Sources and composition of sub-200 nm sea spray aerosol inferred from volatility and hygroscopicity.

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Abstract
Recent modelling has highlighted the importance of pristine environments to the uncertainty in cloud condensation nuclei (CCN) concentrations. A key component to this uncertainty is the emission of sea spray aerosol (SSA) from the surface ocean. The composition and concentration of sub-200 nm SSA remains uncertain, however it provides a significant contribution to global CCN concentrations. The composition of sub-200 nm ambient SSA was measured at the Cape Grim baseline atmospheric station. In addition a purpose built artificial SSA production chamber was also used to measure the composition of laboratory generated SSA. Particle composition was inferred using a volatility hygroscopicity tandem differential mobility analyser (VH-TDMA). Laboratory SSA were produced using biogenically enriched samples from Herron Island, which is surrounded by the Great Barrier Reef, and phytoplankton rich waters from the Chatham Rise (New Zealand).

Observed organic enrichments varied between ambient SSA, which showed a small (less than 5%) organic component, and laboratory generated SSA, which displayed organic volume fractions of up to 47%. Simultaneous measurements using VH-TDMA and transmission electron microscopy (TEM) techniques of a sub-100 nm SSA event observed at Cape Grim displayed contradictory results. VH-TDMA measurements unequivocally show a dominant sea salt fraction via deliquescence and volatility measurements. TEM samples indicated no evidence of sea salt under visual analysis and X-ray spectroscopy. This highlights the possible biases in TEM techniques in the analysis of SSA composition, which are already complicated by spatial and seasonal variations.

An internally mixed non-volatile organic SSA component was observed for laboratory generated SSA from both coral and phytoplankton rich waters. This
supports observations from the North Atlantic and North Pacific oceans. This non-volatile component dominated the volatile organic component, which has been previously observed in South East Pacific waters. The link between the presence of these two organic SSA components and the biogenic activity of the ocean water appears to vary spatially. The use of simple markers for biological activity, such as Chlorophyll-a, falls short of representing this spatial variation.

Bubble generated sub-200 nm SSA produced from water samples taken from the phytoplankton rich Chatham Rise showed a distinct size dependence, with larger particles (up to 150 nm diameter) containing an increasing organic fraction. These results indicate that existing primary marine aerosol emission schemes could provide a significant overestimation of the organic SSA flux and therefore could significantly underestimate the number of potential SSA CCN.
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Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature: QUT Verified Signature

Date: January 2015
1. Introduction

Aerosol emissions and atmospheric processing provide the largest source of uncertainty to estimates of radiative forcing and thus projections of future climate patterns \cite{Andreae_and_Rosenfeld_2008}. Recent modelling studies have identified natural aerosol emissions and the processes these aerosols undergo as a major contributor to the uncertainty of radiative forcing, in excess of the contribution from anthropogenic emissions \cite{Lee_et_al._2011;_2012;_Carslaw_et_al._2013}. This highlights the need for an enhanced understanding of the emissions and atmospheric processes in pristine environments \cite{Carslaw_et_al._2010;_Lee_et_al._2011;_2012}. Aerosols in the marine environment are important for radiative forcing both via the direct scattering of incoming solar radiation (known as the aerosol direct effect) and through their effect on clouds (known as the aerosol indirect effect). The aerosol indirect effect operates via particles acting as cloud condensation nuclei (CCN), sites on which water vapour can condense to form droplets. The concentration, composition and size of CCN influence cloud properties such as lifetime in the atmosphere and albedo, this is the aerosol indirect effect.

Primary marine particles are those that are formed directly from the ocean surface. This occurs when bubbles entrained in the ocean surface layer rise to the surface and burst or from wind and wave action \cite{Lewis_and_Schwartz_2004}. These particles are known as Sea Spray Aerosols (SSA) and are not to be confused with sea salt, which is the inorganic component of SSA. Organic SSA have been attributed to exudates from marine algae and phytoplankton and can be ejected from the ocean surface, along with sea salt \cite{Blanchard_1975}. Identification of the size resolved chemical composition and hygroscopicity (ability to absorb water) of sea spray aerosols (SSA) has been identified as a key aspect of enhancing our understanding of the marine boundary layer. In addition, the current state of knowledge in this area has been classified as low \cite{Meskhidze_et_al._2013}. 
In this study the sub-200 nm ambient SSA composition and concentration is examined via hygroscopicity and volatility measurements from Cape Grim, Tasmania. The ambient marine aerosol composition at Herron Island, Queensland and the Chatham Rise, East of New Zealand has also been characterised. These observations, however, are not covered in detail here due to the lack of observed primary marine aerosol.

Coupled to these measurements are laboratory based SSA observations from Chatham Rise and Herron Island water samples. This study will focus on sub-150 nm diameter particles because marine particle number concentrations are dominated by particles in this size range. In addition the lower limit for CCN active particles in the marine environment generally ranges from approximately 40-120 nm. This lower limit largely determines the CCN concentration and therefore climate implications.
2. Literature review

2.1. Ambient marine aerosol characterisation

This section examines the particle concentrations observed in the remote marine environment and how the sizes of these particles are distributed. In addition the spatial and seasonal variations in marine particle concentrations and size distributions are described. Aitken mode (particle diameter < 80 nm) and accumulation mode (particle diameter between 80 and 600 nm) primary marine aerosol dominate the number concentration and are of most interest with respect to their CCN potential and as such number concentrations are the focus here.

2.1.1. Marine aerosol concentrations

Number concentrations of particles in pristine remote marine environments are relatively low, up to approximately 1000 cm\(^{-3}\). Latitudinal profiles of marine aerosols show average number concentrations for each latitudinal band of between 200 and 800 cm\(^{-3}\). The variability across these bands can be very high and results in concentrations ranging from approximately 0 to 1200 cm\(^{-3}\) [Heintzenberg et al., 2000].

Observations at Mace Head in the North Atlantic [O’Dowd et al., 2013], have indicated that total particle concentrations vary depending on the source and season. Periods when winds transported air masses over the remote marine ocean during 2009 and 2010 concentrations were 353±159 cm\(^{-3}\) for particle diameters greater than 10 nm during high sea-salt background conditions [Bialek et al., 2012]. Averaged winter-time Aitken mode clean marine concentrations were 150 cm\(^{-3}\) in 2002, while the 2002 summer-time average concentration was 293 cm\(^{-3}\) [O’Dowd et al., 2004]. In addition total particle concentrations averaged for January ranged from 200 to 230 cm\(^{-3}\) over 2002-2004 and from 442-493 cm\(^{-3}\) for June averages [Sellegri et al., 2006]. These measurements indicate a clear summertime maximum in remote marine aerosol concentrations in the North Atlantic. This seasonality is associated with enhanced biological activity in the
oceans leading to the production of secondary sulphates and an enhanced number of primary marine organics [O’Dowd et al., 2004].

Cape Grim average particle number concentrations (> 12 nm diameter) during baseline conditions in summer are ~400 cm⁻³ and are 3 to 4 times higher than in winter [Gras, 1995; Fletcher et al., 2007; Gras, 2011]. A similar seasonal variation is observed for the particles greater than 3 nm, with wintertime average concentrations for 1999 and 2000 of 167±103 cm⁻³ and a summertime average of 944±504 cm⁻³ [Jimi et al., 2007]. These figures appear to suggest a similar aerosol concentration and seasonal cycle between the Southern Ocean and the North Atlantic. This cycle has been strongly associated with dimethyl sulphide (DMS) released by phytoplankton during summer months when warmer sea surface temperatures and higher solar radiation increase phytoplankton activity [Ayers and Gras, 1991; Ayers et al., 1995; Jimi et al., 2007].

Continuous particle concentration monitoring is undertaken at Cape Grim and Mace Head, providing excellent sources of marine aerosol concentration data. In addition to these measurements short term, typically of the order of weeks, ship or land based marine aerosol campaigns provide greater spatial variation. Table 1 compares marine aerosol concentrations from a variety of campaign-based measurements. These measurements are characterised by relatively low particle number concentrations, less than 1000 cm⁻³, with high variability between (and within, in some cases) campaigns. This highlights the large role of meteorology and other environmental factors in episodic marine particle concentrations. Care should be taken in interpreting these measurements as average concentrations are taken over relatively short periods, of the order of days, compared to those from research stations, over seasons or years.

A consequence of the relatively small aerosol concentrations in the marine boundary layer is that depletion in concentrations through coagulation is not an important process. Even when concentrations of 104 cm⁻³ are considered, much greater than those observed in clean marine environments, the time required for the particle concentration to be reduced to 10 % of its initial value is of the order
of one month [Lewis and Schwartz, 2004]. As such coagulation is frequently ignored as a loss mechanism in the marine boundary layer.
Table 1: A small sample of observed marine aerosol number concentrations by observations campaign, ocean basin and season.

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Ocean</th>
<th>Year</th>
<th>Season</th>
<th>Minimum diameter</th>
<th>Concentration</th>
<th>Campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Kreidenweis et al., 1998; Murphy et al., 1998]</td>
<td>Macquarie Island</td>
<td>Southern Ocean</td>
<td>1995</td>
<td>Spring/Summer</td>
<td>12 nm</td>
<td>345-768</td>
<td>ACE-1</td>
</tr>
<tr>
<td>[Clarke et al., 2013]</td>
<td>Aeroplane based- Equatorial Pacific</td>
<td>Equatorial Pacific</td>
<td>2007</td>
<td>Spring</td>
<td>10 nm</td>
<td>438</td>
<td>PASE</td>
</tr>
<tr>
<td>[Tomlinson et al., 2007]</td>
<td>Ship based- south-east Pacific</td>
<td>South-east Pacific</td>
<td>2003</td>
<td>Summer</td>
<td>10 nm</td>
<td>398±145</td>
<td>Stratus</td>
</tr>
<tr>
<td>[Tomlinson et al., 2007]</td>
<td>Ship based- south-east Pacific</td>
<td>South-east Pacific</td>
<td>2004</td>
<td>Summer</td>
<td>10 nm</td>
<td>301±100</td>
<td>Stratus</td>
</tr>
</tbody>
</table>
**2.1.2. Marine aerosol size distributions**

The concentration of marine aerosols (along with many other atmospheric constituents) is often modelled using lognormal distributions, chosen because they fit observed concentrations after successive random dilution events [Bencala and Seinfeld, 1976; Seinfeld and Pandis, 2006]. The lognormal distribution as it is often applied to marine aerosol is shown in Equation 1 where \( N \) is the total aerosol number concentration, \( D_p \) is the particle diameter, \( \sigma_g \) is the geometric standard deviation and \( D_{med} \) is the median of the particle size distribution. Commonly aerosol populations are represented as the sum of a number of lognormal distributions, each characterises the production or atmospheric processing mechanism for a population of particles [Jaenicke, 1993; Seinfeld and Pandis, 2006].

\[
\frac{dN}{d\ln D_p} = \frac{N}{\sqrt{2\pi} \ln(\sigma_g)} \exp\left(-\frac{(\ln D_p - \ln D_{med})^2}{2\ln^2\sigma_g}\right) \quad \text{Equation 1}
\]

Marine aerosol size distributions are usually characterised by 3 modes [Seinfeld and Pandis, 2006]:

- the Aitken mode (with \( D_p < 80 \) nm),
- the accumulation mode (with \( 80 < D_p < 600 \) nm), and
- the coarse mode (with \( D_p > 600 \) nm).

The coarse mode commonly represents approximately 95% of the total mass of aerosol particles, but only 5-10% of the number [Seinfeld and Pandis, 2006]. As outlined in Section 2.1.1, the focus in this study is on the ability of marine aerosols to act as CCN, therefore of most interest here are the Aitken and accumulation modes, in which the vast majority of marine aerosols fall (by number). Further to this point, marine accumulation mode can be largely regarded as potential CCN (see Section 2.2.2), therefore sub-200 nm diameter particles will be the focus here.

Marine boundary layer lognormal modes averaged over a variety of observation campaigns are shown in Figure 1 [Heintzenberg et al., 2011]. This includes
observations from the Southern, North and South Atlantic and Indian Oceans, and the Sea of Japan. This provides a very good example of the typical marine size distribution. Ambient marine boundary layer size distributions are characterised by an absence of nucleation mode particles ($D_p < \sim 10$ nm). This is sometimes referred to as being “closed” at the lower size limit and provides evidence for the absence of marine boundary layer nucleation [Heintzenberg et al., 2000; Seinfeld and Pandis, 2006; Heintzenberg et al., 2011]. The minima between the Aitken and accumulation modes is due to the activation of marine aerosols into cloud droplets and is known as the Hoppel minimum [Hoppel et al., 1986]. The Hoppel minimum is dependant on the conditions under which the droplet was formed (see Section 2.2.1 for further details), therefore the boundary between the Aitken and the accumulation mode can vary between about 50 to 100 nm [Hoppel et al., 1986; Sellegri et al., 2006; Blot et al., 2013].

Both the Aitken and accumulation marine aerosol contain a combination of primary (SSA) and secondary components. As with the total concentrations (Section 2.1.1) the proportion of primary to secondary particles in each of these
modes changes with meteorology and other environmental conditions. Normalised size distribution for summer and winter at Mace Head are shown in Figure 2 [Sellegri et al., 2006]. There is a clear enhancement of the Aitken mode in summer to approximately double the concentrations observed in winter. This follows from the observed increase in summertime particle concentrations due to enhanced biological activity mentioned in Section 2.1.1 [O’Dowd et al., 2004; Sellegri et al., 2006]. The Hoppel minimum also shifts to larger sizes during winter, suggesting a change in particle composition or a change in the cloud level saturation ratio, these issues are discussed further in Section 2.2 and 2.3.

![Figure 2: Lognormal fitted normalised aerosol size distributions averaged over clean marine sector conditions during January 2004 (green) and June 2004 (blue) at Mace Head (source: Sellegri et al. [2006])](image)

Depth profiles show that size distributions from the boundary layer (defined as 0 – 600 m in altitude) and boundary upper layer or cloud layer (defined as 600 – 1300 m) are similar and displaying Aitken and accumulation modes separated by a Hoppel minimum [Clarke et al., 2013]. Size distributions from above the boundary layer are shifted to smaller sizes, with free tropospheric distributions having a peak at approximately 40 nm [Clarke et al., 2013; Twohy et al., 2013].
Above the boundary layer clean marine size distributions do not display an accumulation mode or Hoppel minimum, suggesting an absence of cloud processing [Clarke et al., 2013; Twohy et al., 2013]. This supports the idea that new particle formation in the free troposphere is an important source of sub-100 nm particles for the marine boundary layer [Koponen et al., 2002; Quinn and Bates, 2012; Clarke et al., 2013].

### 2.2. Marine aerosol hygroscopicity

The ability of a particle to uptake water (hygroscopicity) is obviously a key characteristic with respect to the probability of a particle act as a CCN. This section describes how the water uptake and hygroscopicity of particles depend on their composition and size (Section 2.2.1) A review of the observed hygroscopic properties of marine particles is also provided in Section 2.2.2.

#### 2.2.1. Hygroscopic growth fundamentals

##### 2.2.1.1. Hygroscopic growth factor

Hygroscopicity is the ability of a particle to uptake water. Hygroscopic particles readily absorb water, while hydrophobic particles repel water. The hygroscopic growth factor is used as the measure of hygroscopicity, this is the ratio of the particle diameter at some reference relative humidity (frequently 90% relative humidity) and the dry particle diameter. That is:

\[
HGF = \frac{d_{RH}}{d_{dry}}
\]

Equation 2

The HGF is dependant on both the particle size and chemical composition. Hygroscopic properties of the remote marine aerosol can be used to infer the chemical composition of the marine aerosol. In addition hygroscopicity is closely linked to the likelihood that a given species or mixture will act as CCN. The HGFs for inorganic substances commonly found in the marine atmosphere, as well as some well-studied organics, are shown in Table 2.
Table 2: HGF, deliquescence relative humidity (DRH) (see Section 2.2.1.2), hygroscopicity parameter (κ) and volatilisation temperature (T_v) for atmospherically relevant species. κ calculated from hygroscopic growth measurements (κ_{HGF}) and from CCN measurements (κ_{CCN}) using κ-Köhler model (see Section 2.2.1.5). Sources: [Fletcher et al., 2007; Petters and Kreidenweis, 2007].

<table>
<thead>
<tr>
<th>Substance</th>
<th>HGF</th>
<th>DRH</th>
<th>κ_{HGF}</th>
<th>κ_{CCN}</th>
<th>T_v (°C)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid (H_2SO_4)</td>
<td>1.68</td>
<td>0%</td>
<td>1.19</td>
<td>0.9</td>
<td>139</td>
<td>[Berg et al., 1998; Clegg et al., 1998; Johnson et al., 2004]</td>
</tr>
<tr>
<td>Ammonium bisulfate ((NH_4)HSO_4)</td>
<td>1.79</td>
<td>40%</td>
<td>-</td>
<td>-</td>
<td>202</td>
<td>[Tang and Munkelwitz, 1994; Berg et al., 1998; Johnson et al., 2004]</td>
</tr>
<tr>
<td>Letovicite ((NH_4)_2H(SO_4)_3)</td>
<td></td>
<td>69%</td>
<td>0.51</td>
<td>0.65</td>
<td>-</td>
<td>[Tang and Munkelwitz, 1994; Clegg et al., 1998]</td>
</tr>
<tr>
<td>Ammonium sulfate ((NH_4)_3H_2SO_4)</td>
<td>1.7</td>
<td>79-80%</td>
<td>0.53</td>
<td>0.61</td>
<td>205 (180 (40 nm))</td>
<td>[Clegg et al., 1998; Prenni et al., 2003; Johnson et al., 2004; Koehler et al., 2006]</td>
</tr>
<tr>
<td>Methanesulfonic acid</td>
<td>1.57</td>
<td>0%</td>
<td>-</td>
<td>-</td>
<td>171</td>
<td>[Johnson et al., 2004]</td>
</tr>
<tr>
<td>Ammonium nitrate (NH_4NO_3)</td>
<td>1.5</td>
<td>61.50%</td>
<td>-</td>
<td>0.67</td>
<td>75</td>
<td>[Lightstone et al., 2000; Johnson et al., 2004; Svenningsson et al., 2006]</td>
</tr>
<tr>
<td>Sea salt</td>
<td>2.2-2.35</td>
<td>75%</td>
<td>-</td>
<td>-</td>
<td>&gt;500 (290 (27 nm))</td>
<td>[Modini et al., 2010a; Fuentes et al., 2011]</td>
</tr>
<tr>
<td>Sodium Chloride (NaCl)</td>
<td>2.45</td>
<td>75%</td>
<td>0.91-1.33</td>
<td>1.28</td>
<td>&gt;600</td>
<td>[Clegg et al., 1998; Koehler et al., 2006; Biskos et al., 2006a; Modini et al., 2010a]</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>1.01</td>
<td>-</td>
<td>&lt;0.006</td>
<td>0.231</td>
<td>-</td>
<td>[Chan and Chan, 2003; Hori et al., 2003; Prenni et al., 2003]</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>1.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[Peng et al., 2001; Prenni et al., 2003]</td>
</tr>
<tr>
<td>Malanoic acid</td>
<td>1.73</td>
<td>-</td>
<td>0.44</td>
<td>0.227</td>
<td>-</td>
<td>[Peng et al., 2001; Pradeep Kumar et al., 2003; Prenni et al., 2003; Koehler et al., 2006]</td>
</tr>
<tr>
<td>Secondary organic aerosol</td>
<td>1.06-1.1</td>
<td>0%</td>
<td>0.009-0.07</td>
<td>0.014-0.229</td>
<td>75-150</td>
<td>[Saathoff et al., 2003; VanReken et al., 2005; Hartz et al., 2006; Varutbangkul et al., 2006; An et al., 2007; Prenni et al., 2007]</td>
</tr>
</tbody>
</table>

2.2.1.2. Deliquescence

Pure crystalline substances, such as sodium chloride and ammonium sulfate, display prompt hygroscopic growth, i.e. a prompt increase in their HGF, at a particular relative humidity (RH). This RH is characteristic for each substance and is known as the deliquescence RH. The deliquescence point is the RH at which particles start to absorb water. Below the deliquescence relative humidity (DRH) the HGF is approximately 1 and at the deliquescence point the HGF increases rapidly. At the DRH enough of the salt is dissolved in the surrounding water vapour and it is thermodynamically more stable for the salt to be in an aqueous rather than solid state [Seinfeld and Pandis, 2006; Biskos et al., 2006a; Mifflin et al., 2009]. When the RH is reduced, however, the water in the particle needs to
evaporate before the particle appears as a dry crystalline salt. This does not generally occur at the DRH, but at a lower relative humidity known as the efflorescence relative humidity (ERH) [Seinfeld and Pandis, 2006]. DRH is dependant the particle composition, with some species experiencing continuous growth with increasing RH. Such species do not display a DRH and include many organics found in the marine environment. In addition there are organic species that are hydrophobic and will not absorb water in sub-saturated conditions. The DRHs for inorganic substances commonly found in the marine atmosphere, as well as some well-studied organics, are shown in Table 2.

A good example of this response to changing RH is observed for ammonium sulfate particles, \((\text{NH}_4)_2\text{SO}_4\), as shown in Figure 3. These particles have a deliquescence point at approximately 80% RH [Fletcher et al., 2007; Johnson et al., 2008]. This means that while increasing the RH up to 80% there will be a negligible change in the particle diameter, but beyond 80% RH the particles will start to absorb water and grow rapidly [Johnson et al., 2008]. Ammonium sulfate particles display a ERH at approximately 30% RH, this means that once the particles have been exposed to a RH greater than the DRH they will have to be exposed to a RH of less than 30% to crystalize into dry particles again.

![Figure 3: Deliquescence, efflorescence curve of 97 nm ammonium sulfate particles. Model HGF based on [Biskos et al., 2006b]. Figure source: [Johnson et al., 2008].](image-url)
Ammonium sulfate is one of a number of species common on the marine environment in the particle phase classified as non-sea salt (NSS) sulfates, so called to be distinguished from sulfate ions present in sea salt. These groups of particles can be distinguished by their respective DRH’s. Non-sea salt sulfates are neutralised by ammonium (NH₄), with the level of neutralisation (the ratio of charges from the ammonium ion to the charges from the sulfate ion) ranging from 0, corresponding with sulphuric acid H₂SO₄, to 1, corresponding with ammonium sulphate (NH₄)₂SO₄. Ammonium bisulfate NH₄HSO₄ and letovicite (NH₄)₃H(SO₄)₂ are also common atmospheric species with neutralisations of 0.5 and 0.75, respectively. The level of neutralization of NSS-sulfate influences the hygroscopic response of the particle [Mifflin et al., 2009]. Sulfuric acid particles don’t display a DRH at all, while for 100 nm particles the DRH for ammonium bisulfate is approximately 40%, for letovicite is approximately 69% and for ammonium sulphate is approximately 80% [Tang and Munkelwitz, 1994; Berg et al., 1998; Johnson et al., 2004; Fletcher et al., 2007].

2.2.1.3. Mixtures
The amount of water absorbed by internally mixed, or multicomponent, particles at their equilibrium vapour pressure tends to follow the Zdanovskii, Stokes and Robinson (ZSR) assumption [Stokes and Robinson, 1966; Chen et al., 1973]. This is that the total volume of water in the particle is the sum of water absorbed due to the individual components. It then follows that the HGF of such a particle is given by the volume fraction weighted sum of the HGF’s of the individual components.

\[
HGF^3 = \sum_i HGF_i^3 \cdot \varepsilon_i \quad \text{Equation 3}
\]

Where \( \varepsilon_i \) is the volume fraction of an individual component and \( HGF_i \) is the HGF for that component. Variations from the ZSR assumption do occur in marine particles, particularly in organic-inorganic mixtures where the surface tension of the particle can be influenced by the organic component acting as a surfactant [Facchini et al., 2000; Modini et al., 2010b].

