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New Particle Formation in Marine Air

A Thesis Presented to
The National University of Ireland, Galway
For the Degree of Philosophiae Doctor

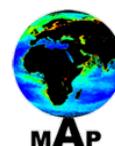
By

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Abstract

Marine aerosols contribute significantly to global climate directly by absorbing or scattering solar radiation, as well as indirectly by altering the reflectance and persistence of clouds. This work presents results of several investigations into the physicochemical properties of particulate matter over the North East Atlantic ocean.

A suite of specifically designed aerosol instrumentation was used to perform an analysis of the characteristics of aerosol size distributions measured in air masses advecting over the Mace Head Atmospheric Research Station during the year 2008. During this time twelve aerosol size distribution clusters were identified as systematically occurring, which were further categorised into four groups with similar characteristics: coastal nucleation category (occurring 21.3 % of the time), open ocean nucleation category (occurring 32.6% of the time), background clean marine category (occurring 26.1% of the time) and anthropogenic category (occurring 20% of the time). Analysis and observations of open ocean new particle production are also reported, where new particle formation events were observed to form a distinct peak in the size distribution with a mode at ~15 nm and grow to a mode of ~50 nm over periods of 24-48 hours, during which time air masses were calculated to have advected over biologically-rich waters in the North Atlantic before detection. A study of size distribution measurements carried out at Mace Head over a seven year period, showed that these nucleation events also exhibit a seasonality, with a monthly average occurrence of 5.7 per percentage occurrence of clean air, peaking in May.

In an investigation of new particle formation from *Laminaria digitata* macroalgae, aerosol nucleation in a range of I₂ (0.3 – 76 ppb_v) and O₃ (<3 – 96 ppb_v) mixing ratios was found to be significant, as well as correlated ($R^2 = 0.95$) with I₂ for low O₃ mixing ratios (<3 ppb_v). In experiments where particle production as a function of laboratory-generated I₂ over a mixing ratio range of 1-8 ppbv was conducted under moderate O₃ mixing ratios (~24 ppbv), a 100-fold

or greater increase in the aerosol number concentrations and mass fluxes was observed compared to the low O_3 experiments. A linear relationship ($R^2 = 0.81$) between particle concentration and I_2 was also found and this relationship suggests an I_2 mixing ratio range of 6-93 ppt_v for particle production events frequently observed at Mace Head. Simulations examining the ability of the modal aerosol microphysical model M7 to predict new particle formation and growth from condensable iodine vapours also yielded large particle number concentrations. From a base case particle concentration of 222 cm⁻³ at radii >15 nm, increases in concentrations to 366 cm⁻³ were predicted from a case where the nucleation was assumed to be from OIO-OIO, 722 cm⁻³ for a case where OIO-H₂SO₄ case was assumed to be involved in the particle formation process, and 1584 cm⁻³ for a OIO-H₂SO₄ case where there was also additional condensing organic vapours. This work shows that despite being characterised by low water solubility, particles containing a large amount of organic matter in addition possess a high CCN activation efficiency. Also, investigation into marine particle size distributions shows that when volcanic ash is present in the marine atmosphere, a bimodal aerosol size distribution can be observed. In an examination of the Eyjafjallajökull ash plumes present in air masses arriving at Mace Head, a clear peak in the mass distribution at a diameter of 600 nm was observed, with the measured particles having been extremely hydrophilic.

This work has elucidated some of the statistical characteristics of marine size distributions as well as providing new information on the underlying mechanisms of observed marine particle nucleation events, which in turn will allow for a more complete understanding of marine aerosols and their impact on climate change.

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New Particle Formation in Marine Air

Thesis Outline

List of Publications

This thesis consists of an introductory review, followed by 6 main research articles, and 4 supporting research articles.

- 1 Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjåraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Gruning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H. G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Lösschau, G. and Bastian, S. (2012). Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions. *Atmos. Meas. Tech.* 5:657-685.

<http://www.atmos-meas-tech-discuss.net/3/5521/2010/amtd-3-5521-2010.html>

- 2 Dall'Osto, M., Monahan, C., Greaney, R., Beddows, D. C. S., Harrison, R. M., Ceburnis, D. and O'Dowd, C. D. (2011). A statistical analysis of North East Atlantic (submicron) aerosol size distributions. *Atmos. Chem. Phys.* 11:12567-12578.

<http://www.atmos-chem-phys-discuss.net/11/21677/2011/acpd-11-21677-2011.html>

- 3 O'Dowd, C., Monahan, C. and Dall'Osto, M. (2010). On the occurrence of open ocean particle production and growth events. *Geophys. Res. Lett.* 37:L19805.

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- 5 Ashu-Ayem, E. R., Nitschke, U., Monahan, C., Chen, J., Darby, S. B., Smith, P. D., O'Dowd, C. D., Stengel, D. B. and Venables, D. S. (2012). Coastal iodine emissions: Part 1. Release of I₂ by *Laminaria digitata* in chamber experiments. *Environmental Science & Technology* 2012 46 (19), 10413-10421.

<http://pubs.acs.org/doi/abs/10.1021/es204534v>

- 6 Monahan, C., Ashu-Ayem, E. R., Nitschke, U., Darby, S. B., Smith, P. D., Stengel, D. B., Venables, D. S. and O'Dowd, C. D. (2012). Coastal Iodine Emissions: Part 2. Chamber experiments into particle formation from *Laminaria digitata*-derived and laboratory-generated I₂. *Environmental Science & Technology* 2012 46 (19), 10422-10428.
<http://pubs.acs.org/doi/abs/10.1021/es3011805>
- 7 Monahan, C., Vuollekoski, H., Kulmala, M. and O' Dowd, C. (2010). Simulating Marine New Particle Formation and Growth Using the M7 Modal Aerosol Dynamics Modal, *Advances in Meteorology*, vol. 2010, Article ID 689763, 9 pages, 2010. doi:10.1155/2010/689763.
<http://www.hindawi.com/journals/amet/2010/689763/>
- 8 O'Dowd, C., Ceburnis, D., Ovadnevaite, J., Martucci, G., Bialek, J., Monahan, C., Berresheim, H., Vaishya, A., Grigas, T., Jennings, S. G., McVeigh, P., Varghese, S., Flanagan, R., Martin, D., Moran, E., Lambkin, K., Semmler, T., Perrino, C. and McGrath, R. (2011a). The Eyjafjallajökull ash plume - Part I: Physical, chemical and optical characteristics. *Atmospheric Environment* 48:129-142.
<http://www.sciencedirect.com/science/article/pii/S1352231011007059>
- 9 O'Dowd, C., Varghese, S., Martin, D., Flanagan, R., McKinstry, A., Ceburnis, D., Ovadnevaite, J., Martucci, G., Bialek, J., Monahan, C., Berresheim, H., Vaishya, A., Grigas, T., McGraw, Z., Jennings, S. G., Langmann, B., Semmler, T. and McGrath, R. (2011b). The Eyjafjallajökull ash plume - Part 2: Simulating ash cloud dispersion with REMOTE. *Atmospheric Environment* 48:143-151.
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- 10 Ovadnevaite, J., Ceburnis, D., Martucci, G., Bialek, J., Monahan, C., Rinaldi, M., Facchini, M. C., Berresheim, H., Worsnop, D. R. and O'Dowd, C. (2011). Primary marine organic aerosol: A dichotomy of low hygroscopicity and high CCN activity. *Geophys. Res. Lett.* 38:L21806.
<http://www.agu.org/pubs/crossref/2011/2011GL048869.shtml>
- 11 Fierz-Schmidhauser, R., Zieger, P., Vaishya, A., Monahan, C., Bialek, J., O'Dowd, C. D., Jennings, S. G., Baltensperger, U. and Weingartner, E. (2010). Light scattering enhancement factors in the marine boundary layer (Mace Head, Ireland). *J. Geophys. Res.* 115:D20204.
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1 Introduction

Particulate matter in the atmosphere arises from both natural sources (e.g. windborne dust, sea spray, volcanoes, and biogenic vapours) and anthropogenic sources (e.g. combustion of fuels associated with transport, industrial processes). Whereas an aerosol is technically defined as a suspension of fine solid or liquid particles in a gas, common usage in atmospheric research refers to the aerosol as the particulate matter component only. Emitted directly from the source as particles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosol) atmospheric aerosol particles are generally considered to be airborne liquid or solid particles that ranges in size from a few nanometres (nm) to tens, or even hundreds, of micrometers (μm) in diameter. Combustion and other high-temperature processes are largely responsible for primary emissions of fine-mode particles [Seinfeld 2006], with mechanical processes such as grinding, entrainment of dust and soil [Duce 1995] and droplet formation by waves generate coarse mode particles [Blanchard *et al.* 1980, Monahan 1986].

