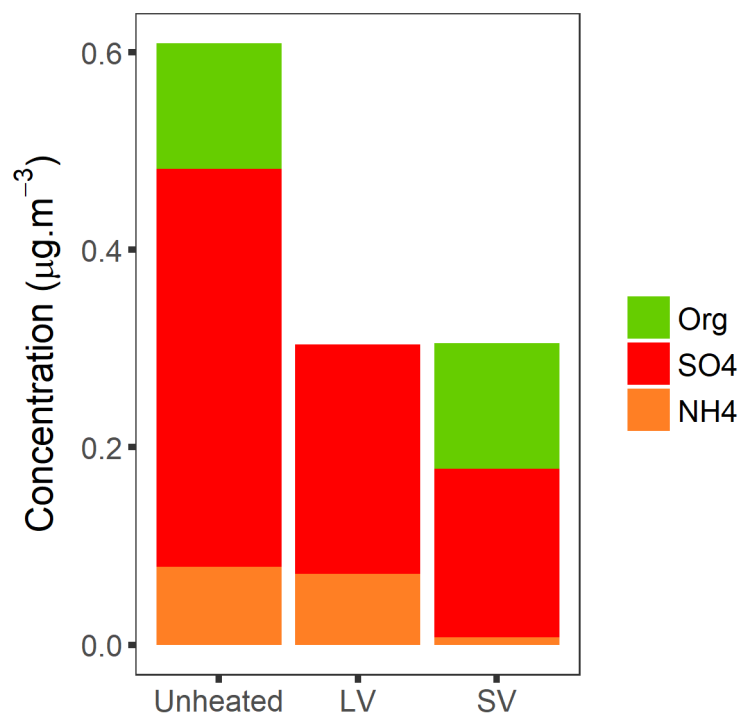


Figure 8: Contribution of sulfates, ammonium and non-refractory organic compounds to the total, semi-volatile and low-volatility fractions of marine aerosol at Cape Grim.

Table 1: Parameters used in the compositional model of marine semi-volatile hygroscopicity

Component	Density (g cm ⁻³)	HGF contribution
OA	1.2 ± 0.1^a	1.0 ± 0.1
Sulfuric acid	1.83 ± 0.01^b	1.95 ± 0.05^c

^a (Ault et al., 2013; Hersey et al., 2009)

^b (Washburn, 1926)

^c (Xiong et al., 1998)

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Table 2: Hygroscopicity of volatility-resolved fractions observed in externally mixed marine aerosol

Classification	Semi-volatile volume fraction	Semi-volatile HGF	Heated HGF	Total HGF	unheated
nss sulfate	0.12 ± 0.02	1.2 ± 0.3^a	1.61 ± 0.02	1.57 ± 0.01	
SSA	0.12 ± 0.02	1.2 ± 0.3^a	2.01 ± 0.05	1.90 ± 0.04	

^a Derived from VH-TDMA measurements of nss sulfate aerosol