2.2.1.4. Size and composition dependence
The formation of a water droplet from the vapour phase involves the transfer of potential energy, the Gibbs free energy, from the vapour to the liquid phase until
the droplet reaches an equilibrium diameter. At this equilibrium diameter there is no net transfer of the Gibbs free energy between the vapour and the droplet. It can be shown that at this equilibrium:

\[ S = \frac{e}{e_s} = e^{\frac{4\sigma V}{eRTD}} \]  \hspace{1cm} \text{Equation 4}

Where \( e \) is the vapour pressure and \( e_s \) is the saturation vapour pressure, \( \sigma \) is the surface tension of the droplet, \( V \) is the molar volume of water, \( R \) is the gas constant, \( T \) is the temperature and \( D \) is the diameter of the droplet.

This implies the greater the curvature of the droplet (i.e. the smaller the droplet), the greater the saturation vapour pressure required to maintain equilibrium, this is the Kelvin effect [Seinfeld and Pandis, 2006]. An intuitive explanation for the Kelvin effect is that a given molecule in a curved surface has fewer neighbouring molecules and therefore fewer attractive forces than a molecule in a flat surface. This results in greater transfer of molecules into the vapour phase and a higher vapour pressure. The Kelvin effect is significant for aqueous particles below approximately 50 nm and up to 200 nm for higher molecular weight organics [Seinfeld and Pandis, 2006].

A cluster of water molecules of the order of a few nanometres is required to overcome evaporation, for the homogeneous nucleation of droplets. Droplet formation theory and observations indicate that to obtain homogeneous nucleation supersaturations of greater than approximately 10% are required. Observations of in-cloud supersaturation show that in the atmosphere droplets are formed at supersaturations of less than 1%. Therefore the Kelvin equation does not adequately explain cloud droplet formation.

Raoult’s law states that the partial pressure of each species in a mixture is equal to the vapour pressure of the pure component of that species scaled by the molar fraction of that species in the mixture. That is:

\[ p_i = p_i^0 x_i \]  \hspace{1cm} \text{Equation 5}

Where \( p_i \) is the vapour pressure of species \( i \) in the mixture, \( p_i^0 \) is the vapour pressure of a bulk sample of species \( i \) and \( x_i \) is the molar fraction of species \( i \) in
the mixture. The total vapour pressure at equilibrium is the sum of the partial vapour pressures for each species. When the water-aerosol system is in equilibrium the Gibbs free energy (G) is minimised and it can be shown that the water activity ($a_w$) is equal to the saturation ratio for a flat surface [Seinfeld and Pandis, 2006]. Giving:

$$S = \frac{p_l}{p_l^s} = x_l = a_w \quad \text{Equation 6}$$

This indicates that for water aerosol mixtures the larger the molar fraction of the aerosol component the lower the saturation vapour pressure required for liquid and vapour phase water equilibrium. In this way the dry particle diameter, through its influence on the aerosol mass, also effects saturation vapour pressure. In addition this law dictates that the vapour pressure required to form droplets is dependent on the species present in the mixture, through their molar mass.

Aqueous particles less than approximately 100 nm are influenced by the Kelvin effect, as well as Raoult’s Law. The saturation ratio of required maintaining equilibrium over a droplet surface is given by the water activity times the Kelvin factor (combining equations Equation 5 and Equation 6).

$$S = a_w \cdot e^{\frac{4\sigma V_w}{RTD}} \quad \text{Equation 7}$$

Where $S$ is the saturation ratio i.e. RH/100, $\sigma$ is the surface tension of the solution, $V_w$ is the molar volume of water, $R$ is the gas constant, $T$ is the temperature and $D$ is the droplet diameter. This is known as the Köhler equation. The Köhler equation indicates that for a given relative humidity the HGF of a particle is dependant on its composition and dry diameter. The Kelvin factor (Equation 4) can be used to correct observed sub-200 nm HGFs.

Figure 4 shows the relationship between water vapour supersaturation and droplet diameter for pure water and (NH$_4$)$_2$SO$_4$ at a range of dry diameters and thus solute masses derived from Equation 7. The curves shown in Figure 4 are known as Köhler curves and can be produced for any species for which the Raoult effect can be calculated. These curves show the droplet diameter at
equilibrium for a given saturation ratio. The peak of the Köhler curve indicates the critical supersaturation (S_c) at which a particle of a given substance with a given dry size (often referred to as the critical diameter, d_c) will activate to form cloud droplets, i.e., act as CCN. Spontaneous growth of the droplet occurs after activation because the supersaturation required for larger droplets decreases. For example, at supersaturations of 0.15% (indicated by the horizontal dashed line in Figure 4) all ammonium sulfate particles greater than or equal to 100 nm will be activated and grow into cloud droplets. Ammonium sulfate particles smaller than 100 nm will not be activated. Particles below their equilibrium curve will shrink through evaporation and those above will grow by condensation until they are in equilibrium [Seinfeld and Pandis, 2006; Biskos et al., 2006c; Andreae and Rosenfeld, 2008].

The Köhler equations do a particularly good job of indicating the required particle size and or/supersaturation required for particles of a known composition to act as CCN. This theory can be used to calculate the expected HGF for a mixture of known composition, these are known as hygroscopic closure studies [Quinn and Coffman, 1998; Swietlicki et al., 1999; Putaud et al., 2000; Hersey et al., 2009]. Frequently in practice calculating the Raoults effect of atmospheric particle mixtures, for which the molar mass ratios are unknown, is not feasible. This is particularly the case when a mixture contains an organic component, which is often the case in marine environments, as the precise composition of the organic is not generally known.
Figure 4: Köhler curves indicate the equilibrium water vapour saturation ratio at 293 K for droplets of pure water shown by the dotted black line. Droplets containing particles with 50 nm, 100 nm and 500 nm dry diameters (and thus various masses) shown in red, green and blue respectively. Water vapour saturation ratio, $S(\%) = 100 \times \frac{p}{(p_0 - 1)}$. Where $p_0$ is the partial pressure of water vapour over the droplet and $p_0$ is the saturated vapour pressure over a flat surface (Source: [Seinfeld and Pandis, 2006; Andreae and Rosenfeld, 2008]).

2.2.1.5. Kappa-Köhler model

To overcome the shortfalls of putting the Köhler equations into practice, models have been developed to estimate the influence of different dissolved species on the saturation vapour pressure. One of the most common models used, and the one used in this study, is known as the κ-Köhler model [Petters and Kreidenweis, 2007; 2013]. This model uses an empirical parameterisation, which is defined by through the hygroscopicity parameter, κ, which is a measure of aerosol water uptake and CCN activity. κ is defined through its effect on $a_w$:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_d}{V_w} \quad \text{Equation 8}$$

Where $V_d$ is the volume of the dry particle and $V_w$ is the volume of water. This relates the water activity to the water uptake rather than to the chemical composition. Substituting Equation 8 into Equation 7 gives the κ-Köhler relationship.
\[ S = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - \kappa)} \frac{4\sigma V_w}{RTD} \quad \text{Equation 9} \]

Where \( D \) is the total droplet diameter and \( D_d \) is the particle dry diameter. The Raoult component can be related directly to observed HGFs in subsaturated conditions, giving:

\[ S = \frac{HGF^3 - 1}{HGF^3 - (1 - \kappa)} \frac{4\sigma V_w}{RTD_p} \quad \text{Equation 10} \]

Kappa describes both super and sub-saturated particles, therefore Equation 8 to Equation 10 can be used to estimate the water uptake behaviour of particles in supersaturated conditions from hygroscopic growth observations in sub-saturated conditions. Of particular interest is whether they will be activated into cloud droplets. In addition, observations of CCN concentrations can be used to infer the sub-saturated HGF of a population of particles, from which the composition may be estimated. Each species has a specific \( \kappa \) value and the overall \( \kappa \) in a mixture is given by:

\[ \kappa = \sum_i \varepsilon_i \kappa_i \quad \text{Equation 11} \]

This mixing rule is a form of the ZSR assumption. The \( \kappa \) values for inorganic substances commonly found in the marine atmosphere, as well as some well-studied organics, are shown in Table 2.
2.2.2. Hygroscopic growth of sea spray

2.2.2.1. HGF measurement

Hygroscopic growth measurements of Aitken and accumulation mode particles are made using a Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA) [Liu et al., 1978; Rader and McMurry, 1986; McMurry and Stolzenburg, 1989]. This instrument uses a pair of differential mobility analysers (DMAs), the first to select particles of a known size from the poly-dispersed ambient sample and the second is operated in with a condensation particle counter (CPC) on the output to act as a Scanning Mobility Particle Sizer (SMPS). In between the two DMAs the aerosol is conditioned to a known relative humidity, frequently 90% RH, and the second DMA/CPC measures the resulting particle size distribution. The HGF can be simply calculated by dividing the measured particle size from the size distribution at the second DMA by the known, initial particle diameter transmitted through the first DMA. The H-TDMA system requires an adequately dried sample aerosol, usually to below approximately 30% as this is below the efflorescence humidity of most species. H-TDMA systems are able to measure particles from 8 nm up to [Väkevä et al., 2002] hundreds of nanometres. The H-TDMA technique is well suited to studies in marine environments because it is able to distinguish between the major constituents of marine aerosols.

Previous studies have generally subdivided the marine Aitken and accumulation mode aerosols into four HGF classes, used to provide guidance on what chemical species are likely to be present in the aerosol.

1. Nearly hydrophobic aerosols, with growth factors ranging from approximately 1.0 to 1.1, are composed of marine organics or are influenced by anthropogenic sources [Berg et al., 1998; Swietlicki et al., 2000; 2008; Bialek et al., 2012].

2. Less hygroscopic aerosols, with growth factors ranging from approximately 1.1 to 1.3, are composed of marine organics [Ovadnevaite et al., 2011b; Bialek et al., 2012].
3. More hygroscopic aerosols, with growth factors ranging from approximately 1.35 to 1.85, are dominated by NSS-sulfates [Swietlicki et al., 2000; Ovadnevaite et al., 2011b; Bialek et al., 2012].

4. Sea salt aerosols (inorganic SSA), with growth factors of more than 1.85, observations of sub-100 nm sea salt is not common and the ideal conditions for their development is uncertain [Zhou et al., 2001; Fuentes et al., 2010a; Modini et al., 2010a; Bates et al., 2012; Bialek et al., 2012].

Caution should be taken when applying these classes because different internal mixtures can result in similar HGFs. For example, SSA internally mixed with less hygroscopic species such as marine organics could be classified in the more hygroscopic class. This could give the impression that the particle is composed of NSS-sulfates. Usually HGFs are considered alongside other measurements to obtain a full picture of particle composition. Despite this limitation regarding the composition of internal mixtures one of the advantages of the H-TDMA technique is the ability to resolve external mixtures. The size distribution obtained by the second DMA and the CPC will have two peaks when an external mixture of two aerosol species, with different HGFs, is present in the sample. The concentration of the two peaks can be used to determine the relative concentration of the species in the sample. This is not common among aerosol composition measurement techniques and is likely to be important with regard to cloud properties [McFiggans et al., 2006]. In addition H-TDMA systems are on-line methods, meaning they provide real time results at a relatively high temporal resolution (approximately 3-5 minutes).

2.2.2. Marine HGFs

H-TDMA measurements in the remote marine environment typically show that the sub-200 nm marine aerosol number concentration is dominated by NSS-sulfates [Berg et al., 1998; Maßling et al., 2003; Johnson et al., 2005; McFiggans et al., 2006; Fletcher et al., 2007; Maßling et al., 2007; Tomlinson et al., 2007; Swietlicki et al., 2008; Allan et al., 2009; Good et al., 2010; Modini et al., 2010b; Bialek et al., 2012]. A small externally mixed SSA component is also sporadically observed in the
remote marine environment [Berg et al., 1998; Zhou et al., 2001; Fletcher et al., 2007; Maßling et al., 2007; Bialek et al., 2012; Lawler et al., 2014]. This component is size dependant and appears to be observed more frequently at sizes greater than 100 nm. The amount of ultrafine SSA has been attributed to wind speed [MårteNSSon et al., 2003; Maßling et al., 2003; MårteNSSon et al., 2010], however wind speed does not appear to consistently explain the relative scarcity of SSA [Berg et al., 1998; Swietlicki et al., 1999; Zhou et al., 2001]. The HGF of SSA and NSS-sulfates are commonly less than that expected from bulk samples (see Table 2), suggesting the presence of an internally mixed less hygroscopic species. This is often attributed to the presence of internally mixed organics with origins from marine phytoplankton and algae [Fletcher et al., 2007; Allan et al., 2009; Good et al., 2010; Modini et al., 2010b; Bialek et al., 2012]. In addition an externally mixed organic component of the sub-200 nm marine aerosol has also been observed [Swietlicki et al., 2000; Maßling et al., 2003; 2007; Dall'Osto et al., 2010; Ovadnevaite et al., 2011b; Bialek et al., 2014].

VH-TDMA measurements at Cape Grim show the presence of SSA in a small proportion of measurements with a number fraction of approximately 15% [Fletcher et al., 2007]. SSA was primarily observed on days with wind speeds greater than 8 ms⁻¹ and for particles greater than 80 nm. HGFs of the SSA mode ranged from approximately 1.8 to 2. Low SSA mode HGFs corresponded with low sulfate mode hygroscopic growth [Fletcher et al., 2007]. This suggests that either the organic component of the SSA was secondary or a larger primary organic fraction was coincident with a larger concentration of condensable organic species, which lowered the sulfate HGF.

H-TDMA measurements in the Southern Ocean during the springtime ACE-1 campaign showed a dominant, ever present NSS-sulfate fraction with HGF ranging from 1.62 at 35 nm to 1.78 at 150 nm [Berg et al., 1998]. In addition an externally mixed SSA fraction with HGF 2.12-2.14 was observed in 40% of measurements at 150 nm and 5% at 50 nm. SSA was not observed at 35 nm. These measurements show a distinct absence of significant concentrations of internally or externally mixed organics. The occurrence of SSA could be linked
with high wind speed conditions in the back trajectory, however these observations are poorly correlated with local wind speed [Berg et al., 1998].

H-TDMA analyses of 30-40 nm particles observed on the east coast of Australia indicated an internal mixture of NSS-sulfate and organic components. Growth factors were approximately 85% of those expected for ammonium sulfate at these diameters [Modini et al., 2009; 2010b]. Volatility measurements indicated that the less hygroscopic organic components suppressed the uptake of water by the sulfate fraction contradicting the ZSR assumption. An increase in HGF of particles after the organic component was removed exceeded that expected under the ZSR assumption, indicating an increase in the HGF of the sulfate component [Modini et al., 2010b]. This phenomenon has not as yet been observed for internal mixtures of organic and inorganic components in SSA, however

H-TDMA observations at Mace Head (North Atlantic) indicate an annual average number fraction of 35-54% modified ammonium sulfate particles, 11-40% SSA and 25-35% organics averaged over 35-165 nm diameter open ocean measurements [Bialek et al., 2012]. The presence of 30 to 165 nm particles with a HGF of 1.3 to 1.5 has been observed. These particles are consistent with SSA with a large organic fraction and appear primarily in summer due to the presence of phytoplankton rich waters [O’Dowd et al., 2004; Dall’Osto et al., 2010; Ovadnevaite et al., 2011b; Bialek et al., 2012]. In addition these particles are in greater concentrations at smaller sizes [Bialek et al., 2012], which is predicted to be due to favourable partitioning of organics into the particle phase at smaller diameters [Oppo et al., 1999]. These particles are distinct from those less hygroscopic particles commonly observed over all ocean basins, which are attributed to NSS-sulfates, with lowered HGFs due to the condensation of organic species [Fletcher et al., 2007; Allan et al., 2009; Good et al., 2010; Modini et al., 2010b; Bialek et al., 2012]. Hygroscopicity measurements alone do not reveal whether these particles are internally mixed with NSS-sulfates or sea-salt. Possibly coupled with the large primary organic fraction is the frequently observed and relatively large sea salt fraction observed at Mace Head, averaging 11-40% for open ocean air masses [Bialek et al., 2012; Lawler et al., 2014]. It
appears that the North Atlantic and Arctic Oceans observe a high proportion of SSA relative to NSS-sulfates, and thus studies examining the primary organic aerosol are somewhat concentrated in these regions [Zhou et al., 2001; O’Dowd et al., 2004; Facchini et al., 2008; Rinaldi et al., 2010].

2.2.2.3. Marine CCN

H-TDMA measurements can be used to determine the hygroscopicity parameter, $\kappa$ via Köhler theory (Section 2.2.1.5). In turn, $\kappa$ provides a relationship between the critical diameter for droplet activation and the supersaturation. Therefore using a size distribution the concentration of CCN at a given supersaturation can be calculated from the HGFs. In this way H-TDMA observations can be directly compared with CCN concentrations, measured at a known supersaturation [Petters and Kreidenweis, 2007; Good et al., 2010; Petters and Kreidenweis, 2013]. CCN concentration can be measured using a CCN counter, which exposes the sample to a set supersaturation and optically counts the number of particles that are activated into droplets [Roberts and Nenes, 2005].

Particle number concentrations at CCN active sizes between supersaturations of 0.04 and 0.4 were observed to decrease with altitude in the southeast Pacific [Clarke et al., 2013]. This is due to a greater proportion of Aitken mode (see Section 2.1), semi-volatile (see Section 2.3.1) particles at and above cloud level (free troposphere). The number of CCN at 0.2% supersaturation in the MBL was 192 cm$^{-3}$ and in the free troposphere was 125 cm$^{-3}$. Entrained free tropospheric particles were determined to provide an immediate contribution of 65% to the marine boundary layer (MBL) CCN, and a further 25% due to subsequent growth in the MBL. The remaining 10% of CCN were attributed to refractory sea salt from volatility measurements [Clarke et al., 2013].

Simultaneous H-TDMA and CCN concentration measurements taken in the tropical Atlantic showed that when using sub-saturated HGFs the estimated CCN number concentration was systematically under-predicted compared to that of measured CCN concentrations. HGFs during this study were within a single dominant mode between 1.56 and 1.74 [Good et al., 2010]. These HGFs suggest a dominant NSS-sulfate fraction with a small, variable organic component and are a good representation of the most commonly observed marine aerosol
McFiggans et al., 2006; Swietlicki et al., 2008; Good et al., 2010]. HGFs at 94% RH were well predicted by the growth factors measured at 90%, suggesting that a change in the hygroscopicity parameter occurs somewhere between 94% RH and activation [Good et al., 2010]. This change was suggested to be either due to non-ideal solution behaviour, surface tension effects or the gradual dissolution of low solubility compounds at high RH. Under-prediction of CCN concentrations was also dependent on supersaturation. H-TDMA derived CCN concentrations under-predicted by approximately 10-20% above 0.2% supersaturation, and increased rapidly with decreasing supersaturations less than 0.2%, to a maximum of approximately 80%. This is an important feature of the HGF, CCN relationship because typical supersaturations for marine stratiform clouds are of the order of 0.1 to 0.4% [Martin et al., 1994; Good et al., 2010; Blot et al., 2013; Twohy et al., 2013]. Similarly, observations of SSA during the late summer at Mace Head have indicated the presence of an organic fraction displaying low HGF and a high CCN activity. This also suggests a discontinuous hygroscopicity parameter between sub- and super-saturated regimes [Ovadnevaite et al., 2011b]. The CCN concentration inferred from H-TDMA measurements in the Arctic, however, overestimated measured values [Zhou et al., 2001]. In addition, removal of measurements at supersaturations of less than 0.2% improved the prediction. Inaccuracies in the prediction are magnified at supersaturations less than 0.2% because this corresponds to the “front edge” of the marine size distribution, therefore a small change in the critical diameter for droplet activation will lead to a large change in potential CCN [Zhou et al., 2001; Good et al., 2010]. Observations at Cape Grim also show an over-predicted CCN concentration from H-TDMA measurements of approximately 25% for measurements from all wind sectors [Covert et al., 1998]. Measurements with wind from the baseline sector and observations with Radon concentrations less than 125 mBeq/m³ show a 20% over-prediction and those with Radon concentrations limited to 50 mBeq/m³ did not display any over-prediction [Covert et al., 1998]. These particles are in the more hygroscopic mode and are likely to be dominated by NSS-sulfates. Radon is a marker for air masses having passed over the continent [Zahorowski et al., 2011]. This suggests that inorganic
salts dominated the marine particles and anthropogenic or continental organic sources were responsible for an under prediction in CCN concentrations.

2.3. Chemical composition of sea spray

Chemical composition of SSA can be measured directly using online methods, such as aerosol mass spectrometry, or offline methods, such as transmission electron microscopy. Online methods analyse particle composition in real time and generally have a high time resolution, of the order of minutes. Offline methods generally have a lower temporal resolution, hours to days, and analyses of composition are undertaken separately to particle collection. Similarly to hygroscopic growth, volatility can be used to infer chemical composition. Coupling volatility with a TDMA is a commonly used method and, as such, volatility is treated as an online method here.

2.3.1. Online methods

A common method of examining particle composition is to heat the particles up until certain components evaporate or dissociate and then analyse what is remaining. This method can provide information on the composition of both the volatile (non-refractory) and non-volatile (refractory) particle fraction. The temperatures at which a number of common atmospheric constituents are fully evaporated or dissociated (volatilisation temperatures) are listed in Table 2. Note that the volatilisation temperature is dependant on the way in which particles are heated and in particular on the residence time of the thermodenuder [An et al., 2007] and as such the values in Table 2 should be treated as a guide.

Non-volatile particle fractions can be analysed using a number of techniques. For example examine the hygroscopic growth after volatilisation can also provide valuable information on the relative water uptake of internally mixed particle components [Johnson et al., 2005; Modini et al., 2010b]. This section will focus on online volatilisation techniques, off-line collection of refractory components will be covered in Section 2.3.2.

Similarly to hygroscopicity, volatility measurements are commonly used in the marine environment because common marine aerosol components display relatively different volatilisation temperatures, as seen in Table 2. In particular,
the refractory sea salt component is commonly examined by volatilising NSS-sulfates and organics [Kreidenweis et al., 1998; Johnson et al., 2005; Tomlinson et al., 2007; Sellegrí et al., 2008]. Non-neutralised NSS-sulfates, H$_2$SO$_4$, can be identified as they volatilise at approximately 140 °C, while the more neutralised fractions volatilise at greater than 150 °C [Fletcher et al., 2007].

Volatility and hygroscopicity measurements of 80 nm ambient wintertime and laboratory generated marine particles undertaken at Mace Head characterises the less hygroscopic particle fraction observed at this location [Sellegrí et al., 2008]. After volatilising to 90 °C a decrease of the order of 50% in the number fraction of less hygroscopic aerosols was observed to the benefit of the sea salt number. This indicates the presence of non-hygroscopic, semi-volatile species. In addition the less hygroscopic particle mode was not observed for laboratory produced marine aerosol and is therefore concluded to be of secondary origin [Sellegrí et al., 2008].

Volatility measurements taken in the south eastern Pacific, off the coast of Chile, indicated that the Aitken and accumulation mode aerosol were comprised of refractory cores (to 250 °C), most likely sea salt, and NSS-sulfates [Tomlinson et al., 2007]. The authors argue that the aerosol hygroscopicity measurements of between 1.36 and 1.49 for sub-200 nm particles indicate a mixture of H$_2$SO$_4$ and that ammonium bisulfate. The relative volatalisation step between 50 and 150 °C was assumed to be entirely due to the dissociation of H$_2$SO$_4$ and the step at 150 to 250 °C was assumed to be entirely due to the loss of ammonium bisulfate. The ratio of ammonium to sulfate concentrations can then be calculated, inferring a neutralisation of 0.56 and 0.23 for the Aitken and accumulation sulfate components respectively [Tomlinson et al., 2007]. These values, however, should be treated with caution as the above method ignores the possibility of an organic component to the semi-volatile marine aerosol as observed elsewhere [Sellegrí et al., 2008; Modini et al., 2010b].