Secondary particles produced from gas to particle conversion processes constitute only a tiny fraction of the natural aerosol budget in terms of mass flux to the atmosphere, but comprise the dominant fraction where particle number flux is concerned. The formation and subsequent growth of particles in the presence of a condensable vapour are processes of significant importance in the atmospheric aerosol system. The formation of these new particles through secondary processes change both the particle size and composition distributions as the size distribution of the aerosol population at a given time is affected by particle growth rates, which in turn are governed partially by particle compositions. This secondary production occurs frequently in the atmosphere

and has been observed at numerous places with very different climatological conditions, such as boreal forests [Mäkelä *et al.* 1997], coastal areas [O'Dowd *et al.* 1998], urban areas [McMurry *et al.* 2005], or the free troposphere [Brock *et al.* 1995]. The nucleation of new particles usually occurs in discrete bursts of very large numbers at their sources, and constitute a distinct 'nucleation mode' in the particle size distribution. The evolution of these bursts, and their changing characteristics over time, can be described using set of differential equations relating the various ambient conditions at the time.

The change in concentration of the newly formed particles, and their successive growth, depends upon the source rate of the condensable vapour species, the number of particles already present the mode, and the flux of new particles. These nucleation and growth events described above can be examined using three equations describing the rate of change of vapour concentration, aerosol particle number concentration and particle growth [Kulmala *et al.* 2001].

The time evolution for aerosol number concentration (N) in size class i can be presented by:

$$\frac{dN_i}{dt} = J_i - CoagS.N_i \quad (1)$$

where J_i is the formation rate of particles and CoagS is the coagulation sink for size i particles. Taking into account the condensable vapour molecules of species X, the time dependence of the vapour concentration (C) can be expressed by

$$\frac{dC}{dt} = Q - CS.C \quad (2)$$

where Q is the source rate of the condensable vapour and CS is its condensation sink to the pre-existing aerosol. The condensation sink (CS), with units of s^{-1} , describes how rapidly condensable vapour molecules will condense on the existing aerosol. Specifically this quantity describes the loss rate of molecules

with diameter d_p , diffusion coefficient D , and mean free path λ_v onto a distribution $n(d_p)$ (or N_i in the discrete case) of existing particles and as such, can be obtained from integrating over the particle size spectrum [Dal Maso *et al.* 2002].

$$\begin{aligned}
 CS &= 2\pi D \int_0^{\infty} d_p \beta_M(d_p) n(d_p) dd_p \\
 &= 2\pi D \sum_i \beta_{M_i} d_{p,i} N_i
 \end{aligned} \tag{3}$$

The transitional correction factor β_M can be expressed as [Fuchs *et al.* 1971]

$$\beta_M = \frac{Kn + 1}{0.377Kn + 1 + \frac{4}{3}\alpha^{-1}Kn^2 + \frac{4}{3}\alpha^{-1}Kn} \tag{4}$$

where Kn is the Knutson number $Kn = 2\lambda_v/d_p$ and α is the mass accommodation coefficient. In Eq. (4), α is assumed to be 1 while Kn can be expressed in terms of particle diameter and the mean free path of the individual vapour molecules [Pirjola *et al.* 1999] as

$$Kn = \frac{2\lambda_v}{d_p} \tag{5}$$

The mean free path λ_v is pressure and temperature dependent and can be determined from the following formula from [Willeke 1976]

$$\lambda_v = \lambda_r \left(\frac{101}{P} \right) \left(\frac{T}{293} \right) \left(\frac{1 + \frac{110}{293}}{1 + \frac{110}{T}} \right) \tag{6}$$

Where P is in kPa and T in K. At 293K and 1 atmospheric pressure, the mean free path λ_r is 0.039 μ m for H₂SO₄.

The growth-rate of particles in the mode can be expressed as:

$$\frac{dr}{dt} = \frac{m_v \beta_m D C}{r \rho} \quad (7)$$

Here, r is particle radius, m is molecular mass of condensable vapour, β_m is transitional correction factor for mass flux, D is the diffusion coefficient, and ρ is particle density. The eq. (7) can be integrated from r_0 to r to obtain:

$$C = \rho \frac{\left\{ \frac{r^2 - r_0^2}{2} + \left[\frac{4}{(3\alpha)} - 0.623 \right] \lambda (r - r_0) + 0.623 \lambda^2 \ln \frac{\lambda + r}{\lambda + r_0} \right\}}{\Delta t D m_v} \quad (8)$$

Where α is the mass accommodation coefficient (i.e. sticking probability) and λ is the mean free path [Kulmala *et al.* 2001]

This value can then be used to find J_1 (the nucleation rate, or formation rate, of 1 nm particles) where 1 nm is assumed to be the size of a new particle.

$$J_1 = J_3 e^{kt} = \left[\frac{dN_3}{dt} + K_3 N_3 \right] e^{Kt} \quad (9)$$

Here N_1 is the number concentration of 1 nm particles N_3 is the number concentration of 3 nm particles. J_3 is formation rate of 3 nm particles. The time t in equations above corresponds to the particle growth time for 1 nm particles to grow to 3 nm and K is a typical coagulation sink during the growth, the actual

value of which is close to K_1 . J_3 can be found by examining the change in concentration of 3 nm particles and the associated coagulation sink:

$$J_3 = \frac{dN_3}{dt} + K_3 N_3 \quad (10)$$

While having small mass, these particles grow quickly through either coagulation, due to their high Brownian velocities, or from condensation of condensable vapour species, and ultimately can indirectly influence climate by the enhancement of cloud condensation nuclei number concentrations.

Once formed, particles can change their size and composition by condensation or evaporation of vapour species, by coagulating with other particles, by chemical reactions, or by activation in the presence of water supersaturation to become fog and cloud droplets. Particles smaller than 1 μm , generally referred to as ‘fine’, in diameter generally have atmospheric concentrations in the range from about ten to several thousand per cm^3 , while those exceeding 1 μm , generally referred to as ‘coarse’, in diameter are usually found at concentrations less than 1 cm^{-3} . The fine and coarse particle modes are distinct in that the two typically, but not exclusively, originate from different sources, are altered in size and composition by different processes, have different composition, optical properties, and differ also in their associated removal mechanisms.

The fine particle mode can further be divided into nucleation, Aitken, and accumulation modes illustrated in Figure 1. The nucleation mode, which can be regarded as particles with a diameter up to about 0.01 μm , accounts for the size range in which the largest particle number concentrations occur, however even at high concentrations particles in the nucleation mode rarely account for more than a few percent of the total aerosol mass. Particles in the nucleation mode are almost primarily as a result of gas to particle conversion processes that arise from the nucleation of atmospheric gas species to form new particles or from the condensation of hot vapours during high temperature combustion processes. Overlapping with the nucleation mode are particles in the Aitken-mode size

range, composed of particles in the 0.01 to 0.1 μm size range. Aitken-mode particles are formed mainly by coagulation and condensation of nucleation-mode particles. Particles in this mode can subsequently grow by condensation of condensable vapours, or by coagulating with other Aitken-mode or larger particles.

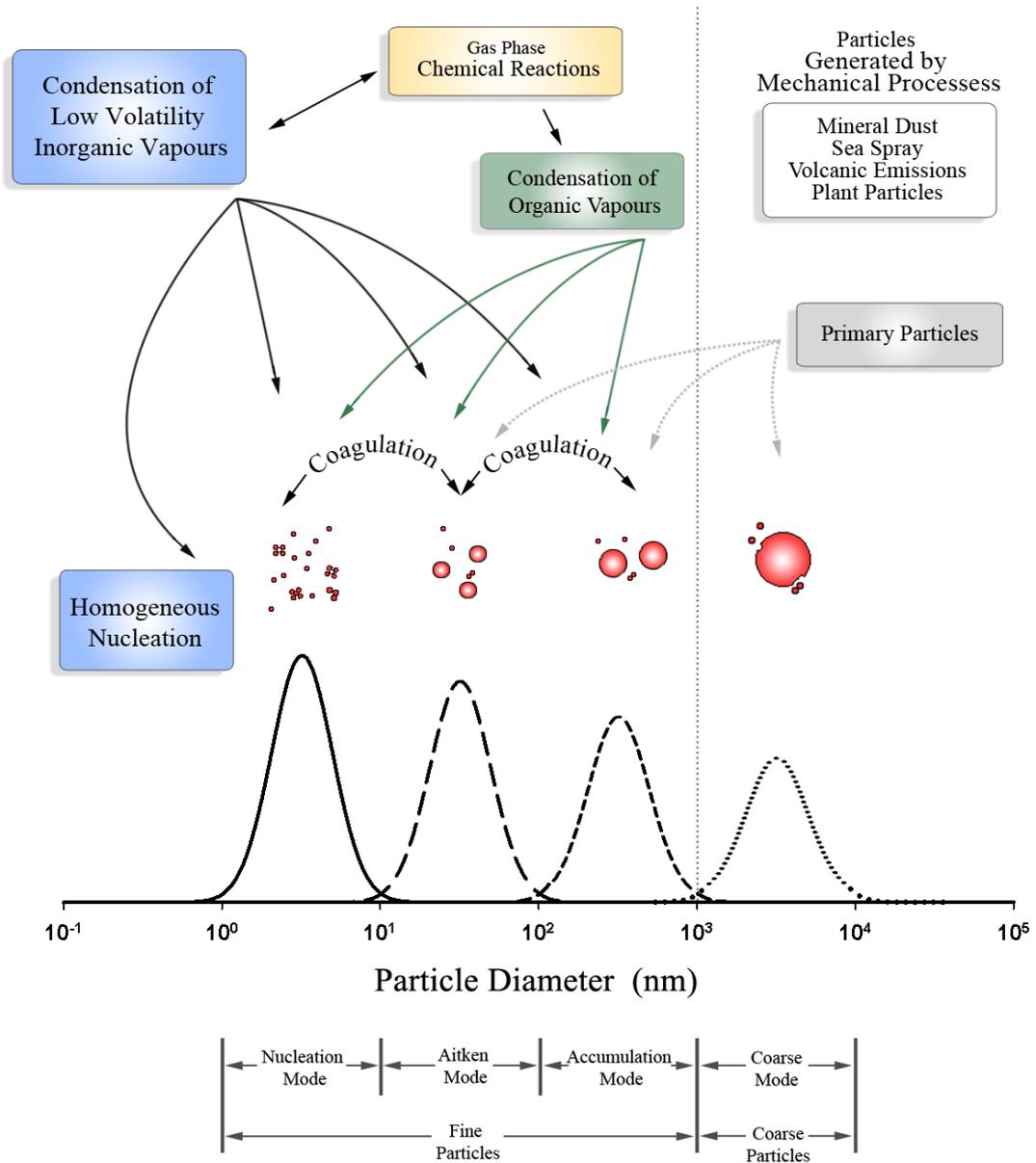


Figure 1. Idealised schematic of aerosol size distribution comprised of four modes; the nucleation, Aitken, accumulation and coarse. Growth and formation mechanisms are also indicated.

The accumulation mode, which can be considered as extending from 0.1 μm to about 1 μm , usually contains the majority of the available surface area, as well as a substantial portion of the overall aerosol mass. The main source of particles in the accumulation mode is from coagulation of Aitken mode particles, as well as growth of Aitken mode particles *via* condensation of vapours causing them to grow into the larger size ranges. In background air, the accumulation mode is usually formed from aqueous phase oxidation of dissolved gases such as SO_2 in clouds and fogs [O'Dowd *et al.* 1999]. In certain environments however, this size range can be predominantly made up of primary particles such as combustion particles or sea salt. The coarse mode in contrast, is composed mostly of primary particles, typically generated through mechanical processes. A small, and perhaps negligible, fraction of the mass in the coarse mode comes from growth of particles from the accumulation mode, but because coagulation of particle in the accumulation mode is very weak, it is only a very small proportion of the mass in that mode is transferred over into the coarse mode. Also, due to their larger size, and thus increased sedimentation velocities, coarse mode particles have a shorter lifetime in the atmosphere. Accumulation mode particles are termed so as they have the longest atmospheric residence times of all sizes due to removal processes having least influence on these sizes.

Particles are eventually removed from the atmosphere by 3 mechanisms: gravitational settling or sedimentation to the Earth's surface; turbulent deposition at the Earth's surface (both processes contributing to dry deposition), scavenging into cloud droplets as well as scavenging by precipitation (both processes contributing to wet deposition). Because wet and dry deposition lead to relatively short residence times in the troposphere, and because the geographical distribution of particle sources is highly non-uniform, tropospheric aerosols vary widely in concentration and composition over the earth. Whereas tropospheric trace gasses have lifetimes ranging from less than a second, for highly reactive gases, to a century or more for non-reactive gases, residence times of particles in the troposphere vary only from a few days to a few weeks.

Despite their low residence times however, aerosols perform an essential function in the atmosphere as we know it as they are directly responsible for the

formation of clouds. As water vapour needs non-gaseous surface to make the transition from a vapour to a liquid, a particle of certain size and composition can become activated to grow to fog or cloud droplets in the presence of a supersaturation of water vapour. These particles are known as cloud condensation nuclei (CCN). At a given mass of soluble material there is a critical value of the ambient water vapour supersaturation below which the particle exists in a stable state, and above which it spontaneously grows to become a cloud droplet of 10 μm or more in diameter. The number of particles from a given aerosol population that have the capacity to act as CCN is therefore a function of water supersaturation or particle composition. CCN number concentrations vary from fewer than 100 cm^{-3} in the remote marine atmosphere, to many thousand cm^{-3} in urban environments.

1.1 Marine Aerosols

Particles in the marine environment constitute one of the most important global natural aerosol systems, as despite their low concentrations, marine aerosols contribute significantly to the global aerosol budget considering the 70% of Earth's coverage by oceans. Having the ability to directly scatter and absorb radiation, aerosols over oceanic regions can potentially increase oceanic albedo directly by the formation of reflective aerosol layers, as well as indirectly by influencing both cloud albedo and precipitation efficiency (and thus increasing cloud lifetimes). This may result in less solar radiation reaching the sea surface, thereby mitigating the effects of greenhouse-gas induced global warming. They also influence biogeochemical cycling, and have substantial impacts on marine ecosystems. These particles are produced from both primary and secondary processes.

1.1.1 Primary Marine Aerosols

Primary aerosol production occurs from the interaction between wind and the ocean surface, resulting in the mechanical production of sea-spray droplets which can comprise both organic and inorganic matter. Sea spray is produced *via* the bubble bursting process typically resulting from whitecap generation, and leads to the production of particles in the range of the submicrometre size up to a few micrometers.

Sea salt comprises the majority of the mass concentration in the marine atmosphere, with a significant fraction occurring in the submicrometre size range, and is the dominant submicrometre scatterer in most oceanic regions [Kleefeld *et al.* 2002]. Sea salt aerosols are produced by a number of physical processes, especially the bursting of entrained air bubbles during whitecap formation [Blanchard *et al.* 1980, Monahan 1986, Monahan *et al.* 1986]. This results in a strong dependence on wind speed, may be the dominant contributor to both light scattering and cloud nuclei number concentrations in those regions of the marine environment where high wind speeds are prevalent and/or other aerosol sources are weak [O'Dowd *et al.* 1997, Murphy *et al.* 1998, Quinn *et al.* 1998]. Due to their high hygroscopicity, sea salt particles are very efficient CCN, however due to the fact that they cover a wide size range (about 0.05 to 10 μm diameter), they also have a correspondently wide range of lifetimes in the atmosphere, making large scale assessment of effects and characterisation difficult [IPCC 2007].