Airborne measurements in the remote equatorial Pacific measured the refractory (at 360 °C) number concentration of condensation nuclei (CN) and CCN in the marine boundary layer, the upper marine boundary layer (at cloud
height) and in the free troposphere. The refractory component at this
temperature is assumed to be sea-salt. In the boundary layer sea salt contributes
57% of CN while in the upper boundary layer it contributes 49% and in the free
troposphere 30%. The decrease in the proportion of sea salt with altitude is due
to a decrease in sea salt concentrations as well as an increase in the
concentration of the volatile component [Clarke et al., 2013]. The authors argue
that approximately 10% of the potential MBL CCN active at 0.2%
supersaturation were refractory sea-salt, while 65% were non-refractory
particles entrained from the free troposphere [Clarke et al., 2013]. In a similar
study volatility measurements were also used to infer that sea salt made up
approximately 20% of the potential CCN number concentration [Blot et al., 2013].

Laser mass spectrometry was used to determine particle composition during the
ACE-1 campaign at Cape Grim [Middlebrook et al., 1998]. Approximately half of the
clean marine particles had an internal mixture of sea salt and an organic
component comprising approximately 10% of the particle mass. Organic
concentration peaks corresponded to periods with sodium sulfate peaks. Sodium
sulfate forms in aged sea salt as the chlorine is depleted and sulfate condenses
onto the surface or sulfate aerosol coagulates with the sea salt [Lewis and
Schwartz, 2004]. Corresponding organic peaks suggest a secondary sulfate source,
similar to that of sodium sulfate. With low sodium sulfate concentrations there
also appeared to be a source of organics, which are thought to be from the
surface ocean. Aerosol mass spectrometer (AMS) measurements from Mace
Head support TDMA techniques from the same location, with a common relative
low organic mass fraction [Dall'Osto et al., 2010], and sporadic high organic events
[Ovadnevaite et al., 2011a]. The high organic fractions observed at Mace Head have
been argued as being of marine origin due to a lack of correlation between the
organic fraction and black carbon concentrations [O’Dowd et al., 2013], as well as
the use of carbon isotope analysis to identify organic sources [Ceburnis et al.,
2011].

### 2.3.2. Offline methods
For offline analyses the sample is collected on a substrate, such as a filter, and
the chemical composition is subsequently determined. The temporal resolution
of sample collection is generally coarser than that of online methods, typically of the order of hours. Size resolved off-line samples are commonly obtained using a cascade impactor, which collects particles at each stage based on their aerodynamic diameter. Similarly to AMS measurements, off-line analysis methods usually provide mass concentrations of particle components, and require a relatively high concentration. As such, off-line measurements of Aitken mode marine particle composition are relatively scarce.

Off-line chemical composition measurements at Mace Head have identified organics as a significant and sometimes dominant contributor to the sub micron primary marine aerosol, especially for sub-200 nm particles [O’Dowd et al., 2004]. There have been a number of off-line chemical composition studies of the marine aerosol at Mace Head [Cavalli et al., 2004; O’Dowd et al., 2004; Ceburnis et al., 2008; Facchini et al., 2008; Rinaldi et al., 2009]. These studies analysed size selected impactor samples using ion chromatography to reveal the concentration of inorganic ions. Water extraction and total organic carbon (TOC) analysis revealed the water soluble organic carbon (WSOC) concentration and thermal evolved gas analysis determined the total carbon (TC) concentration, and thus water insoluble organic carbon concentrations (WIOC) [Matta et al., 2003; Cavalli et al., 2004; Decesari et al., 2011]. In addition the organic composition was analysed using proton nuclear magnetic resonance (HNMR) spectroscopy [Decesari et al., 2000; 2007]. These observations indicated seasonality in the marine aerosol at Mace Head. Periods of high biological activity (spring through to autumn) can result in a dominant sub-micron organic mass fraction replacing a dominant sea-salt fraction observed during periods of low biological activity (winter) [Cavalli et al., 2004; O’Dowd et al., 2004; Yoon et al., 2007; Facchini et al., 2008; Rinaldi et al., 2010]. TOC mass fractions of up to 65% of the accumulation mode have been observed (defined as the 125-500 nm impactor stage) during periods of high biological activity and upwards of 80% of the 60-125 nm impactor stage [Cavalli et al., 2004; O’Dowd et al., 2004]. Note that the fraction of organics appears to vary depending on air mass back trajectories and biogenic activity. Some studies report dominant organics [O’Dowd et al., 2004] while others measurements indicate a sub-200 nm marine aerosol composition similar to that inferred from
hygroscopicity studies, with major contributions from NSS-sulfates and WSOC, particularly methanesulfonic acid (MSA) [Dall’Osto et al., 2010; Rinaldi et al., 2010]. For example [Rinaldi et al., 2010] observed an average NSS-sulfate mass fraction of 50% and water soluble organic matter of 23%, with the remaining contributions from sea salt, ammonium and WIOM.

During periods of low biological activity the TOC contributed 15% to the accumulation mode, which was dominated by sea-salt, 74%. This is due to both the slow down in biological activity and increased wind speeds during winter and appears to be consistent across all studies [Cavalli et al., 2004; O’Dowd et al., 2004; Yoon et al., 2007]. The seasonality observed in Aitken and accumulation mode particle composition follows that observed for concentrations and size distributions at Mace Head (Section 2.1).

There is distinct size dependence to the TOC to sea-salt ratio during periods of high TOC concentrations. This follows that expected from adsorption theory which suggests internally mixed organics will contribute increasing fractions as particle size decreases [Oppo et al., 1999]. A similar relationship was also observed in the hygroscopic growth data suggesting an increasing fraction of organics, internally mixed with either NSS-sulfate or sea-salt (Section 2.2.2.2).

Particle growth events, like that expected with an increased secondary organic concentration, were not observed during periods of TOC concentrations [O’Dowd et al., 2004]. In addition, super micrometre sea salt particles were relatively unaffected by changes in TOC concentration. The authors argue that if the TOC had a secondary source a larger proportion of organics should have condensed onto the large supermicron sea salt condensation sink [O’Dowd et al., 2004]. Little seasonal influence on the supermicron composition, which is dominated by sea-salt, was observed. A primary marine TOC source explains these discrepancies.

During periods of high biological activity the WSOC contribution was 18% and the WIOC was 45% across the accumulation and Aitken modes [O’Dowd et al., 2004]. Gradient flux measurements suggest that WSOC exhibits a downward flux at Cape Grim indicating that it is generally produced aloft and is therefore of secondary origin [Ceburnis et al., 2008]. These measurements showed the reverse
for WIOC, indicating a surface source, consistent with bubble bursting from the ocean [Ceburnis et al., 2008]. In addition laboratory measurements of the primary marine aerosol indicate a similar chemical signature to those observed during high WIOC events at Mace Head (Section 2.4.2). In summary, there is a relative constant secondary sulfate and organic source to Mace Head from spring to autumn, which contributes largely to the observed WSOC concentration. On top of this, sporadic primary organic production leads to enhanced WIOC concentrations due to a dominant organic SSA fraction.

Additional studies in the North Pacific, Southern Indian and Southern Oceans have undertaken similar analyses during periods of high biological activity [Sciare et al., 2009; Claeys et al., 2010; Miyazaki et al., 2010]. Only one of these studies reports sub-micrometre concentrations [Miyazaki et al., 2010] where the authors observed a sea salt mass fraction of approximately 45%, with organics (26%) and NSS-sulfates (23%), the other major contributors. WIOC and WSOC made up approximately equal portions of the TOC concentration. The concentrations of NSS-sulfate, WSOC, sea salt and WIOC suggests a contribution from both marine primary and secondary sources. These results are similar those obtained in the Austral and Southern Indian Oceans [Sciare et al., 2009; Claeys et al., 2010], as well as to that observed at Mace Head in the absence of SSA [Dall’Osto et al., 2010; Rinaldi et al., 2010].

Further sampling over the North Atlantic, Arctic and Southeast Pacific oceans [Russell et al., 2010] observed that organics accounted for 15-47% of the sub-micrometre particle mass. The observed sub-micrometre organic fraction was enhanced by factors of the order $10^2 - 10^3$ compared to that observed in the ocean water. Fourier Transform Infrared (FTIR) spectroscopy revealed that hydroxyl groups were the major organic functional group, comprising between 44 and 61% of the organic mass. This is consistent with sub-micrometre marine aerosol measurements from other locations around the U.S. [Russell et al., 2011]. The hydroxyl concentration was strongly correlated to sub-micrometre Na concentrations and wind speed indicating an association with SSA. This is consistent with scanning transmission X-ray microscopy near edge X-ray absorption fine structure (STXM-NEXAFS) analyses which clearly show an
internal mixture with hydroxyl functional groups coating inorganic sea-salt [Russell et al., 2009]. In addition the both organic and sea salt concentrations increased with an increasing mean diameter of the accumulation mode, suggesting possible cloud processing of this SSA source [Russell et al., 2009].

Electron microscopy and X-ray spectroscopy has also been used to examine summertime particle samples from the Southern Ocean, Macquarie Island and Cape Grim, as part of the ACE-1 campaign [Kreidenweis et al., 1998; Murphy et al., 1998]. The accumulation mode (80 – 200 nm) particles were shown to have a predominantly inorganic composition, with sea-salt number fractions of the order of 15-65% and sulfate number fractions of the order of 25-50%. Organic number fractions range up to approximately 20%. When heated to 300°C only refractory sea salt particles remained [Kreidenweis et al., 1998; Murphy et al., 1998]. For particles between 50 and 150 nm diameters, sea salt was present in 5-25% of the particles at Cape Grim and 5 to 47% of the particles at Macquarie Island. The authors suggest that particles smaller than 100 nm diameter are dominated by ammonium sulfate based on the crystalline structure observed from their diffraction pattern [Murphy et al., 1998]. These results are consistent with existing transmission electron microscopy (TEM) studies from Cape Grim which showed that the number fraction Aitken and accumulation mode particles are dominated by NSS-sulfates, making up greater than 95% of the particle number [Gras and Ayers, 1983]. A small sea salt component made up less than 5% of the total number, and at sizes of approximately 30 nm made up less than 1% of the total number. A third insoluble component, likely to be organics, was also observed to make up less than 1% of the particle number [Gras and Ayers, 1983].

In stark disagreement with the above results are subsequent summertime transmission electron microscopy (TEM) observations from Cape Grim [Bigg and Leck, 2008; Leck and Bigg, 2010]. These observations indicate that the composition of 50 nm diameter particles was not consistent with sea salt or non-sea salt sulfates and resemble organic particles thought to be from the sea surface microlayer [Leck and Bigg, 2010]. X-ray spectroscopy of these particles also revealed that Calcium was the most abundant element detected, along with sulfur. Sodium was near absent, suggesting that very little or no sea salt was
present [Leck and Bigg, 2010]. Authors argue that the observations of sub-200 nm SSA are misinterpretations and that the surface active exopolymers produced by bacteria and algae dominate the sub-200 nm primary marine aerosol [Bigg and Leck, 2008]. A more detailed review and analysis of the composition of the sub-100 nm primary marine aerosol at Cape Grim is available in Section 7.1 [Cravigan et al., 2014]. Further to the results from the Southern Ocean, summertime observations in the high Arctic indicate that the surface microlayer, and more particularly surface active exopolymer secretions of microalgae and bacteria, have a large impact on the marine aerosol composition and therefore CCN [Leck and Bigg, 2005a; 2005b; Bigg and Leck, 2008; Orellana et al., 2011; Karl et al., 2013].
2.4. Laboratory generated SSA

The size dependant chemical composition of SSA and how this relates to seawater composition is poorly understood and has been identified as having a large potential impact in climate modelling [Ganttt et al., 2012a; Meskhidze et al., 2013]. Atmospheric processing confounds measurements of ambient SSA composition and therefore laboratory generation mechanisms have been developed. These methods recreate the bubble bursting process that occurs on the ocean surface (See Section 1). Laboratory generated SSA composition can be directly paired to water phase composition, from which SSA emissions parameterisations are developed for use in atmospheric modelling. Bubble mediated SSA generation techniques indicate that particles are produced down to approximately 10 nm in diameter. When scaled to real oceanic conditions, the bubble chamber data generally suggest SSA should consistently form a dominant fraction of the total marine aerosol [de Leeuw et al., 2011]. The relative scarcity of sub-200 nm SSA in the marine environment is an indicator of the importance of loss mechanisms, such as cloud processing.

2.4.1. SSA generation mechanisms

A number of SSA generation techniques have been developed. These techniques vary in their ability to represent observed surface ocean bubble size distributions and therefore ambient SSA size distributions [Fuentes et al., 2010a]. Comparing primary marine size distributions to ambient size distributions is complicated by secondary impacts on the latter. Studies generally compare size distributions with those observed during high SSA events [Sellegri et al., 2006]. There is some indication that different generation mechanisms correspond to changes in SSA composition, however the direction and magnitude of these changes are not consistent between studies [King et al., 2013; Prather et al., 2013; Collins et al., 2014]. This suggests that differences in the design and operation of bubble-mediated aerosol generators may have an important influence.
2.4.1.1. Sintered glass

The sintered glass approach is the most common method for producing artificial SSA [Sellegri et al., 2006; Keene et al., 2007; Tyree et al., 2007; Sellegri et al., 2008; Modini et al., 2010a; Fuentes et al., 2011; King et al., 2013]. In this method particle free air is passed through porous sintered glass, which is submerged in water. This air forms bubbles, which rise to the surface of the water and burst. The size of the bubble produced using the sintered glass technique is dependant on the pore size of the sintered glass. This technique is common due to the ability to control the particle concentrations by controlling the airflow through the porous glass. There is some evidence to suggest that bubble size distributions using the sintered glass technique do not extend to sizes greater than 1 mm, unlike other techniques [Prather et al., 2013]. Observations have also shown minima in the bubble size distribution at approximately 50-200 μm, which appears to be unique to this technique [Fuentes et al., 2010a; King et al., 2013].

Particle size distributions for the sintered glass technique display a dominant mode at 40-100 nm as seen in Figure 5 [Keene et al., 2007; Fuentes et al., 2010a; Modini et al., 2010a; King et al., 2013; Prather et al., 2013; Long et al., 2014]. Lognormal modes at other sizes are generally much smaller than this primary mode. Observed ambient SSA size distributions are reported to contain an Aitken and an accumulation mode, as seen in Section 2.1.2 [Sellegri et al., 2006]. The primary criticism of the sintered glass technique is that it is effectively mono-modal and therefore does not represent the observed ambient SSA size distributions [Fuentes et al., 2010a; Prather et al., 2013]. Recent observations have suggested that there could be a morphological and therefore compositional influence on the SSA when produced using sintered glass [Collins et al., 2014]. TEM images indicate that SSA from sintered glass techniques are less cubic and may result in a higher organic fraction than those produced using plunging waterfall and wave chamber methods [Collins et al., 2014].

An in situ method for examining SSA has also been developed and is known as the Sea Sweep [Bates et al., 2012]. A housing floats on the ocean surface and a compressed air supply is passed through diffusion stones that are submerged under the water; the aerosol sample is collected from the hood of the housing [Bates et al., 2012]. The bubble generation mechanism and therefore the bubble
and particle size distributions are similar to that for sintered glass techniques [Bates et al., 2012].

Sintered glass SSA production from biologically active regions of the North West Atlantic and North West Pacific showed diurnal variability in the SSA mass and number fluxes [Long et al., 2014]. Following sunrise the SSA flux increased and then decreased again overnight in biologically active waters, this activity was not observed for oligotrophic waters. These results suggest the presence of sunlight–mediated biogenic material can enhance SSA concentrations and, although not measured, SSA composition [Long et al., 2014].

2.4.1.2. Plunging water

Impinging water onto the ocean sample from above entrains air into the surface layer. Turbulent mixing disperses the entrained air in a plume of bubbles, which rise to the surface and burst. This method is commonly applied to laboratory SSA studies [Sellegri et al., 2006; Facchini et al., 2008; Fuentes et al., 2010a; King et al., 2013; Prather et al., 2013]. Bubble size distributions from plunging water methods display a continuous decrease in particle number concentration as the diameter increases [Fuentes et al., 2010a; King et al., 2013] and extend to larger bubble diameters, up to approximately 2-3 mm [Prather et al., 2013]. Size distributions from plunging water are broader than those from sintered glass and display an Aitken and accumulation mode with approximately even concentrations [Fuentes et al., 2010a; Prather et al., 2013]. The presence of 2 modes suggests that plunging water improves the representation of ambient SSA size distributions compared to sintered glass, as seen in Figure 5. Concentrations generated using the plunging water method are generally lower than that from sintered glass techniques [Fuentes et al., 2010b], which leads to a broader size distribution. Low concentrations can also exclude mass based chemical composition measurements for sub-200 nm particles [Collins et al., 2014].

Continuously plunging water has been observed to create surface foam, particularly for water samples highly enriched in organics, which in turn can lead to a larger organic fraction in the aerosol phase [King et al., 2013; Collins et al., 2014]. Corresponding size distributions show an enhanced mode at
approximately 80 nm similar to that observed using sintered glass methods. Pulsed plunging has been used to ameliorate this impact, in this mode the water is plunged on a 4 seconds on/4 second off cycle [Collins et al., 2014]. The pulsed plunging method results in a broad size distribution with lower particle concentrations and a single peak at 160 nm [Stokes et al., 2013].
Figure 5: Typical size distributions for ambient SSA, as well as fritted glass, plunging water and wave breaking generated SSA.
2.4.1.3. Wave chamber
Recent studies have generated SSA using a linear wave channel [Prather et al., 2013; Stokes et al., 2013; Collins et al., 2014], in which breaking waves were induced using a hydraulic paddle. Bubble size distributions of the wave chamber compare favourably with those observed in whitecaps on the open ocean [Prather et al., 2013; Stokes et al., 2013]. In particular the production of bubbles between 3-10 mm in diameter appears unique to this method of bubble-mediated SSA production [Prather et al., 2013; Collins et al., 2014]. Wave chambers provide the closest proxy for ambient marine SSA production. Size distributions from the wave chamber are similar to those observed using the plunging waterfall, with a peak at approximately 160 nm (Figure 5). TEM images indicate that SSA from wave chamber techniques are less cubic than those from the other two methods, indicating a larger proportion of sea salt [Collins et al., 2014].

2.4.2. SSA composition
Observations from sub-200 nm bubble mediated SSA particles generally indicate the presence of sea salt with an internally mixed organic component. This organic component comprises a widely varying fraction of SSA (Table 3) and is observed to be primarily made up of water insoluble polysaccharides, proteins and lipids, exudate from marine algae [Russell et al., 2009; Fuentes et al., 2010a] as suggested by [Blanchard, 1975]. Some studies have also suggested a significant, and sometimes dominant, proportion of externally mixed organics in SSA. [Collins et al., 2013; Prather et al., 2013; Collins et al., 2014]. These externally mixed component do not contain a sea salt component and are shown as number fractions in Table 3. Similarly to the SSA observed in ambient studies, observations show an increase in the organic fraction with deceasing particle size [Keene et al., 2007; Facchini et al., 2008; Prather et al., 2013; Quinn et al., 2014]. Direct measurements of particle composition in the Aitken mode are often not possible due to insufficient SSA mass. Aitken mode composition can be more readily inferred from hygroscopicity measurements, also shown in Table 3. Variable organic fractions are also observed from volatility measurements. Studies in the north west Pacific and north west Atlantic oceans have indicated that the organic component is volatile at somewhere between 230 °C and 600 °C.
Further measurements from the south east Pacific have shown that the primary organic component is volatile below 200 °C, and have used this information to identify the organic volume fraction [Modini et al., 2010a]. The small (8%) and size independent (between 20 and 150 nm) volatile fraction was confirmed using the refractory HGF, which was very similar to that of inorganic sea salt [Modini et al., 2010b].

The variability in SSA organic fractions is largely attributed to spatial and seasonal distribution of marine biogenic material and reflects that reported for ambient marine particle studies. High sub-200 nm organic mass fractions have been observed during periods of high and low biological activity [Keene et al., 2007; Facchini et al., 2008; Ganttt and Meskhidze, 2012; Quinn et al., 2014], and lower organic mass fractions have been observed with relatively high water phase organic composition [Sellegrti et al., 2008; Modini et al., 2010a; Fuentes et al., 2011].

Chlorophyll-a (Chl-a) has been traditionally regarded as a marker for water phase organic activity, and it has been used in organic SSA flux parameterisations [O'Dowd et al., 2004; Vignati et al., 2010; Long et al., 2011]. Recent studies have suggested that Chl-a is not an ideal marker for the organic composition of SSA and that an ever-present pool of dissolved organic matter (DOM) provides the requisite organic matter required for the enrichment of SSA [Fuentes et al., 2010b; 2011; Quinn et al., 2014]. Further arguments suggest that although there are limitations on the applicability of Chl-a for SSA parameterisations it is the best metric currently available with global coverage [Rinaldi et al., 2013]. This highlights the uncertainty remaining with regard to the impact of the water phase on organic enrichment of SSA. It appears increasingly likely that a single metric is not sufficient to represent the complex surface water biology on a global scale.

On top of the natural organic SSA variation, measurement techniques appear to observe different features of the bubble mediated SSA. For example externally mixed organics are observed for both laboratory generated [Collins et al., 2013; Prather et al., 2013] and ambient [Leck and Bigg, 2005a; 2010; Leck and Svensson, 2014] SSA when using X-ray dispersive TEM. Other techniques that are
able to distinguish aerosol mixing state, such as TDMA, do not observe this [Modini et al., 2010a; Fuentes et al., 2011]. The possible influence of measurement technique is confounded by the apparently large natural variability in organic SSA fractions. Inter-comparison studies on common SSA sources are required to resolve this issue.

2.4.3. SSA hygroscopic properties
Organically enriched sea water acts to lower hygroscopic growth by 4-17% compared to that of seawater devoid of organics, suggesting an internal mixture dominated by inorganic salts [Sellegri et al., 2008; Fuentes et al., 2010a; Modini et al., 2010a; Bates et al., 2012]. The organic SSA fraction (discussed in Section 2.4.2) can be calculated using a modified version of the ZSR theory because the HGF probability densities show that the SSA is an internal mixture of sea salt and organics [Sellegri et al., 2008; Modini et al., 2010a; Fuentes et al., 2011]. It is worth noting that the HGF of SSA is lower than that of NaCl due to the presence of species such as NaSO₄. Organic volume fractions calculated by Fuentes et al. [2011] apply NaCl growth factors in the ZSR equation, rather than the commonly used artificial SSA, which could result in enhanced values.