Much research has been carried out in attempts to quantitatively characterize sea spray organics contribution to marine aerosols. A comprehensive study carried out by O'Dowd *et al.* [2004] found that a size segregated chemical characterisation of particles occurring in clean air masses showed a significant organic, both water-soluble and water-insoluble, contribution to marine aerosol, as can be seen in Figure 2. The study showed that marine aerosol chemical composition is determined by the yearly biological cycle occurring in the north Atlantic and that, during periods of high biological oceanic activity, the organic fraction, especially the water insoluble, contributes substantially to the

submicrometer aerosol mass. They suggested that both the water-soluble and water-insoluble organic carbon, but more particularly the water-insoluble carbon, was likely as a result of bubble-mediated primary production. However evidence of SOA was found in coastal nucleation mode particles by Vaattovaara *et al.* [2006], wherein they used an experimental system to look at vapour uptake on recently formed 10nm particles. They found that for certain events, 11-14% of the mass fraction could be identified as organics produced from SOA formation processes, and suggested isoprene maybe responsible

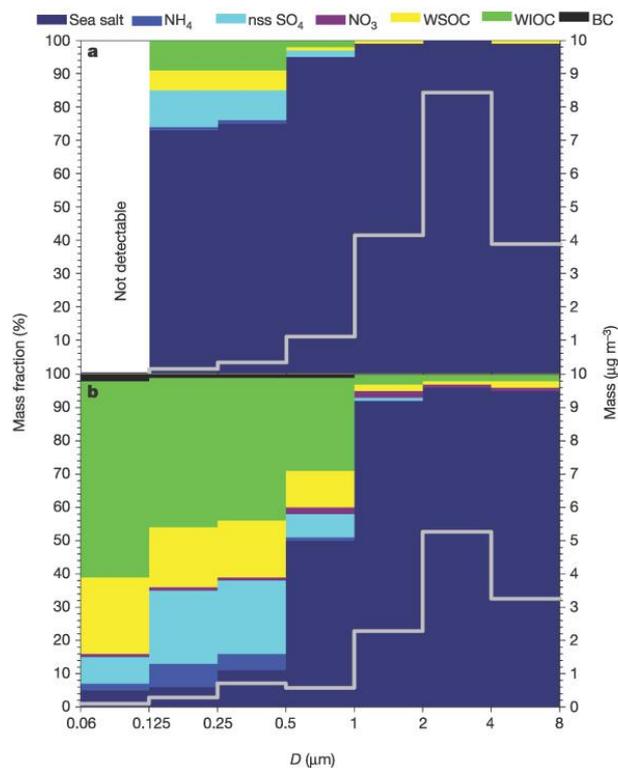


Figure 2. Average size-segregated chemical compositions and absolute mass concentrations for North Atlantic marine aerosols, reported by O'Dowd *et al.* [2004], sampled with a Berner Impactor, for a period of low biological activity (Top) and a period of high biological activity (Bottom). Figure reproduced from O'Dowd *et al.* [2004].

High enrichment factors were reported by Keene *et al.* [2007] and Facchini *et al.* [2008] for water soluble organic material, in nascent lab-produced sea spray particles, contained in sea water. In the study conducted by Keene *et al.* [2007], water soluble organic carbon content was highly enhanced in all aerosol size fractions and the greatest enhancements were found in the smallest size fraction (about 80% of aerosol mass was organic at $0.13\mu\text{m}$). The authors concluded that bubble bursting at the ocean surface produce significant quantities of sub-micron, hygroscopic, organic-dominated particles, implying that this mechanism is a potentially significant global source of climactically relevant particles. Facchini *et al.* [2008] also reported large contributions of organic matter in nascent sub-micron sea spray aerosols, up to $77 \pm 5\%$ in the $0.125\text{--}0.25\mu\text{m}$ size range, however in this case their analysis differentiated between water soluble and water insoluble organic carbon, finding a dominant contribution of water insoluble organic carbon (up to $94 \pm 4\%$ of OC in the $0.125\text{--}0.25\mu\text{m}$ size range). Furthermore, Facchini *et al.* [2008] highlighted that sea spray generated organics are likely to aggregate and form colloids or suspended particles, making the classification of water solubility a complex issue. The differences in the results arising from these two studies, may be attributable to the different organic carbon measurement approach, and/or also to differences in the chemical properties of the sea water used for generating aerosol particles by bubble bursting (oligotrophic Sargasso Sea versus North Atlantic Ocean during algal bloom).

1.1.2 Secondary Marine Aerosols

The secondary fraction derives from gas-to-particle conversion processes which involve biogenically emitted precursors. Following Shaw [1983], the CLAW hypothesis [Charlson *et al.* 1987] proposed a role for the marine biogeochemical sulphur cycle in altering global climate. Charlson *et al.* [1987], proposed a coupled biology – albedo feedback loop arising from dimethylsulfide (DMS) produced by phytoplankton in the ocean. DMS is outgassed by the ocean

into the atmosphere, where it undergoes oxidation by the OH radical to form SO₂ which is further oxidised to form H₂SO₄. H₂SO₄ is thought to participate in binary homogeneous nucleation with H₂O as well as ternary nucleation with NH₃, which subsequently may result in an increase in aerosol, and ultimately to, CCN concentrations.

There is strong evidence to support this hypothesis, such as the correlation between seasonal cycles of DMS, its particulate phase oxidation products (non-sea-salt SO₄²⁻ and MSA⁻), and CCN. At Cape Grim, Tasmania, a remote Southern Ocean measurement site, concentrations of atmospheric DMS, non-sea-salt SO₄²⁻, MSA⁻ and CCN all exhibit peaks in the summer months and have their minima in the winter as is expected for parameters controlled by biological activity [Ayers *et al.* 1991, Ayers *et al.* 1997]. Measurements of DMS and CCN made in the marine boundary layer over the tropical South Atlantic [Andreae *et al.* 1995] and the north-east Pacific Ocean [Hegg *et al.* 1991] reported that 40% to 50% of the variance in CCN number concentrations could be explained by the oxidation of DMS. Also observed in the South Atlantic measurements were significant correlations between non-sea-salt SO₄²⁻ or MSA⁻ mass concentrations and CCN [Andreae *et al.* 1995].

To date various global-scale atmospheric models have been used in sensitivity of CCN to enhanced emissions of DMS for both present-day and globally warmed future scenarios. Woodhouse [2010] reported that for the Southern Hemisphere, the sensitivity during summertime for current DMS fluxes is about 0.07, indicative of a 0.07% increase in total CCN (from all sources) that can be attributed to a 1% enhancement in DMS flux. The sensitivity is lower however for the Northern Hemisphere (0.02%), where the aerosol flux from all sources is greater. It is predicted that global warming will lead to a shallowing of the ocean mixed-layer depth accompanied by an increase in the incident solar radiation in the upper mixed layer. In a scenario where global warming leads to a 50% increase in CO₂ levels, one model result predicts that the DMS flux will increase by 1%, which results in only a ~0.1% enhancement in the global CCN concentration [Woodhouse 2010]. This low sensitivity is due to the relatively large numbers of marine boundary layer CCN arising from non-DMS sources.

Also simulations from various other coupled ocean–atmosphere general circulation models used to study the effect of climate change on marine DMS emissions and CCN and have not found a strong positive global response of sulphate aerosol to increased CO₂ concentration [Carslaw 2010]. This indicates that only very large deviations in the flux of DMS to the atmosphere would lead to a significant impact on CCN concentration.

Recent studies also, have indicated that there may be a potential inconsistency between aerosol modelling predictions and measurements in regards to the number of CCN that are formed as a result of nucleated particles. Kuang *et al.* [2009] found survival probabilities of up to 20 % for observed nucleation bursts and suggested inaccuracies in modelled growth rates from organic condensation as a possible reason for the discrepancy between model results of Pierce *et al.* [2009]. In contrast, Pierce *et al.* [2009] reported findings of low probabilities (10 % or less) of particles growing efficiently to CCN sizes in simulations where nucleation parameterizations were active. The study also found, using a global aerosol model, that global CCN number concentrations have a higher sensitivity to uncertainties in primary emissions than uncertainties in nucleation of new particles. A 12 % global average CCN sensitivity was reported when altering the new particle formation rate by six orders of magnitude. Furthermore, this low sensitivity was credited to reduced survival probabilities at increased nucleation rates. In an extreme case of fast ternary nucleation rates of taken from Napari *et al.* [2002], particle survival probabilities were estimated to be in the order of 10^{-8} .

The CLAW hypothesis also assumed that, for a fixed mass of liquid water in cloud, an enhancement in the CCN number concentration would lead to an increase in cloud albedo. Charlson *et al.* [1987] calculated that a 30% increase in the concentration of CCN would lead to an increase in planetary albedo, enough to decrease the Earth's global mean surface temperature by 1.3 K. In light of the low sensitivity of CCN variance to DMS flux, such a 30% increase in CCN concentration would require a 300% increase in the DMS flux. Also, investigations carried out over the past decade with high-resolution models have found systems that occur on cloud micro- and macro- physical scales that can act

as a buffering mechanism or are counter to the enhancement in cloud albedo that would be attributable to an increase in CCN [Wood 2007, Stevens *et al.* 2009]. This can be a significant as aerosols have an effect on not only cloud microphysics, such as cloud droplet size and number concentration, but also as well cloud macrophysics like cloud fraction, size and morphology [Zuidema *et al.* 2008, Small *et al.* 2009]. For example, for a system of non-precipitating clouds, feedbacks as a result of aerosol perturbations on clouds can lead to a decrease in cloud fraction [Small *et al.* 2009]. A CCN concentration increase results in increased evaporation rates owing to smaller cloud droplets. This increased rate of evaporation results in an increased entrainment of sub-saturated air surrounding the cloud and a decrease in cloud fraction. In cases such as this the effect of aerosol in an increase in cloud albedo is reduced by the decrease in cloud fraction [Zuidema *et al.* 2008]. Model parameterizations that do not take into account these changes in cloud macrophysics as a result of varying CCN number concentrations may not accurately represent the overall effect of aerosol–cloud interactions. Therefore the assumption of a high sensitivity of CCN to the flux of DMS and considering only a highly simplified and hitherto unknown, relationship between aerosol, CCN, and cloud albedo, the Charlson *et al.* [1987] hypothesis likely over-estimates cloud albedo response to varying CCN concentrations.

Also noteworthy is that the CLAW hypothesis assumes that deviations in cloud albedo, surface temperature and/or incoming solar radiation inevitably lead to changes in the production of DMS. While other studies have shown time-series measurements showing a seasonal correlation between levels of downwelling solar radiation and ocean surface mixed-layer DMS concentrations [Toole *et al.* 2004, Vallina *et al.* 2007], these correlations do not elucidate the sensitivity of the DMS production mechanism to changes in solar radiation. Simulations reveal that an increase in the solar radiation to the ocean's upper mixed layer arising from a 50% increase in atmospheric CO₂ levels result in only a minor (~1%) rise in global DMS concentrations [Vallina *et al.* 2007]. Other model calculations show that variations in DMS production arising from changes

in temperature and solar radiation that can cause an effect in ocean primary productivity are minor [Gunson 2006].

Despite important advances in the characterisation and understanding of secondary aerosol formation and transformation processes, some significant open questions remain relating to the global radiative effects of aerosols on climate as well as the global implication of localised phenomena such as nucleation events on precipitation and the hydrological cycle. To quantitatively assess the effects of these processes on climate, the various mechanisms and feedbacks in the aerosol-cloud-climate system at the full range of both temporal and spatial scales needs to be investigated

1.2 Coastal Particle Production Events

In the marine boundary layer, the most active areas for new particle formation are coastal regions, where frequent and significant particle nucleation events have been observed [O'Dowd *et al.* 1998, O'Dowd *et al.* 1999, O'Dowd *et al.* 2002]. Initially it had been thought that sulphur species were the primary chemical component involved in marine nucleation [Shaw 1983, Charlson *et al.* 1987], and although evidence has been found linking particle production and high DMS emissions [Clarke *et al.* 1998], more recent studies to identify a convincing scheme for the reproduction of the observed particle distributions [Grenfell *et al.* 1999] as a result of the role of DMS were not successful. While it was found that a ternary system of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ is likely to result in nucleation occurring in most atmospheric conditions more so than the previously suggested $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system [Kulmala *et al.* 2000], there is typically insufficient H_2SO_4 vapour available to facilitate the growth of nucleated clusters (formed primarily by homogeneous nucleation of embryos of the size of 0.5-1 nm) to measurable sizes of 3 nm (which result from subsequent condensation growth of stable embryonic clusters) or more [Pirjola *et al.* 2000].

Early studies into coastal aerosol production during the ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment - <http://www.uea.ac.uk/~acsoe/>) campaign however suggested that iodocarbons may play a role in coastal nucleation events, as iodocarbon species were observed to exhibit peak concentrations during low tide conditions [O'Dowd *et al.* 1998] when nucleation bursts were seen to occur.

Further studies carried out during the PARFORCE (New Particle Formation and Fate in the Coastal Environment) project [O'Dowd *et al.* 2002] located at Mace Head Atmospheric Research Station in the North-east Atlantic observed nucleation for sulphuric acid mixing ratios > 0.07 ppt (2×10^6 molecules cm^{-3}) but failed to observe any correlation between peak sulphuric acid concentrations and low tide occurrence or nucleation events. A typical case encountered during the PARFORCE campaign is shown in Figure 3. Growth factor analysis of 8 nm particles formed in the events indicated that these particles comprised of some species significantly less soluble than sulphate aerosol. Also a study in which 6-8nm particles were separated onto a TEM stub and analysed using X-ray dispersion techniques, found that particles in all samples contained iodine, and sulphur in most but not all [Mäkelä *et al.* 2002]. In the same study, an examination of biogenic halocarbon emissions from various species of seaweeds identified strong emissions of CH_2I_2 from *Fucus vesiculosus* in particular. The growth-factor data, the strong emission of halocarbons by coastal biota, the tidal related cycle in halocarbons and IO, combined with the fingerprinting of iodine in recently formed particles, suggested a link between the emission and subsequent photooxidation of biogenic iodocarbons leading to the formation of coastal particles through an iodine nucleation mechanism. It remained an open question however whether nucleation over the open ocean is driven by homogenous nucleation of condensable iodine vapours, or whether first, stable clusters are formed through ternary nucleation of sulphuric acid, ammonia and water vapour, followed by rapid growth into detectable sizes by condensation of iodine vapours.

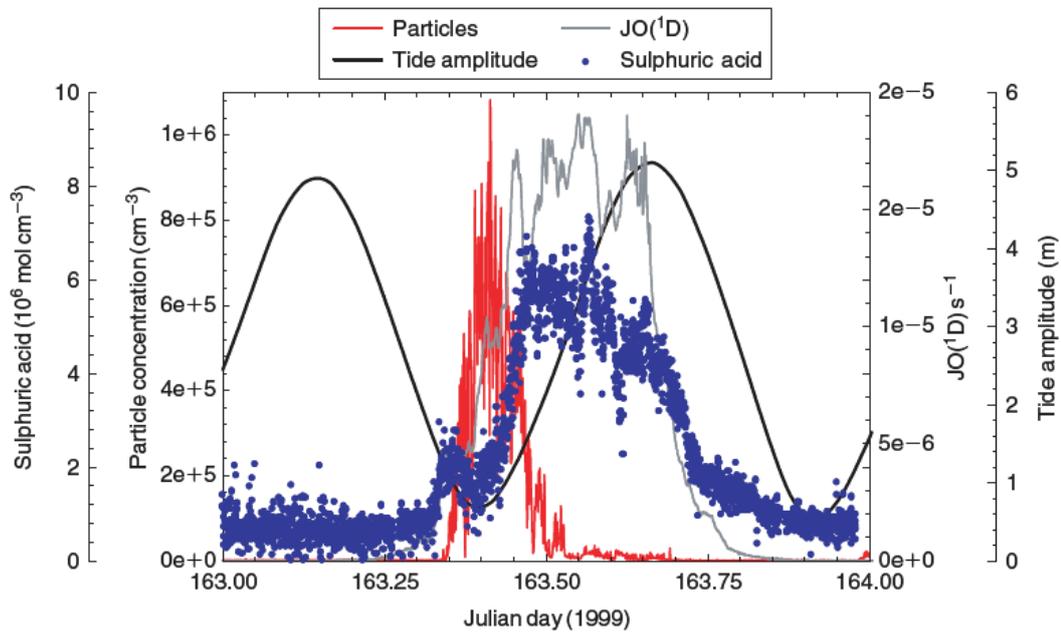


Figure 3. A typical case encountered during the PARFORCE campaign, showing total particle concentration, sulphuric acid concentration, $JO[{}^1D]$ and tide height. (Figure reproduced from O'Dowd, J. *Geophys. Res.* 2002, 107, doi:10.1029/2001JD000555. Copyright [2002] American Geophysical Union.)

Following the PARFORCE findings, O'Dowd *et al.* [2002], confirmed iodine oxides were capable of driving nucleation and growth in the marine environment. Building on the work of Hoffmann *et al.* [2001] and O'Dowd *et al.* [2002], Jimenez *et al.* [2003] corroborated significant particle production from CH_2I_2 in the presence of UV-radiation and O_3 arising from a mechanism proposed to be the dimerisation of OIO into I_2O_4 . Jimenez *et al.* [2003] also suggested however that a further source of condensable material might be needed in order to explain the observations in the atmosphere.