The deviation between CCN counter (CCNc) derived and HGF derived hygroscopicity is low for laboratory nascent SSA [Wex et al., 2010; Fuentes et al., 2011; Bates et al., 2012] in contrast to some observations of ambient SSA [Ovadnevaite et al., 2011b]. This suggests that the organic component of ambient SSA is sourced from a relatively unique subset of marine surface water organics or that it is formed by secondary processes. Hygroscopicity techniques are valuable in determining the SSA composition in the low mass, sub-100 nm range where chemical analyses often cannot measure.
<table>
<thead>
<tr>
<th>Source</th>
<th>SSA source</th>
<th>Water sample</th>
<th>Location</th>
<th>Season</th>
<th>Water composition [μg/L]</th>
<th>Measurement technique(s)</th>
<th>Hygroscopic growth</th>
<th>Particle size</th>
<th>Org. frac.</th>
<th>Weight factor</th>
<th>Organic composition</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinn et al. 2014</td>
<td>Fritted glass (Sea sweep)</td>
<td>High Chl-a taken 315 km off the U.S. East coast.</td>
<td>North West Atlantic</td>
<td>Autumn</td>
<td>POC=228 DOC=1068 Chl-a=7.1</td>
<td>IC, FTIR, EGA</td>
<td>-</td>
<td>&lt;180 nm</td>
<td>52%</td>
<td>mass</td>
<td>Hydroxyl 40% Alkanes 47% Amine 13%</td>
<td>Organic mass by volume was 54% averaged for high and low Chl-a.</td>
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<td>CCNc k=0.9</td>
<td>100 nm</td>
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<td>40%</td>
<td>volume</td>
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<td>Organic composition measurements (FTIR) were undertaken for &lt;1 μm particles.</td>
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<td></td>
<td>CCNc k=0.4</td>
<td>40 nm</td>
<td></td>
<td>80%</td>
<td>volume</td>
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<tr>
<td>Quinn et al. 2014</td>
<td>Fritted glass (Sea sweep)</td>
<td>Low Chl-a taken from Sargasso Sea.</td>
<td>North West Atlantic</td>
<td>Autumn</td>
<td>POC=27.6 DOC=864 Chl-a=0.03</td>
<td>IC, FTIR, EGA</td>
<td>-</td>
<td>&lt;180 nm</td>
<td>48%</td>
<td>mass</td>
<td>Hydroxyl 52% Alkanes 35% Amine 13%</td>
<td>Organic mass by volume was 54% averaged for high and low Chl-a.</td>
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<td>40 nm</td>
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<td>80%</td>
<td>volume</td>
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<tr>
<td>Facchini et al. 2008</td>
<td>Plunging water</td>
<td>Samples taken from up to 400 km off Irelands west coast during MAP campaign.</td>
<td>North East Atlantic</td>
<td>Summer</td>
<td>Chl-a=1.4*10^6</td>
<td>IC, TOC, EGA, HNMR</td>
<td>-</td>
<td>125-250 nm</td>
<td>77%</td>
<td>mass</td>
<td>WIOM 94% WSOM 6%</td>
<td>Both WIOM and WSOM contained: -hydroxylated moieties of sugars (enriched in WIOM), esters and polyols; -aliphatic groups adjacent to carboxyls, amides and acids -aliphatic chains with terminal methyls, typical of lipids (enriched in WIOM).</td>
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<tr>
<td>Prather et al. 2013;</td>
<td>Wave channel</td>
<td>Sampled from coastal waters La Jolla California.</td>
<td>North East Pacific</td>
<td>-</td>
<td>Chl-a=0.18 TOC=830</td>
<td>TEM-EDX, AMS, CCNc, DASH-SP</td>
<td>HGF = 2.4</td>
<td>60-180 nm</td>
<td>OC 26% SS-OC 55%</td>
<td>number</td>
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<td>Collins et al. 2013</td>
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Table 3: Summary of studies using laboratory generated SSA.

| Source | SSA source | Water sample | Location | Season | Water composition [μg/L] | Measurement technique(s) | Hygroscopic growth | Particle size | Org. frac. | Weight factor | Organic composition | Comments |
|--------|------------|--------------|----------|--------|--------------------------|--------------------------|----------------------|---------------|------------|-------------|---------------------|-----------|----------|
| Prather et al. 2013; Collins et al. 2013 | Wave channel | Bacteria added to above. | North East Pacific | - | Chl-a=0.4 TOC=1070 | TEM-EDX, AMS, CCNc, DASH-SP | HGF = 2.2 κ=0.81 | 60-180 nm | OC 62% | SS-OC 28% | number | - | As above except Alteromonas spp. bacter is added. |
| Prather et al. 2013; Collins et al. 2014 | Wave channel | As above, bacteria left to grow ~1 day. | North East Pacific | - | Chl-a=0.1 TOC=1070 | TEM-EDX, AMS, CCNc, DASH-SP | HGF = 2.3 κ=0.21 | 60-180 nm | OC 85% | SS-OC 3% | number | - | As above except Alteromonas spp. bacteria left to grow for approx 1 day. |
| Prather et al. 2013; Collins et al. 2015 | Wave channel | As above with algae added. | North East Pacific | - | Chl-a=2.11 TOC=1640 | TEM-EDX, AMS, CCNc, DASH-SP | HGF = 2.2 κ=0.2 | 60-180 nm | OC 16% | SS-OC 84% | number | - | As above except Dunaliella tertiolecta algae added and left to grow for approx 2.5 days. |
| Bates et al. 2012 | (Sea sweep) | Off the coast of California | North East Pacific | Spring | POC=1100 Chl-a< 15 | IC, TOA, AMS, FTIR CCNc and VH-TDMA | HGF ~ 1.9 | < 1 μm | <4% | mass | non-oxygenated 57.7% (~50% unsaturated) oxygenated 40% | HGF was measured at 50-150 nm and was approximately 10% lower than for artificial SSA. HGF not kelvin or shape factor corrected. |
| Keene et al. 2007 | Fritted glass | Typical of Saragossa Sea | North West Atlantic | Autumn | TOC=840 | IC, TOC | NA | 130 nm | 80% | mass | - | - |
| Modini et al. 2010 | Fritted glass | Collected from Moreton Bay, Brisbane. | South west Pacific | Summer | Chl-a~1-3.2 | VH-TDMA | 2.26 | 71-77 nm | 8% | volume | - | Organic fraction estimated from the difference in volatility between natural SSA samples and artificial SSA and confirmed using HGF. HGF kelvin and shape corrected. |
Table 3: Summary of studies using laboratory generated SSA.

| Source          | SSA source | Water sample       | Location                                | Season | Water composition [μg/L] | Measurement technique(s) | Hygroscopic growth | Particle size | Org. frac. | Weight factor | Organic composition | Comments                                                                 |
|-----------------|------------|--------------------|-----------------------------------------|--------|--------------------------|--------------------------|----------------------|---------------|------------|-------------|----------------|-------------------|--------------------------------------------------------------------------|
| Fuentes et al. 2011 | Plunging water | Seawater proxies  | Based on seawater composition measurements from equatorial Atlantic | -      | DOC=2100-6144            | H-TDMA, CCNc            | HGF=2.05-2.29         | 40-240 nm     | 8.37%      | volume      |                      | Algal exudates used as seawater organic proxies. Results from single exudates reported here, however Fuentes et al. 2011 indicates that mixtures displayed similar results. Inorganic growth factor for NaCl (2.35) was used to calculate organic fraction. Algal species used were Thalassiosira rotula (Diatom), Chaetoceros sp. (Diatom), Emiliana huxleyi (Coccolithophore), Phaeocystis cf. globosa (Prymnesiophyte). |

1. Abbreviations for measurements techniques are:  
   - Ion chromatography (IC)  
   - Fourier transform infra-red spectroscopy (FTIR)  
   - Evolved gas analysis (EGA)  
   - Total organic carbon (TOC). Used on filter extractions, usually to obtain the WSOC concentration.  
   - Proton nuclear magnetic resonance (HNMR)  
   - Differential aerosol sizing and hygroscopicity spectrometer probe DASH-SP  
   - Thermal optical analysis (TOA)  
   - Transmission electron microscopy with energy dispersive X-ray (TEM-EDX)  
   - Aerosol mass spectrometry (AMS)  
   - Cloud condensation nuclei count (CCNc)  
   - Volatility, hygroscopic tandem differential mobility analyser (VH-TDMA).
2.5. Climate influences

The aerosol indirect radiative forcing provides the largest source of uncertainty to climate modelling and thus projections of future climate patterns [Andreae and Rosenfeld, 2008]. Modelling studies have recently been undertaken to quantify the parameters that are most important to this uncertainty [Carslaw et al., 2010; Lee et al., 2011; 2012]. Natural emissions contribute approximately 45% of the variance in globally averaged aerosol forcing since the pre industrial period, while anthropogenic emissions contribute 35%. Natural emissions include volcanic SO₂, marine biogenic emissions of DMS and organics, biomass burning and SSA [Carslaw et al., 2013]. This highlights the need to understand emissions from pristine environments and the atmospheric processing in these environments.

The globally averaged radiative forcing largely provides information on the global temperature change and does not provide information on regional influences, such as changes in the distribution of phytoplankton populations or wind speed patterns [Woodhouse et al., 2013]. It also cannot be simply extended to modelling of parameters such as precipitation. Therefore it is necessary to examine the impact of modelling variables on CCN concentrations. Uncertainties in the droplet activation diameter for stratiform clouds and the diameter at which precipitation scavenging begins, are the two most important marine processes with regard to CCN uncertainty [Lee et al., 2012]. The uncertainty in these 2 parameters currently ranges from 40-125 nm and 80-250 nm, respectively. The droplet activation diameter is of particular importance over the tropospheric and mid-latitudinal oceans, and in particular the equatorial West Pacific. The scavenging diameter is most important in the Southern Ocean along with variability in sea salt emissions. Uncertainty in sea salt emissions vary by 2 orders of magnitude and high wind speeds in the Southern Ocean exacerbate this influence [Lee et al., 2012].

In summary to reduce the uncertainty in modelled marine CCN concentrations an enhanced understanding of the composition dependent activation diameter, the SSA flux and the precipitation sinks for particles in the Aitken and accumulation modes is required. This section briefly relates the observations
reported in Sections 2.1 to 2.4, to the properties most important with regard to reducing modelling uncertainty.

2.5.1. Modelling marine particles

A number of SSA emissions functions (also known as source functions or parameterisations) have been developed relating wind speed to size resolved SSA flux at the oceans surface. At sizes less than 200 nm the SSA flux can vary by approximately 2 orders of magnitude [Lewis and Schwartz, 2004; de Leeuw et al., 2011; Ovadnevaite et al., 2014], highlighting the considerable uncertainty in bubble mediated aerosol production. Source functions tend to over-predict sub-200 nm boundary layer number concentrations [de Leeuw et al., 2011]. Under prediction of SSA concentrations could be the result of stronger than expected SSA sinks, which is supported by a lack of sub-200 nm SSA observed in TDMA measurements [Swietlicki et al., 2008; Cravigan et al., 2014]. For example during high wind events increased SSA production has been shown to be offset by even moderate precipitation rates [Blot et al., 2013]. Scavenging processes have been shown to be particularly important in the Southern Ocean where SSA production is high.

More recent SSA source functions have included parameters such as temperature [Ovadnevaite et al., 2014], Chl-a [Gantt et al., 2011], wave height and wind history [Ovadnevaite et al., 2014]. Parameterisations can use Chl-a, or some other marker for biogenic activity, to estimate organic SSA fluxes. The role of organic SSA on the cloud droplet activation diameter of SSA as yet is difficult to determine due to the uncertainties in Aitken and accumulation mode SSA composition. Estimates have indicated that marine organics could result in a 7% decrease in the aerosol indirect forcing, through a small increase in global CCN concentration of 1.5% [Gantt et al., 2012a]. Areas with high SSA emissions, the Southern, North Pacific and Atlantic Oceans are most strongly influenced.

2.5.2. CCN and cloud processes

The dominant fractions of marine particles, NSS-sulfates and SSA, have high hygroscopicity and therefore activate as CCN at relatively small sizes. Mass is added to these activated particles via aqueous phase chemistry, collision coalescence and gas-to-particle conversion due to their increased size [Blot et al,
2013]. This results in a larger evaporated particle and therefore reduces the number of particles at the critical diameter for droplet activation. This reduction is observed in marine size distributions and is known as the Hoppel minimum [Hoppel et al., 1986] (Section 2.1.2). The Hoppel minimum can be used to estimate the supersaturation at which a population of particles was activated [Blot et al., 2013]. Cloud processing of marine particles can also lead to changes in particle composition, influencing the critical diameter. CCN concentrations have an influence on cloud properties, and therefore radiative forcing and rainfall. For example cloud level observations of CCN have shown that a combination of high droplet number concentrations and lower updraft velocities close to the coast can reduce the cloud droplet size and cloud albedo [Twohy et al., 2013].
2.6. Summary and knowledge gaps

Particle Characterisation
Remote marine environments are characterised by low particle concentrations of less than approximately 1000 cm\(^{-3}\) (Section 2.1.1). Size distributions in these environments are generally bimodal, with an Aitken and accumulation mode separated by a Hoppel minimum (Section 2.1.2). The Hoppel minimum is a result of particle growth associated with cloud processing. Enhanced gas to particle conversion, collision coalescence and aqueous phase chemistry after cloud droplet activation results in growth of the evaporated particle (Section 2.5.2).

Marine aerosol composition
Hygroscopic growth factor and chemical composition measurements indicate that the ambient sub-200 nm remote marine aerosol is dominated by NSS-sulfates, externally mixed with a small and infrequently observed SSA component (Sections 2.2.2 and 2.3).

Sea spray aerosol
When they are observed, sea salt particles frequently make up a small proportion of the sub-200 nm aerosol number concentration. Sea salt concentrations in the clean marine environment vary from approximately 1 cm\(^{-3}\) to 200 cm\(^{-3}\) (Section 3.2.2). SSA emissions parameterisations tend to over-predict concentrations of SSA (Section 2.5.1). The over-prediction of SSA concentrations in the atmosphere are likely to be due to limited understanding of SSA sinks in the atmosphere. For example scavenging from modest enhancements in rainfall have been observed to offset additional production during high wind speed events (Section 2.5). Further observations of size resolved ambient SSA concentrations and corresponding air mass properties are required to identify the atmospheric sinks for SSA.

A dominant organic fraction consistent with SSA enriched with surface active material has been observed in the North Atlantic Ocean during periods of high biological activity (Section 2.3.2).

Laboratory SSA generation methods produce different bubble and particle size distributions, it is unclear the degree to which these influence SSA composition.
Laboratory generated SSA composition indicates a broad range of organic enrichment, with organic fractions of approximately 8-80%, the precise impact of water phase composition is unclear (Section 2.4.2). Mass based chemical composition measurements have a lower size limit of ~60 nm diameter. SSA can be activated into cloud droplets at diameters at or below this lower limit. Volatility and sub saturated hygroscopic growth based estimates of the organic fraction range from approximately 8 to 37% (Section 2.4.2).

Measurements using TEM and X-ray dispersive spectroscopy have also identified an externally mixed organic SSA component in both ambient measurements (Section 2.3.2), and laboratory chamber studies (Section 2.4.2). These results are in stark contrast to those using other methods.

**Vastly varying organic enrichment of SSA and varying SSA mixing states do not correlate well with water phase organic markers.** In addition there appear to be instrumental biases in organic SSA measurements. Further observations are required across a greater variety of ocean basins. These studies need to assess the suitability of ocean water metrics for organic composition, such as Chl-a, for indicating the organic SSA fraction. In addition measurements should be undertaken using multiple measurement techniques to assess the impact of instrumental biases and cover the size range important for activation of SSA into cloud droplets i.e. sub-100 nm.

**Climate**

Natural aerosol emissions and processes in pristine environments such as the remote oceans contribute 45% to the aerosol forcing uncertainty. Key climate modelling parameters for reducing CCN concentration uncertainty include the composition dependant cloud droplet activation diameter, the critical diameter for rainfall induced scavenging and the emission flux of SSA. These variables are of particular importance across the Southern and South Pacific Oceans.
3. **Experimental procedures**

3.1. **Objectives**

Objectives of this study are to:

1. Measure the ambient sub-200 nm volatility and hygroscopicity (and thus inferred composition) of Southern and Pacific Ocean derived SSA.
2. Measure laboratory generated SSA volatility and hygroscopicity (and thus inferred composition).
3. Determine if there is an influence on SSA composition from water phase composition for high biological activity and oligotrophic waters.
4. Determine if the relationship observed differs significantly from that observed elsewhere (e.g. the Northern Hemisphere).

The above objectives were met through investigations undertaken during the following three observational campaigns in the southwest Pacific and Southern Oceans.

1. **Cape Grim.** From 22 November 2007 to 11 December 2007 ambient aerosol observations were undertaken at the Cape Grim Baseline Air Pollution Station (BAPS) on the northwest tip of Tasmania, Australia.
2. The Surface Ocean Aerosol Production pilot study (pre-SOAP) was a ship-based campaign undertaken from 1-12 February 2011 along the Chatham Rise off the east coast of New Zealand.
3. The CORACE (CORal Aerosol Characterisation Experiment) campaign was conducted at the Heron Island Research Station (HIRS, 23°26’34”S, 151°54’48”E) in the southern end of the Great Barrier Reef (GBR) from 26 May to 14 June 2011.
3.2. Methodology

3.2.1. VH-TDMA

Aerosol volatility, hygroscopicity and compositional information were obtained with a custom-built VH-TDMA [Johnson et al., 2004]. This instrument was used during all three observation campaigns, associated equipment for each of the campaigns are outlined in the following sections. The VH-TDMA is a particle sizing instrument that selects particles based on mobility diameter, conditions them, and then measures the resulting particle size distributions using two parallel scanning mobility particle sizers (SMPS), each with a TSI 3010 condensation particle counter (CPC), (TSI 3010, Shoreview, MN, USA), as shown in Figure 6.

The saturator temperature difference was set to 21°C in both 3010 CPCs and the counting efficiencies updated accordingly to extend the lower size limit of the CPCs down to 5 nm diameter [Mertes et al., 1995]. The VH-TDMA combines humidification and volatilisation conditioning to examine hygroscopic properties of the aerosol fraction remaining after volatilisation. It can be used to distinguish between two components of sub-micron heterogeneously mixed particles, and is especially useful in distinguishing between components displaying significantly different hygroscopic properties [Johnson et al., 2004]. The VH-TDMA provides valuable information on the mixing state of marine particles, which is of particular interest because of recent studies highlighting the importance of externally mixed organics [Leck and Bigg, 2005b; 2010; Collins et al., 2013; Prather et al., 2013].
The VH-TDMA measured sub-100 nm mode particles and was run in several operating modes:

1. Volatility mode. For a fixed preselected particle size the humidity was kept constant at relative humidity (RH) 90% and the temperature of the thermodenuder was scanned from room temperature to as high as 500°C (note scanning was stopped when there was no appreciable particle fraction remaining). Changes in the HGF observed during this temperature scan can result from the evaporation of non-refractory components in the thermodenuder (e.g. organics, sulfate).
2. H-TDMA mode. When the thermodenuder was kept at room temperature the instrument operated as a standard H-TDMA. In H-TDMA mode two further modes of operation were utilised: 1) HGF mode where the instrument was operated at fixed 90% RH, and 2) deliquescence mode where the RH was ramped from 60 to 90% in steps as small as 0.5% [Johnson et al., 2008]. Deliquescence curves provide clearer differentiation between different inorganic salts (e.g. ammonium sulfate and sodium chloride) and internally mixed inorganic-organic particles than is possible from HGF measurements at a single RH.

The two primary variables calculated with the VH-TDMA are the temperature dependant HGF and volume fraction remaining (VFR). The VFR is given by:

$$VFR = \frac{d_T^3}{d_0^3}$$

Where $d_T$ is the dry particle diameter at temperature T and $d_0$ is the dry particle diameter at ambient temperature. Assuming a DMA sizing accuracy of ±1% and a RH uncertainty of ±0.6% the VFR and HGF have an uncertainty of ±3% at the 95% confidence level [Modini et al., 2010a].

All VH-TDMA data were inverted using the TDMAinv algorithm [Gysel et al., 2009]. This provides a correction to the measured diameter growth factor distributions, which are a skewed and smoothed version of the actual growth factor probability density function (GF-PDF). Furthermore the measured GF-PDF can contain the contribution from particles with a larger dry diameter but carrying multiple charges because the electrical mobility of these particles is the same as singly charged particles with diameter equal to that set in the pre-DMA [Gysel et al., 2009].

3.2.2. Cape Grim

From 22 November 2007 to 11 December 2007 aerosol observations were undertaken at the Cape Grim Baseline Air Pollution Station (BAPS) on the northwest tip of Tasmania, Australia. The details for these measurements, including instrumentation used, are outlined in Section 7.1.
3.2.3. Surface Ocean Aerosol Production pilot study

The Surface Ocean Aerosol Production pilot study (pre-SOAP) was a ship-based campaign undertaken from 1-12 February 2011 by the New Zealand National Institute for Water and Atmosphere (NIWA). The RV Tangaroa was deployed along the Chatham Rise off the east coast of New Zealand, Figure 7 shows the voyage path. The Chatham Rise is characterised by intensive summer phytoplankton blooms, and is in particular dominated by large coccolithophore blooms, a phytoplankton species identified as a significant source of DMS. This campaign aimed to characterise the ocean-atmosphere interaction for blooms of this type. The production of aerosol precursors in the surface ocean during a coccolithophore bloom and the physical properties and inferred chemical composition of particles in the marine boundary layer were examined.

Regions of phytoplankton bloom were identified via satellite imagery. Continuous on board measurements from the ships underway supply, which draws in ocean water from approximately 7 metres below the surface, were also used to locate blooms. Continuous sampling included measurements of Chl-a, DMS, 660 nm wavelength backscatter (B660) and the partial pressure of CO₂ (pCO₂) in the water. Bloom 1 was located approximately 250 km to the south of the New Zealand North Island (Figure 7) and was identified due to elevated underway Chl-a and DMS concentrations and low pCO₂ concentrations. This region was occupied for 5 days (1/2/2011-6/2/2011). On the 6/2/2011 the ship travelled west for a bloom 2, north west of the Chatham Islands (Figure 7), identified from satellite imagery. This region was characterised over the 8-9/2/2011. B660 was high, which is a marker for the presence of coccolithophores [Tyrrell et al., 1999], however DMS concentrations were unexpectedly low. The ship then travelled west to Bloom 3 (Figure 7) which was identified from the underway observations made during the easterly transect between Blooms 1 and 2. This region was characterised on 10/02/2011 by low pCO₂ concentrations, high Chl-a and DMS concentrations.
Figure 7: Pre-SOAP voyage track coloured by observed Chl-a concentration.

The VH-TDMA was operated during this campaign as described in Section 3.2.1. Particle size distributions were obtained using an SMPS, with a TSI 3080 classifier and a TSI 3772 CPC. Ambient marine aerosol sampling was undertaken during preSOAP, however due to the absence of observed SSA, will not be reported on in detail here. During pre-SOAP water samples were taken and used to generate SSA via the sintered glass production method. 5 litres of sample water were added to a purpose built chamber (cylindrical Perspex chamber 1.5 m in length, 0.2 m in diameter). Particle free compressed air flowed through 2 sintered glass filters, with porosity ranging from 40 to 160 μm, at approximately 10 litres per minute to create bubble mediated SSA, which was sampled by the VH-TDMA and SMPS from the headspace of the chamber.

The following water samples were taken for bubble mediated SSA production:

- 8-February (surface workboat sample taken during bloom 2)
- 9-February (surface workboat sample taken during bloom 2)
- 10-February (surface workboat sample taken during bloom 3)
- 11-February (7-metre depth sample taken just off-bloom 3)

All 7-metre samples were taken from the ships underway supply, which draws ocean water in from the hull, under the ocean surface. Surface samples were taken during workboat experiments, when a small boat launched from the RV Tangaroa for the purpose of taking ocean surface measurements away from the ship.
Bubble mediated SSA volatility and hygroscopicity were compared with volatility and hygroscopicity measurements of artificial sea salt (art SSA) samples. The artificial sea salt was made by dissolving a mixture of analytical grade inorganic salts in ultra pure deionised water. NaCl dominates the mass fraction of sea salt, with contributions from magnesium chloride (MgCl₂), sodium sulfate (Na₂SO₄), calcium chloride (CaCl₂), potassium sulfate (K₂SO₄), sodium bromide (NaBr) and potassium nitrate (KNO₃). Inorganic salt ratios followed those used in [Modini et al., 2010a]. A number of combinations of sea salt solutions were tested with varying ionic compositions and results were averaged to obtain a single temperature dependant VFR and HGF for artificial sea salt. Uncertainties in these values are taken to be either the standard error across multiple artificial sea salt samples or the uncertainty of measurement for the VH-TDMA. The largest of these two values is applied. Artificial SSA contains no organic components and therefore VFR and HGF measurements provide a baseline with which to compare SSA from natural seawater samples.

Measurements were taken at number of pre-selected particle diameters, ranging from 15 to 150 nm. To remove the influence of the Kelvin Effect on the HGFs Equation 8 and Equation 10 were used to convert to bulk HGFs (i.e. where \( a_w = \frac{RH}{100} = 0.9 \)). HGFs of non-spherical particles, such as NaCl, should be corrected for shape effects. Given recent uncertainty surrounding the cubic nature of SSA particles, particularly from sintered glass sources, the shape correction has not been applied here. The underlying assumption is that artificial SSA produced using the sintered glass frits and natural SSA using the same method have a similar shape. The sensitivity of calculated OVF to shape correction is carried out for the CORACE results and described in Section 4.3.

Some preliminary results from ambient measurements taken during the subsequent SOAP voyage in February and March 2012 are also presented for comparison in Section 7.2.

3.2.4. Coral Aerosol Characterisation Experiment
The CORACE campaign was a collaborative research project between QUT (Queensland University of Technology – Brisbane) and SCU (Southern Cross University – Lismore). CORACE-1 was conducted at the Heron Island Research
Station (HIRS, 23°26′34″S, 151°54′48″E) in the southern end of the Great Barrier Reef (GBR) in South Pacific Ocean from 26 May to 14 June 2011. Figure 8 shows the location of HIRS with respect to the GBR and the nearby industrial hub of Gladstone (approximately 85 km away). This experiment aimed to establish whether the DMS and secondary organics produced by coral reefs could influence sub-200 nm aerosol concentration and composition. The VH-TDMA was used during this campaign to characterise the ambient marine aerosol as described in Section 3.2.1.

The second aim of this campaign was to examine the impact of water phase organic matter associated with coral on the composition of SSA. As such laboratory generated SSA from coral waters was also analysed, and is the focus herein. Bubble mediated SSA observations were taken following the methodology outlined for the preSOAP voyage (Section 3.2.3). The following water samples were taken and used to generate laboratory SSA samples:

- 4-June (coral water)
- 6-June (high tide water)
- 7-June (low tide water)
- 5-June (tap seawater)
- 11-June (coral water)
- 13-June (open ocean water)

Water samples collected with coral samples contained are referred to as coral water samples. Note that the coral was removed from the sample before it was used to generate SSA. High tide and low tide samples were collected from local lagoon and tap seawater utilised the HIRS seawater supply, which is drawn from off Herron Island coast. Open ocean water was collected by boat away from Herron Island and surrounding reefs. Natural seawater SSA was compared to that of artificial, organic free SSA to determine the organic fraction of natural samples. The volatile organic fraction was calculated from the difference between the artificial SSA volume fraction remaining and the natural SSA volume fraction remaining averaged over 250 to 450 °C. This temperature range was chosen, as the slope of the VFR is relatively constant over this region. This is because the volatile and semi-volatile organic components have been observed
to evaporate at below 200°C and the refractory components, such as sea salt begin dissociate at above 500 °C [Modini et al., 2010a]. Preselected particle sizes were 50 and 60 nm, therefore the impact of size on the organic fraction is not available from these measurements. Kelvin corrections were applied to the measured HGFs to enable comparison between measurements at different sizes. HGFs and resulting OVF s were calculated with and without a shape correction factor applied to examine the impact of particle morphology. A size independent shape correction factor of 0.90 was used [Biskos et al., 2006c]. This factor was determined by calculating the shape correction factor for 40 nm particles, and was deemed appropriate for use over the small range of particle sizes considered.

Water samples were collected for total organic and inorganic carbon (TOC and TIC) and chlorophyll-a. Analysis of TOC and TIC samples was carried out using an OI Analytical Aurora TOC analyser (OI Analytical, College Station, TX). Absorbance of chlorophyll-a samples was determined by spectrophotometry [APHA, 1998].

![Figure 8: Location of HIRS (green), Gladstone (yellow) and the GBR (dark patches).]
3.2.5. Data analysis
The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Rolph, 2013] was used to identify the air mass properties associated with VH-TDMA observations. These back trajectories were computed using meteorological data from the NOAA/NCEP Global Data Assimilation System (GDAS) [Kanamitsu, 1989]. Using HYSPLIT we obtained 7-day back trajectories for each hour of the 3 campaigns, these were compared to particle measurements at the measurement locations. Of particular interest were the modelled back trajectory altitude, relative humidity, rainfall and mixing height. 6 hourly surface wind speed data observed from the Cross-Calibrated Multi-Platform (CCMP) data set were extracted along the back trajectories. The CCMP data set includes cross-calibrated satellite winds derived from a variety of satellite instrumentation on a 0.25° grid e.g. QuikSCAT, SeaWinds, Windsat [Atlas et al., 2013].
4. Results

4.1. Cape Grim

Section 7.1 examines a high sub-100 nm SSA event observed on 7-8 December 2007 at Cape Grim. VH-TDMA analysis from this event identified two sub-100 nm particle HGF modes. The more hygroscopic mode was identified as being NSS-sulfates as it was volatile between 160 and 180 °C and displayed prompt deliquescence at 80% RH. The very hygroscopic mode was refractory to 300 °C and displayed prompt deliquescence at 80% RH, and was therefore determined to be SSA. The HGF of the very hygroscopic mode suggests that inorganic salts with an organic content of up to 5% dominated SSA.

4.2. Pre-Surface Ocean Aerosol Production study (pre-SOAP)

Laboratory SSA generation results are presented here from the preSOAP voyage. Although ambient air measurements were undertaken, these measurements were dominated by NSS-sulfates and no significant SSA events were observed. This is typical of H-TDMA measurements in the remote marine environment. A summary of the results from a campaign undertaken in the same region, using the same instrumentation, the following year are included in Section 7.2. These results provide an indication of the sub-200 nm ambient marine aerosol over the Chatham Rise.

4.2.1. Laboratory generated SSA

During the pre-SOAP voyage 4 water samples were collected and used to generate primary SSA in a purpose built chamber, as described in Section 3.2.3 and outlined in Table 4. No water samples were taken during bloom 1, B660 values during bloom 2 indicate that it had the highest coccolithophore concentration, as expected. The sample taken from bloom 3 had the highest Chl-a concentration, however the variation between blooms is relatively low.
Table 4: Ocean water sample collection details and properties.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Bloom</th>
<th>Depth (m)</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Water temperature (°C)</th>
<th>Chl-a (µg/L)</th>
<th>B660 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/02/2011</td>
<td>11:00</td>
<td>2</td>
<td>5</td>
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<td>181.94</td>
<td>15.9</td>
<td>0.97</td>
<td>0.13</td>
</tr>
<tr>
<td>9/02/2011</td>
<td>11:00</td>
<td>2</td>
<td>0</td>
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<td>181.62</td>
<td>16.5</td>
<td>0.42</td>
<td>0.11</td>
</tr>
<tr>
<td>10/02/2011</td>
<td>11:00</td>
<td>3</td>
<td>0</td>
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<td>178.75</td>
<td>15.8</td>
<td>1.23</td>
<td>0.11</td>
</tr>
<tr>
<td>11/02/2011</td>
<td>14:00</td>
<td>Outside</td>
<td>3</td>
<td>-43.34</td>
<td>178.83</td>
<td>16.0</td>
<td>0.64</td>
<td>0.11</td>
</tr>
</tbody>
</table>

8-February surface sample

The first sample was taken at approximately 12:00 on 8 February 2011 from the workboat launched off the RV Tangaroa over phytoplankton bloom 2. The size distribution HGF, VFR and organic volume fraction (OVF) of SSA generated from this sample are shown in Figure 10. The size distributions are consistent with that seen for other sintered glass SSA generation studies with a dominant single mode at 100 nm (Figure 10A), which is on the upper end of that observed in previous studies (Section 2.4.1.1). The natural seawater sample VFR follows that of artificial sea salt, with a small volatile organic fraction of 7±5% and 8±5% observed for 45 and 68 nm particles, respectively (Figure 10B). At between 180 and 250°C an increase in the VFR of the natural seawater sample to values above that of the artificial SSA is observed. There is no apparent reason for this and measurements at subsequent, higher temperatures show a lower VFR for natural seawater than that for artificial SSA, which indicates that this could be an instrument artefact.

Kelvin corrected HGF probability distributions for the natural seawater sample displayed a single mode with median HGFs ranging from 1.92 - 2.01 at 60 °C. These particles also displayed reasonably rapid deliquescence at approximately 75%, consistent with the deliquescence point of artificial SSA. This indicates that the SSA is an internal mixture of sea-salt, with a small organic component. HGFs increased by 0.07 - 0.12 from between 60 and 300 °C, however HGFs did not reach that for artificial SSA, suggesting a residual refractory organic component. Across the same temperature range Kelvin corrected HGFs for artificial SSA samples increased by 0.04 (Figure 10C). This suggests that approximately half of
the increase in HGF was due to the volatilisation of inorganic salts in SSA, such as NaSO₄. A small additional increase in natural seawater HGF of 0.03-0.08 is due to the volatilisation of a component not present in the artificial SSA i.e. an organic component. Using the ZSR assumption (2.2.1.3) this corresponds to a volatile organic fraction of 4 to 11%. The volatile organic fraction inferred from HGF measurements at 300 °C are larger than, but consistent with (within experimental uncertainty), those inferred from volatility for sizes except 23 nm.

Total OVF are estimated by adding the volatile organic component inferred from volatility measurements to the organic composition at each temperature inferred from the HGF under the ZSR assumption (Figure 10D). The uncertainty in the total OVF is large, however there is distinct size dependence, with larger particles displaying a larger organic fraction. The OVF should be independent of temperature because volatile components shift from being represented by the HGF to being represented by the VFR as the temperature increases. The observed decreases in the OVF with increasing temperature (Figure 10D) could be due to a suppressed HGF at low temperatures. The water volume uptake for the natural seawater samples 300 °C is 17 to 25 % greater than at 60 °C, suggesting that the water uptake of the refractory component may be suppressed by the volatile organic component. This would act to enhance the change of HGF as the temperature increases and explains the apparent difference between the organic volume fractions indicated by the volatile and hygroscopic measurements.
Figure 9: Deliquescence curves for ambient temperature 47 nm particles generated from surface sample taken on 8-February (A) and 32 nm particles at 400 °C generated from 7 m depth sample taken on 11-February (B). HGFs have not been Kelvin corrected.

Figure 10: Bubble mediated SSA properties from 7m-depth water sample taken on 08/02/2011. Average size distribution, ±1 standard deviation (A). Volume fraction remaining (VFR) indicates the temperature dependant refractory volume (B), error bars represent measurement uncertainty of ±3%. Temperature dependant HGF (C) with ±3% measurement uncertainty. The temperature dependant organic volume fraction (OVF) (D) is the sum of volatile fraction (estimated from VFR) and non-volatile fraction (estimate from HGF).
9-February surface sample
The second sample was taken at approximately 11:00 on 9 February 2011 from the workboat launched off the RV Tangaroa. Size distributions for this sample were mono-modal, peaking at 100 nm (Figure 11A), similar to that observed for the 8 February sample. SSA VFR for this sample indicates a volatile organic fraction ranging from 2±5% for 110 nm particles to 8±5% for 45 nm particles (Figure 11B). Total organic volume fractions (i.e. volatile and non-volatile) inferred from HGF measurements are between 35±5% for 110 nm particles and 18±4% for 22 nm particles at room temperature. These fractions decrease as the temperature increases and the volatile components are removed (Figure 11D). Similarly to the 8-February sample, volatile organic fractions inferred from HGF measurements are larger than those inferred from volatility measurements. The water volume uptake for the natural seawater samples at 300 °C is 7 to 15 % greater than at 60 °C, suggesting that the water uptake of the refractory component may be suppressed by the volatile organic component. Thus the volatile organic volume fraction may be over predicted from the HGFs.
Figure 11: Bubble mediated SSA properties from surface water sample taken on 09/02/2011. Average size distribution, ±1 standard deviation (A). Volume fraction remaining (VFR) indicates the temperature dependant refractory volume (B), error bars represent measurement uncertainty of ±3%. Temperature dependant HGF (C) with ±3% measurement uncertainty. The temperature dependant organic volume fraction (OVF) (D) is the sum of volatile fraction (estimated from VFR) and non-volatile fraction (estimate from HGF).
**10-February surface sample**
The third sample was taken at approximately 11:00 on 10 February 2011 from the surface waters of bloom 3. This bloom displayed the highest Chl-a concentrations. Size distributions for this sample were broader than those for the previous 2 samples, with a peak spanning from 50 to 100 nm (Figure 12A). This is due to variation in the flow rate through the sintered glass between this and previous experiments. SSA VFR for this sample indicates a volatile organic fraction of up to 11±5% (Figure 12B). Total organic volume fractions (i.e. volatile and non-volatile) inferred from HGF measurements are up to 47±12% for 110 nm particles (Figure 12D). Total organic volume fraction and HGF is less variable than for the previous water with increasing temperature. This indicates that the water uptake is not suppressed by the volatile organic component and is supported by a small change in water volume uptake of 3-6% between 60 and 400 °C.

**11-February 7 m depth sample**
The fourth sample was taken at approximately 14:00 on 11 February 2011 from the underway supply. Chl-a concentrations for this sample were relatively low as the sample was taken outside of bloom 3. Size distributions for this sample were similar to those from the 10-February sample, with a peak spanning from 50 to 100 nm (Figure 13A). Volatility measurements for this sample indicate a volatile organic fraction of up to 11±5% (Figure 12B). Total organic volume fractions (i.e. volatile and non-volatile) inferred from HGF measurements are up to 35±10% for 151 nm particles (Figure 12D). Similar to the 10/2/2011 sample total organic volume fraction and HGF values are less variable than for bloom 2 samples. HGFs for 15 nm particles reach a maximum of 2.34±0.07. This is in excess of the artificial SSA HGF and is due to either an instrumental bias or an indication of size dependent variation in the inorganic composition of SSA. Changes in water volume uptake between 60 and 400 °C are low, ±4% for this sample, indicating no suppression of water uptake.

HGFs of the refractory (to 400 °C) bubble mediated SSA component were displayed a relatively prompt deliquescence at between 73 and 75 % RH (Figure 9). HGFs were lower than those for artificial SSA confirming the presence of a
refractory organic component. This organic component deliquesced with the sea salt component, indicating an internal mixture.

Figure 12: Bubble mediated SSA properties from surface water sample taken on 10/02/2011. Average size distribution, ±1 standard deviation (A). Volume fraction remaining (VFR) indicates the temperature dependant refractory volume (B), error bars represent measurement uncertainty of ±3%. Temperature dependant HGF (C) with ±3% measurement uncertainty. The temperature dependant organic volume fraction (OVF) (D) is the sum of volatile fraction (estimated from VFR) and non-volatile fraction (estimate from HGF).
Figure 13: Bubble mediated SSA properties from 7m-depth water sample taken on 11/02/2011. Average size distribution, ±1 standard deviation (A). Volume fraction remaining (VFR) indicates the temperature dependant refractory volume (B), error bars represent measurement uncertainty of ±3%. Temperature dependant HGF (C) with ±3% measurement uncertainty. The temperature dependant organic volume fraction (OVF) (D) is the sum of volatile fraction (estimated from VFR) and non-volatile fraction (estimate from HGF).
4.3. Coral Aerosol Characterisation Experiment

Measurements of the primary marine aerosol generated using the sintered glass technique are presented here. Size distributions of the laboratory generated SSA were relatively constant, with a single mode at 80 nm (Figure 14). The coral water had the highest carbonaceous fraction, both inorganic as measured TIC and organic as measured by Chl-a and TOC (Table 5). Similarly to coccolithophores inorganic carbon from carbonates in coral may provide a source of SSA carbon along with organic carbon species. High tide and tap seawater both had higher organic and inorganic seawater markers than water collected at low tide. This suggests that the diluting effects of high tide are not significant and enhanced organic and carbonate concentrations across the entire region are more important. Corresponding to the large organic and carbonate fraction in the water phase, coral water was also the most volatile (Figure 15), with a volatile organic fraction of 13 ± 5 %. Variation between samples was low however (Figure 15), a further indication that the organic fraction may be driven by larger scale enhancement of biological activity.

Figure 14: Average size distribution for bubble mediated SSA production during CORACE campaign. Error bars indicate ± 1 sd.
Table 5: Summary of VH-TDMA measurements from bubble mediated SSA production and water sample composition. HGFs and calculated OVF s shown with and without shape correction applied to both the natural and artificial SSA measurements.

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Shape + Kelvin corrected</th>
<th>Volatile OVF</th>
<th>Kelvin corrected</th>
<th>Water composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HGF</td>
<td>κ</td>
<td>Total OVF</td>
<td>HGF</td>
</tr>
<tr>
<td>Coral water (June 4)</td>
<td>1.78</td>
<td>0.52</td>
<td>0.5 ± 0.1</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td>Tap seawater (June 5)</td>
<td>1.96</td>
<td>0.72</td>
<td>0.40 ± 0.09</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>High tide water (June 6)</td>
<td>2.03</td>
<td>0.81</td>
<td>0.17 ± 0.09</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>Low tide water (June 7)</td>
<td>1.99</td>
<td>0.76</td>
<td>0.21 ± 0.09</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td>Coral water (June 11)</td>
<td>1.97</td>
<td>0.73</td>
<td>0.23 ± 0.09</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Open ocean water (June 13)</td>
<td>1.88</td>
<td>0.63</td>
<td>0.4 ± 0.1</td>
<td>0.11 ± 0.05</td>
</tr>
</tbody>
</table>

1. Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC).
2. Volatile organic fraction calculated as the average difference between artificial sea salt VFR and natural seawater SSA VFR averaged between 250 and 450 °C.
Figure 15: Temperature dependent volatile fraction remaining (VFR) for SSA generated from natural seawater samples and SSA generated from artificial sea salt (art SSA) samples measured at 50-60 nm. Measurement error of ±6% is indicated for the natural seawater samples and a standard error of ±3% for the artificial SSA. Bottom is magnified version of top.

HGF probability densities for all samples had one mode indicating an internal mixture of organic and inorganic components, consistent with most other SSA observations. The response of HGFs to temperature is more variable than that of volatility. The natural seawater samples display an increasing HGF with temperature. As the non-refractory components, both organic and inorganic, are removed the proportion of species with very high hygroscopicity (e.g. NaCl), increases raising the HGF. Coral water from 4 June displays a significantly depressed HGF relative to that of artificial SSA, even at high temperatures, suggesting a large non-volatile organic fraction. A number of samples display HGFs closer that of artificial sea salt, suggesting low refractory organic fraction.
The total organic fraction, calculated as the sum of the temperature dependant volatile and non-volatile organic fractions show stable values, particularly in between approximately 100 to 450 °C (Figure 17). Total average OVs are shown in Table 5, those calculated using the shape factor correction and those calculated without the shape factor correction are within uncertainty of one another for all samples. At below 100 °C the HGF calculated OVF term dominates and therefore the apparent underestimation at these temperatures indicates that there is no suppression of hygroscopic growth due to the volatile fraction. Above 450 °C the total OVs drop, this is an artefact due to the artificial SSA and natural SSA VFR values converging at these temperatures. This convergence is due to the start of SSA dissociation. At these high temperatures the growth factor probability density functions splits into a number of modes. This is either due to the dissociation of different components of SSA, an instrumental anomaly due to the presence of impurities from the thermodenuder at these high temperatures or the combination of these two influences (Figure 18).
Deliquescence measurements of the coral water sample from 4 June shows reasonably prompt deliquescence at 72 to 75% RH, this is broadly consistent with artificial SSA, although it appears that the large organic fraction influenced the deliquescence behaviour of the SSA. Most notably water uptake occurred before this deliquescence, with a HGF of 1.2 at 70%RH.

5. Discussion/Implications
Water samples taken for bubble mediated SSA production during the pre-SOAP voyage displayed Chl-a concentrations ranging from 0.42 to 1.23 μg/L. Samples taken during the CORACE campaign had Chl-a concentrations ranging from 0.26
to 6.22 μg/L. These values are somewhat typical for bubble mediated SSA production studies carried out elsewhere and are largely representative of large-scale phytoplankton blooms and organically enriched coastal regions. There have been recent bubble mediated SSA studies with Chl-a concentrations of this order of magnitude \cite{Modini et al., 2010a; Prather et al., 2013], as well as those from more phytoplankton rich and oligotrophic waters \cite{Quinn et al., 2014]. Organic volume fractions observed in this study were up to 47%, similar to those observed for both phytoplankton rich and oligotrophic waters in the North East Pacific and North West Atlantic oceans \cite{Quinn et al., 2014]. SSA organic volume fractions observed during pre-SOAP displayed a poor correlation with Chl-a concentrations, supporting findings from the North East Pacific and North West Atlantic oceans indicating that an ever-present pool of DOM is available for organic SSA enrichment \cite{Quinn et al., 2014}. A relatively small number of observations were taken during the pre-SOAP voyage and therefore the relationship between water and SSA composition is difficult to establish.

The small quantity of samples taken during CORACE also hinders the attribution of SSA composition to water phase composition. Volatile organic fractions do not display a dependence on any of the measured indicators of biological activity in the water column (Figure 20). There does, however, appear to be some dependence of the total organic fraction on Chl-a, TOC and TIC, particularly in highly enriched waters with Chl-a concentrations greater than approximately 1 μg/L. This indicates that the refractory organic component may be more closely linked to the water phase than the volatile component. These observations do not support previous measurements indicating a lack of dependence of SSA organic enrichment on Chl-a concentrations \cite{Quinn et al., 2014].
Ubiquitous DOM as the source of SSA organics is also not supported by measurements from Cape Grim [Cravigan et al., 2014], where a very low organic fraction, less than 5%, was observed for summertime ambient sub-100 nm SSA particles. In addition laboratory generated mediated SSA studies elsewhere have shown similarly low organic fractions for cases with relatively high Chl-a concentrations [Modini et al., 2010a]. Questions remain about the suitability of Chl-a as a surrogate for the organic enrichment of sub micrometre SSA concentrations, particularly on a global scale [Quinn et al., 2014]. An argument has been made, that Chl-a is the best available surrogate [Rinaldi et al., 2013], however this conclusion is based on observations from the North Atlantic and does not account for regional variation. It is possible that the effectiveness of various surrogates varies regionally and seasonally. For example the spatial variation within the results reported here alone appear to have a dramatic impact on the usefulness of Chl-a as a marker for organically enriched SSA.

Figure 20: CORACE laboratory generated SSA OVF compared to Chl-a concentrations (A), total organic carbon (TOC) concentrations (B) and total inorganic carbon concentrations (C).
Previous studies have consistently observed an increasing organic fraction with decreasing particle diameter [O’Dowd et al., 2004; Facchini et al., 2008; Prather et al., 2013; Quinn et al., 2014]. Mass based composition methods are commonly used, and therefore the size dependant organic fraction over the Aitken mode is not captured. Lower size limits are down to 60 nm and compositions are averaged over broad stages, for example 60-120 nm [O’Dowd et al., 2004]. SSA organic fractions in these lowest size modes are up to 80% [O’Dowd et al., 2004; Facchini et al., 2008; Gantt et al., 2012a]. As such characterisation of the variation in sub-100 nm SSA composition is rare and largely limited to hygroscopicity based techniques. CCNc measurements from the North Atlantic and Pacific Oceans have shown a maximum SSA organic fraction of approximately 80% at 40 nm, decreasing to 40% at 100 nm [Quinn et al., 2014] (Figure 21). Corresponding with the decrease in OVF the hygroscopicity parameter, \( \kappa \), was 0.4 at 40 nm and 0.9 at 100 nm. Observed OVF values from the preSOAP voyage display the opposite trend, with an average OVF of 13 % at diameters less than 30 nm and an average OVF of 37% at diameters larger than 130 nm (Figure 21). This is consistent with observations from Cape Grim which show an increasing HGF, indicating SSA composed entirely of sea salt at 16 nm [Cravigan et al., 2014] (Section 7.1). These Cape Grim observations and those taken during preSOAP support recent observations of an SSA flux mode at approximately 20 nm [Ovadnevaite et al., 2014].