In further investigations, Burkholder *et al.* [2004] used an aerosol model which implemented a kinetic nucleation scheme, coupled to an aerosol dynamics model, to examine the possible implications of iodine oxide nucleation in the

marine boundary layer . Simulations were ran for recently published field measurements of OIO and IO [Alicke *et al.* 1999, Allan *et al.* 2001] of ~0.5 ppt and 2-5 ppt respectively. They concluded that new particle formation with single component homogenous nucleation of OIO is efficient, but found that concentrations reported by the field measurements were not sufficient to reproduce significant aerosol production either in the coastal or open ocean marine boundary layer. It was estimated however, that steady state concentration of ~10 ppt would yield 10^6 particles cm^{-3} within 10-20 minutes and be more consistent with measurements recorded at Mace Head. For IO also, it was found that a value significantly higher than that reported in field measurements, 50-100 ppt, would be needed to reproduce the observations at Mace Head. Most field measurements however, have been carried out using a long path differential optical absorption spectroscopy (LP-DOAS), which provides a spatial average along the DOAS light path. This means however, that DOAS measurements will not accurately resolve inhomogeneously distributed concentrations [Peters *et al.* 2005], and given that most tidal regions are only a fraction of a kilometre, both OIO and IO concentrations could reach 10 ppt and 50-100 ppt respectively, when occurring in localised ‘hot-spots’ along the coastal regions.

It had initially been assumed that CH_2I_2 was the main driver of coastal nucleation event, observations of molecular iodine (I_2) in the coastal boundary layer [Saiz-Lopez *et al.* 2004] at Mace Head indicated that I_2 , rather than iodocarbons, may be the dominant source of coastal reactive iodine. Work by McFiggans *et al.* [2004] investigated the formation of iodine-containing particles from kelp and proposed new mechanisms for coastal I_2 production. As a result, this high source of molecular iodine could explain the observed levels of OIO, and was supported by field observations [Saiz-Lopez *et al.* 2004, Saiz-Lopez *et al.* 2006] of I_2 ranging from 20 ppt during the daytime to more than 80 ppt at night.

Based on this recently published new information on the role of I_2 in new particle formation from seaweeds, to quantify the amount of I_2 emitted, as well as the new particles formed by a given amount of seaweed, Sellegri *et al.* [2005], used a simulation chamber filled with selected species of seaweeds from the

Mace Head area and flushed with particle-free atmospheric air. It was found that total particle concentrations and particles in the 3–3.4 nm size range produced in the chamber are positively linearly correlated with gaseous I_2 concentrations emitted by the seaweeds, with a typical source rate of $2800 \text{ particles cm}^{-3} \text{ ppt}_{[I_2]}^{-1}$ in the 3–3.4 nm size range [Sellegrì *et al.* 2005]. In the same study, field measurements of iodine concentrations at Mace Head and hotspots in the vicinity were found to be of the order of 30 ppt and 110 ppt respectively. Further model simulations [Pirjola *et al.* 2005], examining the formation of thermodynamically stable clusters by dimer formation of OIO vapour, where the iodine precursor was assumed to be molecular I_2 emitted from seaweed, derived a range of I_2 fluxes from 5×10^8 to $1.5 \times 10^9 \text{ cm}^{-3} \text{ s}^{-1}$. The calculations showed that for the lower I_2 flux, I_2 reached a steady-state concentration of $3.2 \times 10^9 \text{ cm}^{-3}$ and for the higher flux, a concentration of $1 \times 10^{10} \text{ cm}^{-3}$. The steady state was reached in less than 150 seconds, with predicted growth rates of 3-6 nm particles varying in the $1.2\text{-}3.6 \text{ nm min}^{-1}$ range, which were in good agreement with previous field and laboratory measurements of I_2 [Saiz-Lopez *et al.* 2004, Sellegrì *et al.* 2005].

1.3 Open Ocean Particle Production Events

In contrast to the coastal environment, both the mechanisms of formation of new particles over the open ocean, and the chemical species driving the production, is much less clear, principally due to the lack of observed nucleation events combined with the much lower concentrations of open ocean precursor species resulting in much less intense production events when they do occur, ultimately rendering them extremely challenging to elucidate. In essence, the significantly reduced biogenic emissions, when compared to those in the coastal environment, presents great difficulty in making clear and unambiguous measurements.

Early investigations into the source of new particles in the remote marine regions have proved conflicting, with the two likely sources being identified as nucleation in the marine boundary layer and entrainment from the free troposphere. It was found that an approximately linear dependence exists between CCN concentrations and DMS flux of over $2.5 \mu\text{mole m}^{-2} \text{ d}^{-1}$ under

typical remote marine conditions, however for lower fluxes practically all the SO₂ produced by DMS photooxidation is predicted to be heterogeneously converted to sulfate in sea-salt aerosol particles [Pandis *et al.* 1994, Russell *et al.* 1994]. Conversely, Raes [1995] concluded that free troposphere-marine boundary layer exchange is likely to be an important mechanism that can explain both the observed levels of CN and CCN in the marine boundary layer and their lack of short-term variability. Raes also argued free troposphere aerosols to be self-preserving in areas of large-scale subsidence such as the subtropics and also that entrainment of free troposphere aerosols in the marine boundary layer quenches new particle formation within the marine boundary layer. Subsequently, Covert *et al.* [1996] reported an intermittent ultrafine mode at diameters less than 25 nm, wherein it was suggested that the concentration and dominance of one mode over another depended on the relative strength of the entrainment of ultrafine and Aitken particles from the free troposphere into the marine boundary layer. However, ultrafine particles have been observed to occur in polar marine air masses in the Antarctic region [O'Dowd *et al.* 1997] and also in the tropical regions. Clarke *et al.* [1998] presented evidence of *in-situ* particle nucleation relating to the natural DMS cycle based on real-time observations of dimethylsulphide, sulphur dioxide, sulphuric acid (gas), hydroxide, ozone, temperature, relative humidity, aerosol size and number distribution, and total aerosol surface area. This would suggest that new particles in the marine boundary layer can arise from both processes although the importance of either process or if one dominates over the other is not yet fully understood.

A recent study by Ehn *et al.* [2010] recorded clear measurements from ship-borne measurements of new particle production in the northeast Atlantic, and can be seen in Figure 4. An examination of air mass back trajectories showed no continental contact for at least three days previous, implying that this was purely a marine new particle formation event. Making a comparison between the particle mode mean radius recorded on the measurement cruise and at Mace Head, a growth rate of 0.4 nm h⁻¹ was calculated for the measured plume.

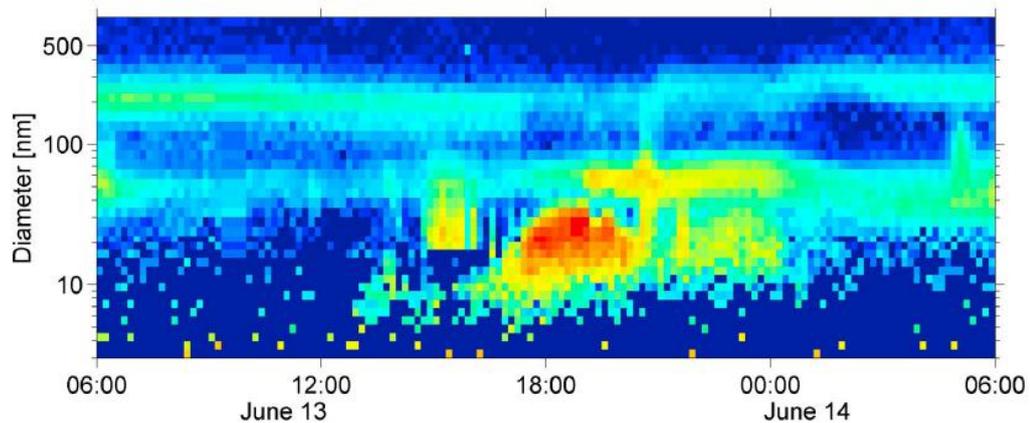


Figure 4. Aerosol number size distribution recorded by Ehn et al. (2010), during ship-based measurement in the north east Atlantic, on the 13th June 2006 on board the Celtic Explorer. (Figure reproduced from Ehn *et al.* [2010], *J. Geophys. Res.*, 115, D18218, doi:10.1029/2010JD014292, Copyright [2002] American Geophysical Union.)