Primary marine aerosol emission schemes developed for use in climate modelling exclusively show increasing organic fractions with decreasing SSA diameter [Gantt and Meskhidze, 2012; Gantt et al., 2012b]. Results from this study indicate that these schemes could provide a significant overestimation of the organic SSA flux and therefore could significantly underestimate the number of potential SSA CCN.

The variation between observations reported here and those reported by Quinn et al. [2014] highlight the importance of the water phase organic composition to sub-100 nm SSA composition. These differences suggest an as yet un-reported regional variation in the organic content of the surface ocean water, corresponding to a variation in sub-100 nm organic OVF. A significant difference
in the OVF calculated from HGF and that calculated using CCNc measurements is also a possible source for the observed variation.

Figure 21: Hygroscopicity parameter, $\kappa$ (left), and OVF (right) as a function of particle diameter observed from preSOAP laboratory bubble mediated SSA generation.

A volatile organic fraction of up to 13% is consistent with that observed in the Pacific and Atlantic Oceans [Modini et al., 2010a; Quinn et al., 2014]. The absence of non-volatile organics in SSA generated from South West Pacific Ocean waters [Modini et al., 2010a] contradicts measurements reported here, and others [Quinn et al., 2014]. In addition the volatile organic component was observed to suppress the water uptake of the sea salt component for some samples taken along the Chatham Rise, but not others. This was not observed at all for measurements from Herron Island waters and has not been reported in the literature. This indicates water uptake suppression could be controlled by the presence of a particular organic component in the water phase. Bloom 2 was dominated by coccolithophores at the end of their life cycle, however further SSA observations coupled to water composition are required.

The majority of studies examining the organic component of SSA have concluded that SSA is an internal mixture of sea salt and organics based either on the original theory presented in [Blanchard, 1975] or on subsequent observations, particularly from TDMA [Modini et al., 2010a; Fuentes et al., 2011] and single particle analysis techniques [Middlebrook et al., 1998; Murphy et al., 1998]. SSA observed during both the preSOAP and CORACE experiments displayed a single deliquescence curve and a mono-modal HGF probability density function. This clearly supports the notion of SSA being an internal mixture of sea salt and
organics. Recent studies have indicated that sub micrometre SSA is dominated by an externally mixed organic component using TEM and single particle AMS methods [Leck and Bigg, 2010; Prather et al., 2013; Collins et al., 2014]. It has been shown however that TEM observations of an entirely organic ambient SSA fraction are misleading as TDMA observations show an unequivocal dominance in the sea salt fraction (Section 7.1) [Cravigan et al., 2014]. Instrument biases complicate analyses of the contribution of organics to SSA, which already contains significant spatial and seasonal variations.

Organic volume fractions calculated using shape corrected HGFs were within the uncertainty of those calculated without a shape correction factor. This however assumes that both the natural and artificial SSA are of similar morphology. Further observations, using TEM methods are required to characterise any composition dependant variability in shape from the SSA generation system used here.

The implications of a high concentration sub-100 nm SSA event observed at Cape Grim are described in Section 7.1. High wind speed back trajectories and a compressed boundary layer appear to have contributed to this dominant SSA event, as well as the absence of precipitation sinks for SSA [Cravigan et al., 2014]. As expected the increased sea salt fraction resulted in an estimated enhancement in CCN concentrations of 8-9%.
6. Conclusions and further work
The composition of sub-200 nm ambient and laboratory generated SSA were measured at the Cape Grim baseline atmospheric station and using a purpose built artificial SSA production chamber, respectively. Observed organic enrichments varied between ambient SSA, which showed a small (less than 5%) organic component, and laboratory generated SSA, which displayed organic volume fractions of up to 47%.

Ambient SSA was observed in a single, short-lived event. Back trajectories indicate that the SSA was produced 1500 km away in the Southern Ocean, highlighting the possible long-range transport of sub-100 nm SSA. The scarce observation of sub-100 nm SSA in the literature and reported here (during pre SOAP and CORACE) highlight the importance of SSA sinks, as well as the potential importance of SSA as CCN. Simultaneous measurements using VH-TDMA and TEM techniques of the sub-100 nm SSA event displayed remarkably dissimilar results. TEM collections showed no evidence of sea salt at approximately 50 nm diameters under visual analysis and X-ray spectroscopy. VH-TDMA measurements unequivocally showed the presence of a sea salt component via deliquescence and volatility measurements. Sub-100 nm sea salt concentrations of 110-290 cm⁻³ corresponding with number fractions of up to 69% were observed. This discrepancy highlights the potential for biases in TEM analysis of the chemical composition of marine aerosols, which are already complicated by spatial and seasonal variations. Inter-comparison studies are required to characterise the potential biases in instrumentation.

Laboratory generated SSA volatility and hygroscopicity measurements from both a coral reef region and a phytoplankton rich region of the South West Pacific indicate the presence of an internally mixed non-volatile organic component to sub-200 nm SSA. This component tends to dominate the volatile organic SSA fraction. These results support recent measurements showing that the organic fraction of SSA is dominated by a refractory component and that the volatile organic component typically comprises approximately 10-15% of the total SSA
volume [Quinn et al., 2014]. Measurements elsewhere have also observed no refractory organic SSA component [Modini et al., 2010a] suggesting that it may not be due to an ever-present pool of dissolved organic matter, as recently thought. An ever-present pool of dissolved organics may, however, describe the volatile organic component of SSA, which appears to consistently have a volume fraction of approximately 10-15%.

High chlorophyll-a, total organic carbon and total inorganic carbon concentrations appear to provide an indicator for the organic enrichment of SSA for coral waters. This relationship was not observed for phytoplankton rich waters. In addition water phase markers for biogenic activity did not provide an indicator for the volatile organic fraction. There appears to be a greater complexity in the composition dependant transfer of organics from the water to the aerosol phase than that described by single metrics such as Chl-a and dissolved organic carbon. Measurements coupling SSA composition to more detailed water phase characterisation is required.

Bubble generated sub-200 nm SSA produced from water samples taken from the phytoplankton rich Chatham Rise showed a distinct size dependence. Larger SSA particles displayed an increasing organic fraction up to 150 nm. This is surprising as previous measurements show an increase in organic fraction with decreasing size down to 60-120 nm. These mass based techniques do not capture the variability across the sub-150 nm size range as well as VH-TDMA techniques are able to. These measurements also contradict recent sub-100 nm measurements taken using a CCNc, which show an increasing organic SSA fraction with decreasing particle diameter. This discrepancy may be due to variation in the SSA organic composition between the two studies or due to instrumental biases. Only better characterisation of the organic SSA dependence on the water phase composition and measurement technique inter-comparisons will resolve this issue. Results from this study indicate that existing primary marine aerosol emission schemes could provide a significant overestimation of the organic SSA flux and therefore could significantly underestimate the number of potential SSA CCN.
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7. Appendices

7.1. Observation of sea salt fraction in sub-100 nm diameter particles at Cape Grim.

Observation of sea salt fraction in sub-100 nm diameter particles at Cape Grim
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Abstract
Volatility-hygroscopicity tandem differential mobility analyser (VH-TDMA) measurements were used to infer the composition of sub-100 nm diameter Southern Ocean marine aerosols at Cape Grim in November and December 2007. This study focuses on a short lived high sea spray aerosol (SSA) event on 7-8 December with two externally mixed modes in the Hygroscopic Growth Factor (HGF) distributions (90% RH), one at HGF > 2 and another at HGF ~1.5. The particles with HGF > 2 displayed a deliquescent transition at 73-75% RH, and were non-volatile up to 280°C, which identified them as SSA particles with a large inorganic sea salt fraction. SSA HGFs were 3 – 13% below those for pure sea salt particles, indicating an organic volume fraction (OVF) of up to 11 – 46%. Observed high inorganic fractions in sub-100 nm SSA is contrary to similar, earlier studies. HGFs increased with decreasing particle diameter over the range 16 – 97 nm, suggesting a decreased OVF, again contrary to earlier studies. SSA comprised up to 69% of the sub-100 nm particle number, corresponding to concentrations of 110-290 cm⁻³. Air mass back trajectories indicate that SSA particles were produced 1500 km, 20-40 hours upwind of Cape Grim. Transmission electron microscopy (TEM) and X-ray spectrometry measurements of sub-100 nm aerosols collected from the same location, and at the same time, displayed a distinct lack of sea salt. Results herein highlight the potential for biases in TEM analysis of the chemical composition of marine aerosols.
**Key points:**
- Characterisation of high concentration sea spray aerosol (SSA) event.
- Sub-100 nm SSA organic volume fraction of up to 11 – 46% and size independent.
- Free tropospheric entrainment coincided with enhanced SSA concentrations.

**Keywords:**
marine aerosol, sea spray, CCN, hygroscopic growth, deliquescence, Cape Grim, entrainment.

**Index terms:**
Aerosols and particles (0305), Air/sea constituent fluxes (0312), Constituent sources and sinks (0322), Troposphere: constituent transport and chemistry (0368), Clouds and aerosols (3311).
1. Introduction

The remote marine aerosol, free from direct continental influences, plays an important role in the global climate by directly scattering incoming solar radiation and acting as cloud condensation nuclei (CCN) [Andreae and Rosenfeld, 2008]. Recent modelling has highlighted the need for a greater understanding of aerosol forcing in pristine environments, indicating that natural emissions make up 45% of the variance in aerosol forcing since 1750 [Carslaw et al., 2013]. Sea spray aerosols (SSA) are an important marine aerosol class. They are primary particles produced from the bursting of bubbles at the oceans surface or from wind shear. Observations at or near cloud level have indicated that SSA can contribute significantly to the marine CCN. For example, SSA formed 20% of the total potential CCN at supersaturations between 0.2 and 0.43 during a recent study in the mid-latitudeal Pacific Ocean [Blot et al., 2013]. Despite the climatic importance of primary marine aerosols there are significant uncertainties regarding the production mechanisms and chemical composition of the sub-100nm diameter SSA. In particular, the factors that control SSA concentrations in the atmosphere and the organic enrichment of sub-100nm diameter primary marine aerosols relative to water biology are poorly understood [Gantt and Meskhidze, 2013].

Recent studies have simulated the production of SSA in-situ and under controlled laboratory conditions by bubbling air through seawater [Modini et al., 2010], by continuously plunging water [Fuentes et al., 2010], and/or through wave action [Prather et al., 2013]. These methods have consistently detected a dominant mode in the SSA number distribution at sizes less than 100 nm dry diameter [Fuentes et al., 2010; Modini et al., 2010; Bates et al., 2012] with the exception of the wave chamber method, where a dominant mode centred at 160 nm was observed [Prather et al., 2013]. All of the systems produce particles down to 10 nm in diameter. When scaled to real oceanic conditions, the bubble chamber data generally suggest SSA should consistently form the largest fraction of the total marine aerosol in remote environments [de Leeuw et al., 2011]. In addition, a recent parameterisation has suggested the presence of an SSA flux mode at approximately 20 nm [Ovadnevaite et al., 2014]. Despite this, observations of sub-100 nm diameter SSA particles in the marine boundary layer (MBL) are relatively scarce, even under high wind conditions. It is not understood why this is the case [Berg et al., 1998; Kreidenweis et al., 1998; Zhou et al., 2001; Lewis and Schwartz, 2004; Swietlicki et al., 2008], although loss processes such as wet deposition likely play an important role [Blot et al., 2013]. Tandem Differential Mobility Analyser (TDMA) data illustrate the scarcity of SSA observations well. TDMA techniques are well suited to the study of remote marine aerosols since they are able to differentiate the main marine aerosol types i.e. SSA, non-sea salt sulfates (nss-sulfates) in external mixtures of particles with diameter as small as 8 nm [Väkevä et al., 2002; Swietlicki et al., 2008]. TDMA studies suggest that nss-sulfates dominate the ambient, sub-100 nm diameter, marine aerosol outside the surf zone [Berg et al., 1998; Fletcher et al., 2007;
Swietlicki et al., 2008; Allan et al., 2009; Good et al., 2010b]. A more scarce externally mixed SSA component is also observed [Berg et al., 1998; Fletcher et al., 2007; Swietlicki et al., 2008]. When SSA are observed, they comprise 11-40% of the sub-165 nm number fractions at Mace Head, Ireland (North Atlantic) [Bialek et al., 2012], 11-14% of the sub-100 nm number fractions in the West Atlantic [Swietlicki et al., 2000], 12-15% in the Pacific [Berg et al., 1998], 23% in the open Southern Ocean [Berg et al., 1998] and 1-15% at Cape Grim, Australia (Southern Ocean) [Gras and Ayers, 1983; Fletcher et al., 2007]. An exception to this pattern is the very high proportions of sub-100 nm SSA (95-100%) observed in the Arctic, but only in 3-7% of all measurements at 35 and 50 nm [Zhou et al., 2001].

The Southern Ocean is a particularly interesting region for SSA due to the higher than global average wind speeds and thus strong potential for SSA production. Further observations of the marine aerosol at Cape Grim using electron microscopy and X-ray spectroscopy of individual particles identify number fractions of SSA of 5-25% in the 50-150 nm size range. These fractions correspond to SSA number concentrations of the order of 30 to 100 cm$^{-3}$ [Murphy et al., 1998a; 1998b]. Values for the open Southern Ocean range from 1 to 150 cm$^{-3}$ for particles greater than 80 nm diameter [Bates et al., 1998; Kreidenweis et al., 1998; Murphy et al., 1998b; Lewis and Schwartz, 2004]. Observations of sub-100 nm SSA in the Southern Ocean are sparse and studies report widely varying SSA concentrations, from 1 to 171 cm$^{-3}$ [Bates et al., 1998; Kreidenweis et al., 1998; Murphy et al., 1998b; Lewis and Schwartz, 2004]. Further observations of sub-100-nm SSA particles are required to assess the importance of the Southern Ocean as a source of SSA and thus CCN.

The chemical composition of SSA under different oceanic and meteorological conditions is also an active area of research. It is known that nascent SSA is comprised of internally and externally mixed inorganic (sea salt) and organic fractions. Table summarises results from some recent studies, which examined the composition of nascent SSA. TDMA analyses of laboratory generated SSA particle composition reveals internally mixed organic mass fractions on the order of 5-27% for sub-200 nm particles [Modini et al., 2010; Fuentes et al., 2011]. Off-line chemical composition measurements of ambient [O'Dowd et al., 2004; Rinaldi et al., 2010] and laboratory generated [Keene et al., 2007; Facchini et al., 2008] SSA particles have identified much larger organic fractions of up to 80% for sub-200 nm particles in the North Atlantic. Ambient TDMA observations in the North Atlantic (Mace Head) displayed externally mixed non-hygrosopic particles, consistent with primary organics with a small sea salt component, contributing up to 75% of the Aitken mode ambient particle number [Ovadnevaite et al., 2011]. Flux measurements [Ceburnis et al., 2008] and an increasing ambient organic mass with decreasing particle size [O'Dowd et al., 2004; Facchini et al., 2008] have provided evidence that the large observed organic fraction is predominantly primary, with a relatively small contribution from secondary organics.

Primary marine organics have also been observed using particle analysis by laser mass spectrometry at Cape Grim [Middlebrook et al., 1998; Murphy et al., 1998a]. These authors argued that a small sodium sulfate fraction in these particles and the presence of iodine, which was correlated with organic concentrations,
indicated relatively freshly emitted SSA. This is consistent with simultaneous depletion of iodine and chlorine and accumulation of sodium sulfate from the marine boundary layer observed at Cape Grim, which suggest a primary iodine source [Murphy et al., 1997]. Average organic mass fractions in SSA were approximately 10% for particles between 1.6 and 3 μm in diameter [Middlebrook et al., 1998; Murphy et al., 1998a]. This organic mass fraction was variable ranging from 5 to 50% and authors suggest it may have been enhanced at the lower end of the observed size range, ~170 nm. These results are broadly consistent with observations of a residual component, the difference between the ionic and gravimetric mass, which comprised 21% (0.23 μg/m³) of the Southern Hemisphere mid-latitudes submicron mass [Quinn et al., 2000]. A submicron carbon mass concentration of 0.23 μg/m³ was also observed via proton elastic scattering analysis at Cape Grim, suggesting a similar organic component [Andreae, 1982].

Adsorption theory predicts that during rough sea conditions the enhanced concentration of surfactant organic matter at the ocean surface saturates the SSA adsorption process. A surfactant organic matter film of approximately the same thickness develops on SSA independent of particle size and will therefore form increasing fractions of total particle volume as particle size decreases [Oppo et al., 1999]. The majority of size-resolved SSA organic volume or mass fraction measurements have supported this theory through the observation of increasing primary organic fractions in SSA with decreasing particle size [O’Dowd et al., 2004; Rinaldi et al., 2009; Quinn et al., 2014]. However, this trend has not been observed in all experiments [Modini et al., 2010].

Externally mixed organics have also been explicitly identified in SSA. X-ray analysis of transmission electron microscopy (TEM) samples and single particle mass spectrometry measurements for ambient marine and wave chamber aerosols have indicated external mixtures. These external mixtures are dominated by organics with contributions from organic particles to the overall sub-100 nm particle population, ranging from approximately 80 to 100% [Bigg and Leck, 2008; Leck and Bigg, 2010; Prather et al., 2013]. Of particular note are the ambient observations from Cape Grim, which are characterized by an absence of sea salt in the sub-100 nm particle fraction. These particles are hypothesised to be primary particles from the sea surface microlayer [Bigg, 2007; Leck and Bigg, 2010]. A small fraction of individual 0.2 to 2μm, externally mixed bacterial cells have also been identified in TEM samples over the Southern Ocean [Pósfai et al., 2003].

A seasonal trend has been observed in the organic enrichment of SSA particles at Mace Head, with higher organic fractions thought to be largely comprised of a primary organic fraction, observed during the biologically active summer months [O’Dowd et al., 2004]. However, recent research suggests the ever-present pool of oceanic dissolved organic matter (DOM), composed primarily of saccharides, proteins and processed, recalcitrant organic molecules, provides sufficient matter for organic enrichment of SSA to occur even in non-productive regions [Burrows et al., 2014; Quinn et al., 2014]. These studies and the observations of high internally and externally mixed organic fractions in small SSA particles lead to the suggestion that organics will dominate sub-100 nm SSA composition in most oceanic conditions. This raises questions about the
importance of sea salt in sub-100 nm SSA. The previously mentioned TDMA studies indicate externally mixed SSA with large by sea salt fractions, however the precise organic fraction of the SSA component is unknown [Berg et al., 1998; Fletcher et al., 2007; Swietlicki et al., 2008]. In addition recent cloud level studies in pristine conditions also identify sea salt particles down to 40 nm in diameter from atmospheric and in-droplet sampling using TEM [Twohy et al., 2013] and volatility techniques [Blot et al., 2013]. These observations provide an indication that sub-100nm sea salt plays a role in marine cloud formation.

Here we present observations from a unique, short lived and particularly strong SSA event, which occurred in clean Southern Ocean air masses over 2 days in summer 2007 at the Cape Grim Baseline Air Pollution Station (BAPS) on the north-west tip of Tasmania, Australia. We use aerosol hygroscopicity and volatility measurements to identify sub-100nm SSA composition and discuss the conditions under which this SSA was produced and transported to Cape Grim. The case study does not necessarily provide an indication of the long-term average sub-100 nm aerosol composition at Cape Grim. This unique SSA event was selected as a case study because it contributes to our understanding of the chemical composition of sub-100 nm ambient SSA and the factors that control SSA concentrations in the atmosphere.

2. Experimental methods

2.1. Cape Grim Baseline Monitoring Station

From 22 November 2007 to 11 December 2007 aerosol observations were undertaken at the Cape Grim BAPS on the north-west tip of Tasmania, Australia. These observations were aimed at examining the properties of the naturally occurring marine aerosol. Here we focus on measurements taken from 7 – 8 December, when a particularly strong SSA event was observed from the station.

The Cape Grim BAPS is situated 94 m above sea level, well located for examining clean air from the Southern Ocean. Winds from the south-west, the baseline sector (190° to 280°), typically traverse across several thousand km of the Southern Ocean [Gras, 2009]. Modelling of air flow around the Cape Grim station indicates that sampling from the 10 m inlet (104 metres from sea level) delivers air with a source height over the near ocean ranging from 10 to 30 m, when the air is from the baseline sector, suggesting that observations are unlikely to be influenced by local sources such as wave breaking [Baines and Murray, 1994]. In addition to the wind direction a minimum wind speed of 7 km/hr (1.94m/s) was used in this study to determine baseline conditions, this is consistent with previous aerosol monitoring at Cape Grim [Gras, 2009]. Total particle number and radon concentrations are also commonly used as indicators of baseline conditions in Cape Grim and these measurements are reported along with our results.
2.2. Instrumentation

Total aerosol concentrations were measured using two condensation particle counters (CPCs), a TSI 3010 and 3025 (TSI, Shoreview, MN). The 3010 CPC has a detection size limit of 10 nm at the lower end of its range, while the 3025 has a detection size limit of 3 nm. The number of 3-10 nm diameter particles can be obtained from the difference in the concentrations reported by these two instruments providing information on the concentration of nucleation mode particles. Aerosol size distributions from 15 to 737 nm were obtained using a scanning mobility particle sizer, consisting of a TSI 3071 Differential Mobility Analyser and TSI 3776 CPC. Black carbon concentrations, inferred from light absorption, and radon concentrations were measured as markers for continental air and pollution at a time resolution of 60 min. Details of light absorption and radon measurements at Cape Grim can be found in Gras [2011] and Zahorowski et al. [2004].

Further aerosol properties and compositional information were obtained with a custom-built VH-TDMA [Johnson et al., 2004]. The VH-TDMA is a particle sizing instrument that selects particles based on mobility diameter, conditions them, and then measures the resulting particle size distributions using two parallel scanning mobility particle sizers (SMPS), each with a TSI 3010 CPC. The temperature difference between the saturator and the condenser was set to 21°C in both 3010 CPCs and the counting efficiencies updated accordingly to extend the lower size limit of the CPCs down to 5 nm diameter [Mertes et al., 1995]. The VH-TDMA combines humidification and volatilisation conditioning to examine hygroscopic properties of the aerosol fraction remaining after volatilisation. It can be used to distinguish between two components of sub-micron heterogeneously mixed particles, and is especially useful in distinguishing between components displaying significantly different hygroscopic properties [Johnson et al., 2004]. The VH-TDMA provides valuable information on the mixing state of marine particles, which is of particular interest with recent studies highlighting the importance of externally mixed organics [Leck and Bigg, 2005b; 2010; Collins et al., 2013; Prather et al., 2013].

The VH-TDMA measured sub-100 nm mode particles and was run in several operating modes:

1. Volatility mode. For a fixed preselected particle size the humidity was kept constant at relative humidity (RH) 90% and the temperature of the thermodenuder was scanned from room temperature to 280°C. During this mode the particle volume fraction remaining (VFR) can be calculated from the first SMPS using:

\[ VFR = \frac{d_T^3}{d_i^3} \]

Where \( d_T \) is the particle diameter at temperature, \( T \) and \( d_i \) is the initial particle dry diameter. The growth factor (VH-GF) observed by the second SMPS is due to both volatility and hygroscopic growth and is given by:

\[ VH-GF = \frac{d_{90,T}}{d_i} \]
Where \( d_{90,T} \) is the particle diameter after being exposed to 90\%RH and passing through the thermodenuder set to temperature, \( T \). Changes in the HGF observed during this temperature scan can result from the evaporation of non-refractory components in the thermodenuder (e.g. organics, sulfate).

2. H-TDMA mode. When the thermodenuder was kept at room temperature the instrument operated as a standard H-TDMA. In H-TDMA mode two further modes of operation were utilised: 1) HGF mode where the instrument was operated at fixed 90\%RH, and 2) deliquescence mode where the RH was ramped from 60 to 90\% in steps as small as 0.5\% [Johnson et al., 2008]. Deliquescence curves provide clearer differentiation between different inorganic salts (e.g. ammonium sulfate and sodium chloride) and internally mixed inorganic-organic particles than is possible from HGF measurements at a single RH.

### 2.3. Data analysis procedures

The HGF is defined as the ratio of humidified particle diameter to dry particle diameter and is commonly measured at 90\%RH. HGF provides information on particle composition [Berg et al., 1998; Zhou et al., 2001; Swietlicki et al., 2008]. Previous studies have generally partitioned the marine sub-100 nm aerosols into four HGF classes, used to provide guidance on what chemical species are likely to be present in the aerosol. The aerosol composition is inferred from the known HGFs of common species [Tang and Munkelwitz, 1994] and H-TDMA field data [Swietlicki et al., 2008].

1. Nearly hydrophobic aerosols, with growth factors ranging from approximately 1.0 to 1.1, are composed of marine organics or are influenced by anthropogenic sources [Berg et al., 1998; Swietlicki et al., 2000; 2008; Bialek et al., 2012].
2. Less hygroscopic aerosols, with growth factors ranging from approximately 1.1 to 1.3, are often composed of marine organics [Ovadnevaite et al., 2011; Bialek et al., 2012].
3. More hygroscopic aerosols, with growth factors ranging from approximately 1.35 to 1.85, are commonly dominated by nss-sulfates [Swietlicki et al., 2000; Ovadnevaite et al., 2011; Bialek et al., 2012].
4. Sea salt aerosols (inorganic SSA), with growth factors of more than 1.85, observations of sub-100 nm sea salt is not common and the ideal conditions for their development is uncertain [Zhou et al., 2001; Fuentes et al., 2010; Modini et al., 2010; Bialek et al., 2012].

Inferring chemical composition purely from particle HGFs can be problematic since different internal mixtures can result in the same HGF. For example, sea salt and sulfate particles could both be classified in the more hygroscopic class when internally mixed with less hygroscopic material. In this study HGFs are examined alongside particle volatility and deliquescence data, providing a more complete picture of particle composition and mixing state.

All VH-TDMA data were inverted using the TDMAinv algorithm [Gysel et al., 2009]. The resulting growth factor probability distributions were used to
determine the median HGF for each mode. The 95% confidence interval in the median or the experimental uncertainty of ±3% [Modini et al., 2010], whichever value was greater, was applied to represent the uncertainty. Uncertainties ranged from ±3% at between 22 and 55 nm to ±6% at 16 nm. To estimate the change in CCN concentration with changing particle composition, the κ parameter was calculated using the measured HGFs for a range of particle diameters [Petters and Kreidenweis, 2007]. A critical dry diameter, beyond which particles are activated as CCN, for each super-saturation was calculated and size distributions used to determine the fraction of particles exceeding the critical diameter.

2.4. Back trajectory analysis

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Rolph, 2013] was used to identify the air mass properties associated with observations of high SSA concentrations. These back trajectories were computed using meteorological data from the NOAA/NCEP Global Data Assimilation System (GDAS) [Kanamitsu, 1989]. Using HYSPLIT we obtained 7-day back trajectories for each hour of the campaign, these were compared to particle measurements at Cape Grim, particularly SSA concentrations. Of interest in the baseline sector was the modelled back trajectory altitude, relative humidity, rainfall and mixing height. 6 hourly surface wind speed data observed from the Cross-Calibrated Multi-Platform (CCMP) data set were extracted along the back trajectories. The CCMP data set includes cross-calibrated satellite winds derived from a variety of satellite instrumentation on a 0.25° grid e.g. QuikSCAT, SeaWinds, Windsat [Atlas et al., 2013].

In addition the UK Met Office Numerical Atmospheric-dispersion Modelling Environment (NAME) was used to create back trajectory probability plots and ensure clean marine background air origin [Jones et al., 2007].

3. Results and Discussion

3.1. Event characterisation

Size distribution data from the 7 – 8 December 2007 indicate there was a developing accumulation mode from 13:00 to 15:00 on 7 December, coincident with enhancement of an Aitken mode, resulting in an increase in total particle concentrations from approximately 450 to 900 cm⁻³ (Figure 1). Following this a bimodal marine aerosol size distribution was observed [Sellegri et al., 2001; Lewis and Schwartz, 2004; Heintzenberg et al., 2011] containing a larger Aitken mode, initially with a peak at 23 nm, and an accumulation mode with a peak at 145 nm. This suggests previous cloud processing of the aerosol had occurred,
with those particles over 70 nm having previously been activated and readily growing into the accumulation mode, whilst smaller particles remained inactivated leading to a Hoppel minimum at 70 nm [Hoppel et al., 1986]. On 8 December, the peak of the Aitken mode grew slowly from approximately 23 nm in the morning to approximately 60 nm at 18:00. Total particle concentrations increased substantially after 10:00 (Figure 1), primarily driven by an increase in the concentration of 3 – 10 nm nucleation mode particles. These particles may have contributed to the Aitken mode growth observed in the afternoon on 8 December through coagulation.

Modelled back trajectories show a clean, Southern Ocean origin for air masses arriving at Cape Grim during the period from 19:00 7 December to 07:00 8 December (Figure 2). Local wind speed and direction at Cape Grim from 12:00 7 December to 06:00 8 December were also indicative of air masses arriving almost entirely from the clean marine sector (Figure S4) [Gras, 2009]. After 06:00 local wind direction shifted slightly north resulting in intermittent baseline conditions. By 10:00 baseline conditions had finished completely. Consistent with the local meteorological data at 07:00 – 10:00 8 December there was a slight shift in the path of the modelled back trajectories demonstrating the air mass came closer to the Australian mainland near the major city of Melbourne. From 12:00 7 December to 18:00 8 December black carbon concentrations ranged from 1.3 to 10 ngm⁻³, and radon concentrations ranged from 27 to 80 mBqm⁻³, which is consistent with the values observed for baseline periods at Cape Grim [Zahorowski et al., 2011].

Entrained particles from the free troposphere are a possible cause of the increases in particle concentrations observed on 8 December. This is consistent with previous studies at Cape Grim by [Gras et al., 2009], where peaks in the concentration of 3-10nm particles were observed following the passage of cold fronts. Gras and co-workers have convincingly argued the concentration enhancements are due to nanoparticle-rich free tropospheric air rapidly mixing to the surface in the turbulent postfrontal atmosphere. Enhancements of approximately 100 cm⁻³ and peaks of 300-500 cm⁻³ are typically observed 9—11 hours after the passage of a front, and are separated by 8-11 hour intervals. Synoptic charts (Figure S6) and observed pressure (Figure S3) indicate that a cold front passed Cape Grim at approximately 05:00 7 December. Immediately following the front concentrations of 3-10 nm particles were initially greater than 150 cm⁻³ due to continental influences. By 11:00 the wind direction settled into the baseline sector and concentrations were low, 50 cm⁻³. Hourly average nanoparticle concentrations of 70 to 170 cm⁻³ occurred from 15:00 7 December until 10:00 on 8 December, consistent with the postfrontal observations by [Gras, 2009]. Sharp increases in concentration to peaks above 1000 cm⁻³ were observed after 10:00 8 December. These enhancements are larger and sharper than those previously observed in postfrontal conditions at Cape Grim. The sharp concentration peaks correspond with the end of baseline conditions as defined by wind speed and direction and the shifting of the air mass trajectory closer to the major city of Melbourne, which suggests that they could be the result of intermittent intrusions of anthropogenically-influenced air. Despite the sharp increases in nucleation mode particle concentrations radon and black carbon concentrations remained low until approximately 18:00. This is
potentially because the lower time resolution black carbon and radon measurements failed to capture the sharp, intermittent concentration increases. After 18:00 8 December particle, black carbon and radon concentrations (Figure S1) all increased signifying the complete establishment of polluted conditions at Cape Grim.

### 3.2. Hygroscopic growth factors

The VH-TDMA was run mainly in the H-TDMA mode during the 7 – 8 December event. Observations of sub-100 nm particle hygroscopicity at 90% RH from the afternoon of 7 December (16:30) to the afternoon of 8 December (15:00) indicate an external mixture of at least two distinct types of aerosols, one in the more hygroscopic mode with raw growth factor of 1.45 to 1.65, and another in the sea salt mode with growth factor 1.95 to 2.1 (see Figure 3A and Figure S5). HGF corrections due to shape and Kelvin effects are described in the remainder of this section. The observed HGFs are consistent with an external mixture of predominantly nss-sulfates and SSA. These will subsequently be referred to as the nss-sulfate and SSA modes, respectively. Strong justification for these mode assignments is presented in the following sections.

The HGF probability distribution (Figure S5) was used to estimate the number fraction of particles in each mode. Figure 1C shows the time series of the SSA mode number fraction. Small fractions of externally mixed sea salt were initially observed between 15:00 and 16:30 7 December. By approximately 05:30 on 8 December SSA number fractions reached as high as 69%. The increase in the proportion of the SSA mode (15:00 7 December to 05:30 8 December) coincided with postfrontal enhancements in nanoparticle concentrations (section 3.1). The number fraction of SSA particles decreased after 06:00 8 December, corresponding with a shift in wind direction signalling intermittent baseline sector measurements. After 10:00 baseline conditions had ended completely and after 18:00 no SSA particles were observed. During the peak of this event SSA particle number fractions were variable but almost exclusively greater than 0.2.

When the SSA mode fraction reached its maximum value measurements of the HGF at different sizes were conducted between 7:30 and 8:40 on 8 December. Considerable fractions (24-50%) of SSA particles were detected at all particle sizes examined between 16nm and 97 nm diameter. Figure 3A shows the HGF of the two modes as a function of particle size as well as the Kelvin and shape corrected HGFs for both modes. Freshly emitted SSA has a non-spherical shape and can be described with the NaCl shape correction factor [Niedermeier et al., 2008; Wise et al., 2009; Modini et al., 2010]. SSA can become more spherical via atmospheric processing [Laskin et al., 2012] and a higher organic content [Laskin et al., 2012; Ault et al., 2013]. In this study a case with no shape factor adjustment (i.e. spherical SSA), and a case with a size dependant shape-factor for NaCl, ranging from 1.20 to 1.23, was applied to the SSA mode to provide a lower and upper limit for the HGF of the SSA. A constant shape factor of 1.02 was applied to the sulfate mode [Biskos et al., 2006b; 2006c].

In addition, for the comparison of HGFs across particles of different sizes the influence of the Kelvin effect had to be negated. This was achieved by converting
HGFs measured at 90% RH to bulk growth factors (i.e. where water activity = RH = 90%) using a single parameter representation of hygroscopic growth, κ [Petters and Kreidenweis, 2007]. The Kelvin corrected, and shape and Kelvin corrected HGFs are referred to as ‘K corrected’ and ‘K/shape corrected’ HGFs in Figure 3A.

The Kelvin corrected HGF for the SSA particles, without shape factor correction, ranged from $2.05 \pm 0.09$ at 95 nm to $2.3 \pm 0.1$ at 16 nm. The measured Kelvin and shape corrected HGF for the SSA mode ranged from $2.3 \pm 0.1$ at 95 nm to $2.5 \pm 0.2$ at 16 nm. Kelvin and shape corrected HGFs for 16 nm SSA and nss-sulfate particles exceeded the HGFs for artificial SSA and laboratory (NH$_4$)$_2$SO$_4$, respectively. This suggests that the ambient particles were more spherical than laboratory analogues. Overnight HGFs were higher than observed during size resolved measurements on the morning of 8 December (triangle compared to circle markers Figure 3A), this may indicate a change in the SSA morphology.

Assuming that the suppression of the Kelvin corrected SSA HGFs (without shape factor correction) is entirely due to the presence of an internally mixed organic component, an upper bound for the organic volume fraction can be calculated via the Zadanovkii-Stokes-Robinson (ZSR) assumption [Stokes and Robinson, 1966; Chen et al., 1973]. ZSR calculation were made using measured SSA HGFs (without shape factor correction), an artificial sea salt HGF of 2.35 and a HGF for the organic fraction of 1 and 1.5 [Peng et al., 2001; Gysel et al., 2004; Mikhailov et al., 2004; Fuentes et al., 2011]. Assuming an organic growth factor of 1, the average sub-100 nm organic volume fraction was 26%, ranging from 11% at 16 nm to 37% at 95 nm. An assumed organic growth factor of 1.5 yielded an average sub-100 nm organic volume fraction 33%, ranging from 14 to 46%.

Alternatively aging of the SSA could have enhanced the sulfate component to the detriment of more hygroscopic species such as NaCl. Thus, the suppression of HGFs relative to artificial sea salt is possibly due to an ambiguous combination of inorganic sea salt ageing and the presence of both primary and secondary organic components. Therefore, the 11 – 46% SSA organic volume fractions should be considered as upper limit estimates.

### 3.3. SSA number concentrations

The size dependent SSA number fractions observed between 7:30-8:40 am 8 December were multiplied by the average total aerosol size distribution during this time period to estimate the SSA size distribution up to 100 nm diameter, (Figure 3B). Lower and upper bound estimates of the SSA size distribution were derived based on the range of total particle concentrations (284 - 363 cm$^{-3}$) and SSA number fractions (at the single particle size at which most measurements were taken, 95 nm, 26 – 49 %) measured during the time period 7:30 to 8:40. The lower and upper bound size distribution estimates correspond to integrated sub-100 nm SSA particle concentrations of 41 and 109 cm$^{-3}$, respectively.

The integrated sub-100 nm SSA concentrations estimated for the period 7:30 – 8:40 8 December were scaled by measured SSA number fractions (Figure 1C) to estimate integrated sub-100 nm SSA particle concentration over the entire 2-day
event (Figure 1E). This scaling procedure assumes that the shapes of the SSA and total particle size distributions were constant from 7 – 8 December, which is not strictly true (Figure 1A), so these calculated concentrations should be considered as approximate estimates only. The peak SSA number fraction of 0.69 observed at approximately 05:30 8 December corresponds to sub-100 nm SSA particle concentration in the range 110 – 290 cm⁻³.

### 3.4. Volatility

To further confirm that the observed highly hygroscopic particles were SSA with a large sea salt fraction the VH-TDMA was run in volatility mode from 9:10 to 10:15 on 8 December. A particle size of 56 nm was preselected and the temperature of the thermodenuder was ramped from room temperature to 280°C. The VFR and VH-GFs at 90% RH of the non-volatile particles remaining at each temperature step were examined. The number fraction of the SSA mode during this period was up to 0.4 based on the HGF probability distribution. The VFR showed a population of particles evaporating at 160-200°C. This corresponded with a reduction in the VH-GF of particles in the more hygroscopic mode (HGF 1.5) (Figure 4). This combined volatility and hygroscopic behaviour closely matches that observed for laboratory generated ammonium sulfate [Fletcher et al., 2007; Swietlicki et al., 2008], which is also displayed in Figure 4. At 280°C particles in the SSA mode had a VFR of 0.90 ± 0.05, the VFR of artificial SSA at this temperature is 0.93 ± 0.03 [Modini et al., 2010]. This, in combination with the very high HGF, is strong evidence for SSA with a very small volatile organic or enhanced sulfate fraction, but does not exclude the presence of non-volatile organics (Figure 4).

### 3.5. Deliquescence

Dependence of the HGF on relative humidity was examined by two separate deliquescence scans conducted between 22:00 7 December and 00:00 8 December. During this period the number fraction of SSA mode particles was up to 0.15 (Figure 1). Three distinct populations of particles were observed in the deliquescence scans (Figure 5). For one group of particles there was a prompt increase in growth factor to 1.8 at 73-75% RH. This is consistent with the deliquescence of sea salt [Berg et al., 1998; Biskos et al., 2006a]. Furthermore, the HGFs above 75% RH of these particles closely matched those of modelled and measured sodium chloride and sea salt [Fletcher et al., 2007], as already discussed above with reference to the continuous HGF measurements at 90% RH. The deliquescence, volatility and growth factor of this mode provides compelling evidence that it is SSA, with a large (>50% by volume) inorganic sea salt component.

For another group of particles reasonably prompt deliquescence was observed at approximately 78-80% RH, which matches the deliquescence RH of ammonium sulfate [Biskos et al., 2006b; Fletcher et al., 2007]. In addition the HGF for this mode above 79% RH closely matched that modelled for ammonium sulfate
[Fletcher et al., 2007]. The third group of particles did not display prompt deliquescence and was characterised by a continuous increase in growth factor from 1.3 at 65% RH to 1.4 at 80% RH. This behaviour is consistent with nss-sulfates containing an ammonium to sulfate ratio less than that for ammonium sulfate, referred to as partially neutralised nss-sulfates. One such nss-sulfate is ammonium bisulfate, which has a deliquescence RH of 40% RH [Tang and Munkelwitz, 1994; Fletcher et al., 2007].

There was a distinct increase in the proportion of ammonium sulfate to the detriment of the partially neutralised sulfate fraction over the time between the two deliquescence scans, shown in Figure 5. Additional growth factor measurements at 74-76% RH were used to separate the partially neutralised sulfate and ammonium sulfate, and to calculate the number fraction of partially neutralised nss-sulfates. These number fractions are shown in Figure 1D. At 12:00 7 December the aerosol was composed entirely of partially neutralised sulfate particles. Between 18:00 and 00:00 the fraction of partially neutralised nss-sulfates decreased from 0.6 to 0 (Figure 1). At 15:00 nanoparticle concentrations increased and sparse HGF measurements indicate that the SSA was first observed between 15:00 and 22:00. This suggests that the ammonia, SSA and nucleation mode particles all arrived in the same air mass.

4. Implications

Hygroscopic growth, volatility and deliquescence measurements of sub-100 nm ambient marine particles at Cape Grim during this event identified high concentrations of SSA with a large proportion of inorganic salts (greater than 50% by volume) down to 16 nm in diameter. The SSA number fraction reached a maximum of 0.69 early on 8 December 2007, which corresponds to sub-100 nm SSA concentrations of 110-290 cm$^{-3}$. The full SSA size distribution most likely peaks at a diameter greater than 100 nm [Prather et al., 2013; Lewis and Schwartz, 2004]. Therefore total SSA concentrations were likely substantially higher than the sub-100 nm SSA concentrations reported here. Previous observations in the Southern Ocean have observed SSA concentrations for particles greater than 80 nm in diameter of up to 170 cm$^{-3}$ [Kreidenweis et al., 1998]. High SSA concentrations will enhance CCN concentrations, with possible climate implications.

4.1. Sea spray composition

Very few ambient marine observations are characterised by sub-100 nm SSA fractions of greater than 0.5, with measurements particularly scarce in the Southern Hemisphere (Table 2). Previous summertime studies of ambient SSA in the north Atlantic [O’Dowd et al., 2004] and in situ, artificially produced SSA in the north Pacific [Quinn et al., 2014], observed an increasing SSA organic fraction, up to approximately 80%, with decreasing particle size. The ambient SSA organic fraction was identified as predominantly primary, however did contain a secondary organic component [O’Dowd et al., 2004; Ceburnis et al.,
Results from our study are not consistent with relationships observed in O’Dowd et al. [2004] and Quinn et al. [2014]. Contrary to the above studies the observed organic volume fraction from the HGF measurements was up to 11 – 46 %, and increased HGFs with decreasing particle sizes down to 16 nm in diameter suggested a decreasing organic fraction. The results herein are broadly consistent with submicron organic mass fractions of 5-50% previously observed in the Southern Ocean [Quinn et al., 2000; Middlebrook et al., 1998; Murphy et al., 1998a; Andreae, 1982]. Other studies looking at sub-100 nm SSA artificially produced in-situ in the North Pacific [Bates et al., 2012], have observed a HGF suppressed by 10% relative to artificial sea salt and independent of the particle size. SSA observed in this study displayed similarly suppressed HGFs and were also non-volatile (to 280 °C), suggesting that if there are any internally mixed organic components they were non-volatile. This study provides a unique characterisation of hygroscopic and volatile properties of summertime sub-100 nm SSA with a dominant (greater than 50%) inorganic component.

TEM images of 50nm particles collected between 08:00 and 16:00 8 December 2007 are not consistent with sea salt or ammonium sulfate and resemble organic particles thought to be from the surface ocean microlayer [Leck and Bigg, 2010]. These particles appeared to be made up of aggregates of 5 nm particles held together in a transparent matrix [Leck and Bigg, 2010]. In addition high resolution X-ray spectrometry of particles during this period identified calcium as the element detected with the highest concentration, along with sulfur. Sodium was near absent in the TEM-samples indicating that little to no sea salt was present [Leck and Bigg, 2010]. A similar composition was observed by the same authors in other oceans using the same methodology [Leck and Bigg, 2005a; Bigg and Leck, 2008; Leck and Bigg, 2008]. The chemical composition, both in terms of the organics observed but even more important in terms of the inorganic composition, reported by [Leck and Bigg, 2010], is in contrast with the observations herein. We have shown clear evidence of a large fraction (~50%) of highly hygroscopic (HGF~2), refractory (up to 280°C) sub-100 nm particles that deliquesced around 74% RH. This combination of properties provides unambiguous evidence of the presence of large numbers of sub-100 nm SSA with a large proportion (greater than 54% by volume) of inorganic salts. It is unclear whether the absence of sea salt in TEM samples resulted from misattribution of sea salt due to the presence of a non-volatile organic component or an absence of sea salt particles resulting from inadequate sampling statistics (only 10 particles sampled on 8 December 2007 are discussed by Leck and Bigg [2010]; 4 imaged by TEM, and 6 analysed by X-ray spectrometry). These results bring into question the applicability of TEM data to provide quantitative and representative data on the composition of atmospheric aerosols, and could have consequences for observations in other ocean basins.

Observations of primary marine aerosols have been undertaken using a wide range of techniques and indicate great spatial and seasonal variation in composition. Simultaneous measurements using online and offline methods are rare and this study highlights the potential for biases in analysis techniques to influence marine aerosol measurements, which are already complicated by spatial and seasonal variations. Further inter-comparison studies are needed to appropriately quantify the composition of sub-100 nm SSA.
4.2. SSA source

Air mass back trajectories for periods during which the highest proportion of SSA were observed at Cape Grim were characterised by relatively high altitude, and thus low pressure and temperature, as well as low relative humidity and rainfall (Figure 6). There were two high surface wind speed periods in the back trajectories spanning the high SSA event. The first was 20-40 hours preceding the arrival of the air mass at Cape Grim and involved wind speeds of 10.2 - 19.9 ms\(^{-1}\). The second was approximately 100 hours upwind of Cape Grim and involved wind speeds of 12 - 18.5 ms\(^{-1}\). The high surface wind speed periods correspond to locations approximately 1500 km and 3200 km west and southwest of Cape Grim, respectively. Ocean surface wind speeds were similar for back trajectories from 15:00 7 December to 17:00 8 December, suggesting that the SSA production was relatively constant for these back trajectories.

Peak SSA concentrations corresponded with a minimum in atmospheric turbulence at Cape Grim, the boundary layer depth falling from 1060 m at 17:00 on 7 December to 650 m at 4:00 on 8 December. This indicates that the relatively constant source of SSA was ejected into an increasingly compressed boundary layer, which resulted in increased SSA concentrations from 7:00 on 7 December to 4:00 on 8 December. Following this the boundary layer rose and the SSA concentrations dropped again. Back trajectories corresponding to the highest SSA fractions had periods above the boundary layer, particularly from 110 to 140 hours before the air mass reached Cape Grim (Figure 6). This suggests that the arrival of air masses with high SSA concentrations at Cape Grim coincided with sulfates from the free troposphere.