This occurrence of open ocean production events was corroborated by another study in which the examination of air masses during the EUCAARI campaign at the Mace Head Atmospheric Research Station, Dall'Osto *et al.* [2010] detected a recently-formed nucleation mode with average particle number concentrations of $800\text{--}900\text{ cm}^{-3}$ and which was considered representative of off-shore nucleation and growth in clean marine air. This newly formed mode was typically detected at sizes larger than 10-15 nm, in contrast to the coastal nucleation mode which is detected as a very recently-formed mode of 3-5 nm diameter. The “open ocean” nucleation mode detected at Mace Head is observed to grow from 15 nm – 40-50 nm over many hours and occurs predominantly in marine polar air masses (See Dall'Osto *et al.* [2010] for full description of air mass classifications). During these events, the nucleation mode accounted for ~30% increase in particle number concentration associated with polar marine air compared to air masses with a marine tropical origin in which new particle formation is rarely observed.

These particle plumes were estimated to have a growth rate of $\sim 1 \text{ nm h}^{-1}$, and a source region of $\sim 600 \text{ km}$ offshore.

In the events examined by Ehn *et al.* [2010] and Dall'Osto *et al.* [2010], a peak of nucleation mode particles was seen to occur and the mode mean radius increase over time indicating particle growth over time. The question of whether this new particle production occurs from nucleation of clusters in the marine boundary layer or *via* entrainment from the free troposphere is still not conclusively answered; however, evidence suggests that the former may be the most likely explanation in the aforementioned studies. In order for the continued growth such as for the plumes observed at Mace Head in both cases, an entrainment mechanism would require either a small scale entrainment moving continuously offshore, or else a large scale entrainment of clusters and condensable vapours. For the small scale entrainment this seems unlikely as the entrainment region would have to be moving against the prevailing wind. Also large scale entrainment, while possible to result in large scale particle production in the marine boundary layer [Raes 1995, Covert *et al.* 1996], would also require a significant source of condensable vapours to drive the growth observed in measurements. Condensable vapours of these concentrations may arise from anthropogenic activities however black carbon mass concentrations recorded during these events do not corroborate this hypothesis, and also the free troposphere is not regarded as a dominant source of natural condensable vapours.

To answer these questions more conclusively, a larger data set would be required so that both a number of events could be taken for analysis, and also any observed pattern in terms of seasonality would aid in the elucidation of the underlying processes.

1.4 Secondary Organic Aerosol Formation

Secondary organic aerosol (SOA) can form in the marine boundary layer through a number of different processes. Biogenic volatile organic compounds, emitted by the sea surface, or their oxidation products, can be involved in new particle formation events *via* nucleation of stable clusters and subsequent growth to

larger sizes. These biogenic volatile organic compounds and related oxidation products can also condense onto pre-existing particles, contributing, sometimes significantly, to the particulate mass. SOA can also derive via chemical transformation, occurring on the particle surface [Eliason *et al.* 2004, Maria *et al.* 2004] or in the aqueous phase [Peter 2003], by compounds present in the condensed phase. One of the best known SOA components in marine atmosphere is methanesulfonic acid (MSA), resulting from the oxidation of DMS [Shaw 1983, Charlson *et al.* 1987]; however other formation processes, involving different precursors, such as biogenic isoprene [Meskhidze *et al.* 2006], have also been postulated. Vertical profiles made by Greenberg *et al.* [2005] of the concentration of several alkyl halides, as well as isoprene, from the surface to 200 m, using a tethered balloon platform near Mace Head indicated a surface source of isoprene, determined from examining the vertical gradients which showed decreasing concentration with height. Also, using a combined empirical relationship for isoprene production rate with MODIS satellite chlorophyll observation, Palmer *et al.* [2005] estimated isoprene fluxes in the range from 0.37 ppt s^{-1} – 37.18 ppt s^{-1} (10^7 – $10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$), which could account for a significant source of SOA. Meskhidze *et al.* [2006] proposed that secondary organic aerosol, formed from the oxidation of phytoplankton-produced isoprene, can affect chemical composition of marine cloud condensation nuclei and influence cloud droplet number. Their results are consistent with the evidence that the CCN concentration in remote marine regions follows a seasonal trend, with a maximum in spring-summer [Yum *et al.* 2004], and also with work by Sorooshian *et al.* [2009] who found increased average CCN activity during periods of increased chlorophyll a levels, which likely results from both size distribution and aerosol composition changes. Conversely however, recent studies [Irwin *et al.* 2010, Prisle *et al.* 2010, Fuentes *et al.* 2011] show a reduction in CCN activity upon the incorporation of marine organics into the particle composition. This would suggest that marine organics are not ideally suited as a CCN contributor; however increases in CCN concentrations in areas of high biogenic organic emissions would imply a significant role in the evolution of oceanic particles.

This thesis primarily aims to address the follow questions identified as being the most important relating to marine new particle production:

- **What are the statistical characteristics of marine size distributions observed over the NE Atlantic?**

A significant impediment to the study of naturally produced aerosol dynamics and impact on climate is the lack of comprehensive examinations over longer time periods. A longer time series of aerosol and meteorological measurements collected over an entire year, would allow for an in-dept study of aerosol production mechanisms, and monthly trends over the North-East Atlantic.

- **What are the characteristics of coastal new particle production events and what do laboratory studies reveal or elucidate?**

New particle formation in the coastal environment has been a subject of much study in recent years. The role of exact gas-phase species and their relative roles in the nucleation process however are still poorly understood. In particular, iodine containing compounds, released from coastal flora, has been implicated in new particle formation in several studies on coastal nucleation. Despite the detection of significant levels of both iodocarbons and molecular iodine having been detected, its role in the frequently observed particle bursts is still not known. Quantification of the ability of molecular iodine to form particles measured at a high time resolution, both spatially and temporally, in different phases simultaneously, would yield valuable information about rates of formation and the time scales involved with the various processes affecting the aerosol size distribution.

- **Does open ocean particle production (nucleation) occur and if so, how often?**

While new particle formation in a coastal setting has been the subject of many investigations, whether it occurs frequently in the open ocean is still not fully known. This is due mainly to the lack of definitive measurements of open ocean nucleation events, owing both to the difficulties of acquiring these measurements as well as the greatly reduced aerosol precursor gas-phase species, making the resultant aerosol number concentrations much more difficult to observe. Elucidation of the frequency of open ocean nucleation events in the North Atlantic, the seasonality of events, as well as the characteristics of these particle populations would greatly further understanding of the underlying open ocean particle production mechanisms.

- **What is the relative role of sulphuric acid, iodine oxide, and condensable vapours in open ocean particle production and which nucleation mechanism is likely to be involved?**

Critical to the understanding of the production mechanism of both open ocean and coastal nucleation events is knowledge of the role and concentrations of the aerosol precursor gasses, as well as other compounds which affect other aerosol dynamics such as condensational growth. It would be valuable to reproduce, through modelling of aerosol microphysical processes, particle concentrations previously observed at the Mace Head atmospheric research station, using the main compound's identified to date such as sulphuric acid, iodine oxide, and condensable vapours. This would identify the sensitivity of the particle production mechanism to each compound, as well as indicate the concentrations of gas phase precursors needed to reproduce published measurements.

In addition, the work contributed to peripheral questions of importance to marine aerosol characterisation along with ash cloud aerosol characterisation:

- How does marine aerosol scattering respond to changes in relative humidity and how does this respond to changes in chemical composition?
- What is the role of sea spray enriched with organic matter in water uptake and cloud droplet activation?
- What are the physical and chemical properties and water content of ash cloud aerosol?

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2 Summary of Papers

This thesis consists of 10 papers published in peer-reviewed journals. Two are as lead author, one as effective lead author, and seven with minor to moderate to major roles.

Paper 1: Contributing Author – moderate role

Particle mobility size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions

This paper results from several instrument inter-comparison workshops conducted within the European infrastructure project EUSAAR (European Supersites for Atmospheric Aerosol Research), and summarizes experimental results from the intercomparison of 10 custom-built as well as commercially available particle mobility size spectrometers (e.g. SMPS, DMPS, TDMPS). In this study, number size distributions from 20 to 200 nm, determined by mobility size spectrometers of different design, were used in the development of technical standards for a minimum requirement of mobility size spectrometry for atmospheric aerosol measurements. Technical recommendations are given for atmospheric measurements including continuous monitoring of flow rates, temperature, pressure, and relative humidity for the sheath and sample air in the differential mobility analyser. Also a new uniform data structure was introduced for saving and disseminating data with the EMEP (European Monitoring and Evaluation Programme) framework. The author was responsible for modifying the SMPS hardware and software to adhere to EUSAAR guidelines, all of the analysis of the NUIG particle size distribution data, and provision of this data for publication. Related work in background support to this paper centred on realtime web casting and database provision of Mace Head SMPS size distributions.