There was no precipitation associated with the high surface wind event 1500 km west of Cape Grim. This supports cloud level measurements in the Pacific where increased SSA production during high wind speed events were observed to be offset by even modest increases in precipitation [Blot et al., 2013].

4.3. Contribution to CCN

Meteorological observations, back trajectory modelling and nanoparticle measurements all indicate that increased SSA concentrations were associated with entrainment of air from the free troposphere. The size distribution of particles over the period when SSA was observed indicates the presence of a Hoppel minimum at 63 to 82 nm (Figure 3B). The Hoppel minimum is apparent in the total aerosol size distributions, but is unclear in the SSA size distributions (Figure 3B). Although it is unclear whether there were SSA particles that were previously activated into cloud droplets, the high measured HGFs indicate that the SSA particles could make a contribution to the cloud level CCN in this region during periods with sufficient updraft velocity.

To examine the enhancement of CCN concentrations due to the high SSA fractions observed during the SSA event sub-100 nm HGFs were used to estimate single hygroscopicity parameters (κ) for both the SSA and nss-sulfate modes [Petters and Kreidenweis, 2007]. The κ parameters were then used to calculate
CCN concentrations at 25°C. Two cases were considered to investigate the effect of high SSA fractions on CCN concentrations. The first case is an external mixture of 40% nss-sulfate and 60% SSA, representing nominal values for the peak of the high SSA event. The second case was 100% nss-sulfates representing conditions with no sub-100 nm SSA. Using the calculated \( \kappa \) values the critical diameter was calculated as a function of supersaturation. CCN concentrations were calculated by integrating the size distributions above the critical diameter. The CCN activation ratio is the ratio of CCN concentration to condensation nuclei (CN) concentration. CN concentrations were calculated by integrating the entire size distribution. An average size distribution for the period 6:00 to 9:00 8 December 2007 was used for the high SSA mode case and an average over 10:00 to 15:00 7 December for the case with no sub-100 nm SSA. The total integrated concentrations for the high SSA particle case and no SSA particles case were 347 and 368 cm\(^{-3} \), respectively. Therefore the enhancements in absolute CCN concentrations shown in Figure 7A were due to the increased proportion of SSA, rather than an increase in overall particle concentrations.

The supersaturation at which a population of particles were initially activated into droplets can be estimated by applying the particle diameter at the Hoppel minimum as the critical diameter for droplet formation [Blot et al., 2013]. Estimated supersaturations range from 0.25 to 0.38% and 0.13 to 0.2% using the \( \kappa \) calculated from the HGFs for the nss-sulfate and SSA modes, respectively. This provides a guide for the typical cloud supersaturation in the Southern Ocean south of Australia during the study period. Enhancement of the CCN activation ratio is observed with the presence of sea salt (Figure 7). The enhancement in the CCN activation ratio is 8.4% at 0.2% supersaturation and 8.7% at 0.4% supersaturation. It should be noted that the skill of subsaturated H-TDMA measurements to represent CCN concentrations is an ongoing research question. For example Good et al. [2010a] identified an increase in the disagreement between measured CCN number concentration and that calculated using H-TDMA methods with supersaturations below 0.2%. Nevertheless an enhancement in CCN with increasing sea salt is to be expected due to its hygroscopic properties. Determination of the influence of the enhancement of CCN concentrations on cloud properties requires further modelling.

5. Conclusions

Large concentrations of sub-100 nm SSA particles ranging in size from 16 to 97 nm diameter were observed at Cape Grim, Tasmania in clean, marine conditions on 7 – 8 December 2007. Two externally mixed modes were observed in the HGF distributions, the SSA mode with very high HGFs and another mode with moderate HGFs. The moderate HGF mode displayed volatility consistent with ammonium sulfate and prompt deliquescence at 79-80% RH, providing strong evidence that this mode is dominated by nss-sulfates. The SSA particles were refractory (up to 280 °C) and they deliquesced promptly at 73-75% RH, which further confirmed their identity as SSA particles with a large proportion of inorganic sea salt. The HGFs at 90% of the ambient SSA particles were suppressed relative to those for pure sea salt, which suggests the inorganic sea
salt may have been internally mixed with a non-volatile organic component. Continuous HGF measurements provided a temporal characterisation for the SSA event. Number fractions of the SSA mode peaked at 69%, corresponding to an estimated sub-100 nm SSA concentration of 110-290 cm⁻³.

Measurements of sub-100 nm inorganic SSA are scarce, particularly for the Southern Hemisphere. The observation and characterisation of 16 to 97 nm diameter SSA is a unique set of measurements. Based on the measured HGFs, the organic volume fraction of the SSA was calculated to be 11 – 46%. This result is contrary to summertime primary marine aerosol observations from the North Atlantic and Pacific Oceans [O’Dowd et al., 2004; Facchini et al., 2008; Quinn et al., 2014], which show a greater sub-100 nm organic fraction. Additionally, these previous studies observed increased organic enrichment with decreasing particle size. In this study, HGFs increased with decreasing particle size, which indicates the possibility of a reduced organic fraction at smaller sizes. Discrepancies in observed size dependant organic SSA fraction suggest that organic enrichment is not necessarily spatial uniform during periods of high biological activity. Simultaneous TEM and X-ray spectrometry of sub-100 nm mode aerosols collected from the same location, and at the same time, displayed a distinct lack of sea salt and appear to be made up of organic aggregates and microgels [Leck and Bigg, 2010]. As strong evidence of the existence of a large sea salt fraction (high HGF, non volatile up to 280°C, deliquescence at 75% RH) has been presented in this study we highlight the potential biases of other techniques in analysis of the chemical composition of marine aerosols. Further inter-comparison studies are needed to properly quantify the composition of sub-100 nm SSA.

Analysis of air mass back trajectories indicated that the SSA particles observed at Cape Grim were produced 1500 km upwind in the Southern Ocean during high wind speed events (12-20 ms⁻¹). The arrival of SSA particles at the site coincided with moderate increases in 3-10 nm particle concentrations (hourly averages of up to 170 cm⁻³), which were likely due to the entrainment of air from the free troposphere following the passing of a cold front [Gras et al., 2009]. We suggest the dropping boundary layer on the morning of 8 December could have contributed to an enhanced SSA number fraction. Although this event does not provide information on the long-term sub-100 nm particle composition at Cape Grim it provides details on the ambient SSA composition and the factors that control SSA concentrations in the atmosphere.

Acknowledgements

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Table 1: Organic fraction observed from nascent SSA measurements.

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Season</th>
<th>Measurement technique (s) ¹</th>
<th>Particle size</th>
<th>Organic Fraction ²</th>
<th>Weighting factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinn et al. 2014</td>
<td>North West Atlantic</td>
<td>Autumn</td>
<td>CCNc</td>
<td>100nm ; 40 nm</td>
<td>40% 80%</td>
<td>volume</td>
</tr>
<tr>
<td>Facchini et al. 2008</td>
<td>North East Atlantic</td>
<td>Summer</td>
<td>IC, TOC, EGA, HNMR</td>
<td>125-250nm</td>
<td>77%</td>
<td>mass</td>
</tr>
<tr>
<td>Prather et al. 2013; Collins et al. 2013</td>
<td>North East Pacific</td>
<td>Autumn</td>
<td>TEM-EDX, AMS, CCNc, DASH-SP</td>
<td>60-180 nm</td>
<td>OC 26% SS-OC 55%</td>
<td>number</td>
</tr>
<tr>
<td>Keene et al. 2007</td>
<td>North West Atlantic</td>
<td>Autumn</td>
<td>IC, TOC</td>
<td>130 nm</td>
<td>80%</td>
<td>mass</td>
</tr>
<tr>
<td>Modini et al. 2010</td>
<td>South west Pacific</td>
<td>Summer</td>
<td>VH-TDMA</td>
<td>71-77 nm</td>
<td>8%</td>
<td>volume</td>
</tr>
<tr>
<td>Fuentes et al. 2011</td>
<td>Model equatorial Atlantic seawater</td>
<td>-</td>
<td>H-TDMA, CCNc</td>
<td>40-240 nm</td>
<td>8-37%</td>
<td>volume</td>
</tr>
</tbody>
</table>

¹ CCNc (cloud condensation nuclei counter), IC (ion chromatography), TOC (total organic carbon), EGA (evolved gas analysis), HNMR (proton nuclear magnetic resonance), TEM-EDX (transmission electron microscopy with energy dispersive x-ray), AMS (aerosol mass spectrometry), DASH-SP (differential aerosol sizing and hygroscopicity spectrometer probe).

² All assumed to be internally mixed with sea salt except for [Prather et al., 2013], which indicates an external mixture of organics (OC) and sea salt internally mixed with organics (SS-OC).
Figure 1: Time series of particle size distributions (A), particle number concentration (B), number fraction of SSA mode particles (C), number fraction of partially neutralised (pn) nss-sulfates (D) and the concentration of sub-100 nm SSA (E) from 12:00 7/12/07 to 18:00 8/12/07. Particle number concentrations measured using TSI3010 CPC (blue), TSI3025 (red) and the difference between TSI3025 and TSI3010 (green). SSA mode defined by HGF>1.85 at 90% RH. Horizontal bars in C show periods when particle deliquescence (Del.) and volatility (Vol.) were being measured. Partially neutralised (pn) nss-sulfate measured as number fraction of more hygroscopic mode at 74-76% RH. Sub-100 nm SSA estimated from size dependant very high HGF fraction and size distribution.
Figure 2: Air origin probability density maps for the Cape Grim monitoring station, 4am 8/12/2007 to 1 pm 8/12/2007 [Jones et al., 2007].

Figure 3: HGF at 90% RH for the SSA (red, pink and grey) and nss-sulfate (blue and light blue) particles at mobility diameters from 16 to 97 nm (A). Dark markers are Kelvin and shape factor corrected, light markers are raw HGFs and grey markers are Kelvin (not shape) corrected SSA. Kelvin and shape corrected growth factors for 95 nm particles observed overnight are represented by triangles. Size distributions for average total (green) and sub-100 nm SSA (red) particles (B). All observations taken between 07:30 and 08:40 8 December. Range in size distributions represents variation in concentration and SSA fraction between 07:30 and 08:40.
Figure 4: Volatility of 56 nm ambient marine aerosol observed during high SSA mode event on 8 December 2007 at Cape Grim. Temperature scan undertaken between 09:10 and 10:15 8 December 2007. Normalised number fraction indicated by colour scale. Growth factor is ratio of heated, humidified (90% RH) particle diameter to initial particle diameter, 56 nm. Volatility of laboratory generated (NH₄)₂SO₄ particles displayed for reference.
Figure 5: Deliquescence of 95nm ambient marine aerosol particles at Cape Grim, 22:00-23:00 (A) and 23:00-23:59 (B) 7 December 2007. Normalised number fraction indicated by colour scale. Modelled (NH₄)₂SO₄ and laboratory measured artificial SSA (not shape corrected) are indicated by white circles and black lines, respectively [Fletcher et al., 2007]. Deliquescence relative humidity (DRH) for NaCl [Biskos et al., 2006a] and (NH₄)₂SO₄ [Fletcher et al., 2007; Johnson et al., 2008] indicated with white lines.
Table 2: Selected sub-100 nm primary marine aerosol observations. SSA fractions are maximum fractions indicated in study. SSA fraction in TDMA studies identified by HGF, and therefore generally contain a large fraction of inorganic sea salt.

<table>
<thead>
<tr>
<th>Source</th>
<th>Particle Diameter (nm)</th>
<th>Location</th>
<th>Season</th>
<th>Method</th>
<th>Sea spray fraction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bialek et al. [2012]</td>
<td>35-165</td>
<td>Mace Head/ North Atlantic</td>
<td>All</td>
<td>H-TDMA</td>
<td>11-40%</td>
</tr>
<tr>
<td>O’Dowd et al. [2004]</td>
<td>60-125</td>
<td>Mace Head/ North Atlantic</td>
<td>Spring/Summer</td>
<td>Filter samples, Ion</td>
<td>64% b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>chromatography</td>
<td></td>
</tr>
<tr>
<td>Mårtensson et al. [2003]</td>
<td>35</td>
<td>Tenerife/ West Atlantic</td>
<td>Summer</td>
<td>H-TDMA</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Tenerife/ West Atlantic</td>
<td>Summer</td>
<td>H-TDMA</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>73</td>
<td>Tenerife/ West Atlantic</td>
<td>Summer</td>
<td>H-TDMA</td>
<td>14%</td>
</tr>
<tr>
<td>Fletcher et al. [2007]</td>
<td>100</td>
<td>Cape Grim (Southern Ocean)</td>
<td>Summer</td>
<td>VH-TDMA</td>
<td>15%</td>
</tr>
<tr>
<td>Berg et al. [1998]</td>
<td>35</td>
<td>Pacific Ocean</td>
<td>Spring</td>
<td>H-TDMA</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Pacific Ocean</td>
<td>Spring</td>
<td>H-TDMA</td>
<td>13%</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>Pacific Ocean</td>
<td>Spring</td>
<td>H-TDMA</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Southern Ocean</td>
<td>Spring/summer</td>
<td>H-TDMA</td>
<td>23%</td>
</tr>
<tr>
<td>Zhou et al. [2001]</td>
<td>35</td>
<td>Arctic Ocean</td>
<td>Summer</td>
<td>H-TDMA</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Arctic Ocean</td>
<td>Summer</td>
<td>H-TDMA</td>
<td>95%</td>
</tr>
<tr>
<td>This study</td>
<td>16-97</td>
<td>Cape Grim</td>
<td>Summer</td>
<td>VH-TDMA</td>
<td>69%</td>
</tr>
</tbody>
</table>

* Number fraction unless otherwise stated. SSA fraction identified as SSA due to the presence of a sea salt component (from HGF, see Section 2.3), unless otherwise stated.

b Mass fraction, SSA assumed to be comprised of sea salt and water insoluble organic matter [O’Dowd et al., 2004; Ceburnis et al., 2008; Facchini et al., 2008], dominated by organics (<10% sea salt).
Figure 6: Hourly back trajectories (7 day) for the high SSA mode event 7-8 Dec. Back trajectory map (A), altitude (B), relative humidity (C) and mixing ratio (D) shown on top, left to right. Surface wind speed (E), pressure (F), relative humidity (G) and rainfall (H) shown on bottom left to right. Back trajectories during the high SSA event are coloured by hourly averaged SSA fraction measured at Cape Grim and all other trajectories during the measurement campaign are shown in grey.
Figure 7: CCN concentrations (A) and activated fraction, ratio of CCN conc. to CN conc. (B). 60% SSA aerosol/40% sulfate (red line) is bounded (red shading) by the CCN activated fraction calculated using minimum and maximum k from HGF measurements at all measured sizes (including uncertainty). 100% sulfate aerosol (blue line) is bounded (blue shading) by the CCN activated fraction calculated using minimum and maximum k from HGF measurements at all sizes (including uncertainty). All calculations for 25°C.
4. Supplement

Introduction

Figure S1 and Figure S2 show the measurements used as identifiers of influence of continental air masses or other pollution events for the entire campaign and the high SSA period, respectively. The baseline sector, identified using the method outlined in Gras et al. [2009], is identified in blue. The figures show that during the high SSA event, particularly during the onset, the air was largely from the baseline sector, this is confirmed by low radon and black carbon concentrations.

Figure S3 and Figure S4 show the meteorological measurements taken throughout the entire campaign and during the high SSA event, respectively. The measurements show a sharp change in wind direction, simultaneous with a drop in pressure, likely to be associated with passing of a cold front (see Figure S6). This change in wind direction brings baseline sector air, which brought high SSA concentrations. In addition RH shows a decrease over the period during which the front passes and the SSA was observed.

HGF probability distributions, Figure S5, were used to calculate HGFs for sea salt and sulfate modes. The median HGF for each mode was obtained and the 95% confidence interval in the median for each mode was applied as the uncertainty in the HGF. This is particularly relevant for Figure 3.
Figure S1: CPC3025, black carbon and radon concentrations for the entire campaign, 22 Nov – 10 Dec 2007.

Figure S2: CPC3025, black carbon and radon concentrations for high SSA period, 12:00 07 Nov – 18:00 08 Nov 2007.
Figure S3: Meteorological observations for the entire campaign, 22 Nov – 10 Dec 2007. Wind direction, wind speed, atmospheric pressure and water vapour mixing ratio included.
Figure S4: Meteorological observations for high SSA period, 22 Nov – 10 Dec 2007. Wind direction, wind speed, atmospheric pressure and water vapour mixing ratio included.
Figure S5: Hygroscopic growth factor probability distributions for 15-97nm particles from the morning of 8/12/2007.
Figure S6: Mean sea level pressure charts for high SSA period [BoM, 2013].

References
7.2. Marine Aerosol Hygroscopicity and Volatility, Measured on the Chatham Rise (New Zealand)

Marine Aerosol Hygroscopicity and Volatility, Measured on the Chatham Rise (New Zealand)

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Abstract. The Surface Ocean Aerosol Production (SOAP) study was undertaken in February/March 2012 in the biologically active waters of the Chatham Rise, NZ. Aerosol hygroscopicity and volatility were examined with a volatility hygroscopicity tandem differential mobility analyser. These observations confirm results from other hygroscopicity-based studies that the dominant fraction of the observed remote marine particles were non-sea salt sulfates. Further observations are required to clarify the influences of seawater composition, meteorology and analysis techniques seasonally across different ocean basins.

Keywords: Marine aerosol, hygroscopicity, volatility, ammonium sulfate.
PACS: 92.20.Bk; 92.60.Mt; 82.33.Tb

Introduction

This study considers the composition of Aitken and accumulation mode remote marine particles observed at the Chatham Rise (East of New Zealand; latitude 42°S-44°S, longitude 174°E-177°E). These observations were undertaken during the IGBP-SOLAS Surface Ocean Aerosol Production (SOAP) voyage in February/March 2012 on board the research vessel RV-Tangaroa (NIWA, Wellington, New Zealand). The Chatham Rise is located in the southern Pacific Ocean and is characterized by intensive summer phytoplankton blooms. These blooms lead to high organic concentration in the water and high dimethyl sulfide concentrations in the water and gas phase.

Composition of the abundant Aitken and accumulation mode remote marine aerosol has important direct and indirect climate influences [1]. Modeling indicates that the marine organic aerosol parameterization has a significant impact on the aerosol indirect forcing [2]. Despite the importance of this aerosol source there are significant uncertainties surrounding the production mechanisms, processing and resulting ultrafine marine aerosol composition.

Typically hygroscopicity measurements indicate that the remote marine aerosol is dominated by particles with a moderately high hygroscopic growth factor (HGF) (~1.6), with a small contribution from very high HGF particles (~2), and low HGF particles (~1.3). This is consistent with an external mixture dominated by non-sea salt sulfate with sea salt aerosol (SSA) and organics and/or anthropogenic pollution [3].

The composition of sulfate particles varies depending on the ambient ammonia concentration and level of neutralization. The hygroscopic response of sulfates can provide an indication of neutralization. Sufficiently neutralized particles, such as
ammonium sulfate, display prompt deliquescence from solid to aqueous as the relative humidity is increased. In the presence of particles of intermediate neutralization no deliquescence is observed [4].

SSA is produced by bubble bursting at the ocean surface and is infrequently observed. SSA is rarely a dominant contributor to the sub 100nm diameter remote marine aerosol [3]. Wind speed is thought to be a key driver of SSA concentration [5]. Dominant organic contributions to the remote marine aerosol have also been observed, especially for sub 100nm particles during periods of high biological activity [6]. These measurements display relatively minor contributions from non-sea salt sulfates across all size ranges at times of both high and low biological activity [6].

Laboratory observations of artificially generated primary marine aerosols yield internally mixed SSA/organic aerosols with Aitken and accumulation mode organic volume fractions of 7-58% using hygroscopicity methods [7,8], and up to 80% using other methods [9].

Method/instrumentation

Atmospheric ultrafine Aitken and smaller accumulation mode particles (30-150nm diameter) were studied using a Volatility Hygroscopicity Tandem Differential Mobility Analyser (VH-TDMA) [10]. The VH-TDMA uses parallel Scanning Mobility Particle Sizers (SMPS) to examine particles of a pre-selected size that have been conditioned to high humidity and/or high temperature. Compositional information was obtained by exposing particles to a controlled relative humidity (20-90%) and observing the resultant hygroscopic growth. Further information is obtained from changes in the size and hygroscopic growth as particles are exposed to high temperature (25-550°C).

In addition the remote marine aerosol distribution and concentration was characterized using an SMPS (WCPC3781) and 2 condensation particle counters (CPC3007, CPC3010). Black carbon measurements were taken with an Aetholometer as a marker for ship pollution. Complementing the VH-TDMA measurements are observations from an ultra-fine organic TDMA (UFO-TDMA). This instrument examines the change in preselected particle size (10<d<50nm) after being exposed to ethanol vapor, providing information on an organic volume fraction (OVF) [11].

The RV-Tangaroa route was designed to maximize the time spent in waters with high biological productivity and efforts were made to minimize the influence of ship pollution on atmospheric measurements. This resulted in the examination of areas with a broad range of water biology and chemistry under a variety of meteorological conditions.

Observations and discussion

H-TDMA selected observations indicate that the 30-150 nm diameter marine aerosol was dominated by particles of moderately high hygroscopicity with fractions of the total number of ambient particles at the preselected size ranging from approximately 0.6 to 1. This is consistent with high concentrations of non-sea salt sulfates. Smaller contributions from externally mixed particles with very high hygroscopicity (number fraction of up to approximately 0.3) and low hygroscopicity (number fraction of up to approximately 0.4) were also observed. The aerosol composition appears to be broadly consistent with observations from other locations using hygroscopicity methods [3].

Volatility measurements of 50 nm particles taken within (15 February) and outside of phytoplankton blooms (2 March) are shown in Fig. 1. These particles had a HGF of
1.5 and an OVF of 6-12% an indication that they are moderately hygroscopic non-sea salt sulfates. Fig. 1 indicates that the aerosol is volatilized at approximately 150°C, presenting further evidence for the dominance of non-sea salt sulfates. Measurements taken from within and outside of the phytoplankton bloom are remarkably similar, suggesting that in this case the water composition hasn’t played a significant influence on Aitken mode particle composition.

**FIGURE 1.** Volatility of 50 nm marine aerosol particles from within phytoplankton bloom (15 February) and outside of bloom (2 March).

**FIGURE 2.** Deliquescence of 50 nm marine aerosol particles from outside of phytoplankton bloom (26 February).

Figure 2 shows the deliquescence measurements of 50 nm particles outside the phytoplankton bloom. The growth of ~1.6 observed at 90% RH is a further evidence for the dominant presence of non-sea salt sulfates. An increase in the HGF above 1 is observed above approximately 70% RH, indicating that the dominant proportion of particles had neutralization greater than or equal to that of letovicite [4]. A reasonably prompt deliquescence can be seen between approximately 76% and 79% relative humidity, this is consistent with the deliquescence point of ammonium sulfate for 50 nm particles. The hygroscopic response suggests that the aerosol is dominated by ammonium sulfate and that ambient ammonia concentrations were high, possibly due to biogenic emissions. The UFO-TDMA also observed the dominance of ammonium sulfate on the early morning of 26th by an OVF value of 6%.

These observations confirm results from many other hygroscopicity-based studies indicating that the dominant fraction of the observed remote marine particles were non-sea salt sulfates. It appears that the composition of the secondary sulfate particles was relatively constant, indicating limited response to changes in the water biology surrounding the ship or a constant regional source. There were no atmospheric observations indicating a significant proportion of primary organics, despite measurements being undertaken in biologically active waters. Further observations
are required to clarify the influences of seawater composition, meteorology and analysis techniques seasonally across different ocean basins.

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