Paper 2: Contributing Author - major role

A statistical analysis of North East Atlantic (submicron) aerosol size distributions

This paper presents extensive analysis of the physical characteristics of aerosol size distributions measured in air masses advecting over the Mace Head Atmospheric Research Station for the year 2008. Analysis of the aerosol size distributions was carried out by using k-mean cluster analysis techniques, which allowed for examination of the degree of similarity and difference between the individual observations to define the groups, and assign groups memberships. Twelve clusters were identified as systematically occurring, which could be further categorised into four groups with similar characteristics: coastal nucleation category (occurring 21.3 % of the time), open ocean nucleation category (occurring 32.6% of the time), background clean marine category (occurring 26.1% of the time) and anthropogenic category (occurring 20% of the time). The author was responsible for all of the particle size distribution collection, a major part of the analysis, and a minor part of the writing.

Paper 3: Contributing Author – effective lead role.

On the occurrence of open ocean particle production and growth events

This paper presents new results from the Mace Head Atmospheric Research Station highlighting case studies in where episodes of new particle production and growth over the North East Atlantic are explored. Taking as a case study a 12 day period in August 2009, size distribution measurements made by a nano-scanning mobility particle sizer (nano-SMPS) and scanning mobility particle sizer (SMPS) instruments covering a size range from 3 nm to 500 nm were examined over time. Events were seen to form a distinct peak in the size distribution with a mode at ~15 nm and grow to a mode of ~50 nm over periods

of 24-48 hours, while air masses were calculated to have advected over biologically-rich waters in the North Atlantic before detection. In an extensive analysis of size distribution measurements carried out at Mace Head over a seven year period, events were also seen to exhibit seasonality, with a monthly average occurrence of 5.7 per percentage occurrence of clean air, peaking in May, while no events were seen to occur outside the months of March to September. The author was responsible for all of the particle size distribution collection, the majority of the analysis, and a secondary role in writing.

Paper 4 & 5: Contributing Author Part 1; Lead Author Part 2.

Coastal iodine emissions: Part 1. Release of I₂ by *Laminaria digitata* in chamber experiments

Coastal Iodine Emissions: Part 2. Chamber experiments into particle formation from *Laminaria digitata*-derived and laboratory-generated I₂

In this study, I₂ emissions from 25 *Laminaria digitata* (Phaeophyceae) samples were investigated in a simulation chamber in order to investigate the particle forming ability of inter-tidal macroalgae. Experiments were carried out using incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) while a nano scanning mobility particle sizer (nSMPS) was built and operated continuously to measure particle number size distributions from 3 nm to 20 nm. A scanning mobility particle sizer (SMPS), with a measurement range of 10 nm – 500 nm, was also used in conjunction with the nSMPS to measure particle number size distributions for several chemical experiments in which a flow through the chamber was applied. Emission of I₂ was seen to occur in four stages: moderate emissions from partially submerged samples (stage one), followed by a strong release by fully emerged samples (stage two) and slowing or stopping of I₂ release (stage three) while in some specimens later pulses of I₂ were evident (stage four). A clear increase in the aerosol number concentrations in the 3 nm to 20 nm size range was observed under low O₃ conditions (<3 ppb_v),

where also aerosol mass fluxes (assuming I_2O_4 gas-to-particle conversion) and particle number concentrations were linearly correlated ($R^2=0.7$ and 0.95 , respectively) with I_2 mixing ratios. Additional experiments into particle production as a function of laboratory-generated I_2 , over a mixing ratio range of 1-8 ppb_v, were conducted under moderate O_3 mixing ratios (~ 24 ppb_v) where a clear, 100 - fold or greater, increase in the aerosol number concentrations and mass fluxes was observed compared to the low- O_3 experiments. A linear relationship ($R^2 = 0.81$) between particle concentration and I_2 was found, and scaling the laboratory relationship to aerosol concentrations typical of the coastal boundary layer suggests a I_2 mixing ratio range of 6-93 ppt_v. Aerosol number concentrations produced, in this case from I_2 , are more than a factor of 10 higher than that produced from CH_2I_2 for the same mixing ratios. The author was responsible for all of the aerosol measurements, aerosol analysis, integrated analysis with focus on gas-to-particle production and a major part of the writing as lead author of Part 2.

Paper 6: Lead Author

Simulating marine new particle formation and growth using the M7 modal aerosol dynamics model

In this paper the modal aerosol microphysical model M7 was evaluated for its ability to predict new particle formation and growth under conditions characterising the clean marine atmosphere. Three different particle nucleation schemes were used in a number of simulations to examine kinetic self nucleation of OIO, nucleation via OIO activation by H_2SO_4 and nucleation via OIO activation by H_2SO_4 with condensation of a low volatility organic vapour. The kinetic OIO self-nucleation scheme was found to increase the background aerosol population ($N = 300 \text{ cm}^{-3}$) by 65% for $r > 15\text{nm}$, decreasing to 2% for $r > 50\text{nm}$. Activation of OIO by H_2SO_4 vapours increased the aerosol population by 226% for $r > 15\text{nm}$, decreasing to 0.5% for $r > 50\text{nm}$. When the latter case was

considered with an additional condensable low volatility vapour with a mixing ratio of 0.45ppt (1.2×10^7 molecules cm^{-3}), the largest increase in aerosol concentration was observed where the aerosol concentration increased by 615% for sizes $r > 15\text{nm}$ and by 15% for $r > 50\text{nm}$. It was concluded from the simulations that while there were significant increases in Aitken (defined operationally as particles in a lognormal distribution whose mode mean diameter was between between 10 nm and 100 nm) mode particle number concentrations, increases were most notable in cases where nucleation occurred in the presence of a condensable organic vapour. As a specific case study the model results were compared to a measured open ocean nucleation event which was also modelled by a sectional model, results demonstrated good agreement, and the feasibility of using a modal modelling system. In this case where the total aerosol concentration was 300 cm^{-3} , after a nucleation burst via activation of OIO by H_2SO_4 vapours, and subsequent growth by a low volatility organic vapour, peak Aitken mode particle concentrations exceeded 3000 cm^{-3} , while the concentration at the end of two days of simulations at sizes $r > 15$, $r > 25$, $r > 35$, and $r > 50 \text{ nm}$ were 1585 cm^{-3} , 556 cm^{-3} , 230 cm^{-3} , and 126 cm^{-3} , respectively, suggesting that the combination of iodine oxide activation by sulphuric acid and subsequent growth by an organic vapour can significantly impact on the marine aerosol population number concentration. The author was responsible for most of the simulations, analysis and a major part of the writing.

Paper 7 & 8 Contributing Author Part 1 & 2 – moderate role.

The Eyjafjallajökull ash plume Part I: Physical, chemical and optical characteristics

The Eyjafjallajökull ash plume Part 2: Simulating ash cloud dispersion with REMOTE

This paper examines the physical, chemical, and optical properties of the Eyjafjallajökull ash plume that was detected at the Mace Head atmospheric

research station between April 19th 2010 and May 18th 2010. Throughout this period an array of particle measurement instruments were used to measure the ash plume characteristics, including size distributions, which were sampled using a TSI nano-Scanning Mobility Particle Sizer (SMPS) between 3 and 20 nm, and a standard SMPS operating size distribution scans between 20 and 500 nm. These SMPS measurements in conjunction with an aerosol particle sizer (APS) allowed for the calculation of the mass size spectrum for the measured plume. Results show that the ash size distribution was bimodal with a supermicron mode of 2.5 μm in diameter while the submicron mode varied between 185 nm to 395 nm during the low and high explosive phases respectively. Findings also show that the physical size and chemical composition of the ash plume aerosol result in very efficient CCN. The author was responsible for all of the analysis of the particle size distribution data.

Paper 9: Contributing Author – moderate role.

Primary marine organic aerosol: A dichotomy of low hygroscopicity and high CCN activity

In this paper high time resolution measurements of the physicochemical properties of primary marine organic sea spray are presented. Continuous measurements of marine aerosol in clean air masses were undertaken at Mace Head by an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer, a scanning mobility particle sizer (SMPS), a Droplet Measurements Technology CCN counter, and a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA). Results show that primary marine organic sea spray aerosol exhibit a low hygroscopic growth factor but also a high CCN efficiency. It is suggested that this effect relates to the enrichment of marine hydrogels in sea spray aerosol. Using the size distribution data, an innovative approach was taken to achieve closure between lab studies and observations at Mace Head by combining the weighted mean size from the

SMPS to the aerosol mass spectrometer (AMS) chemistry, to provide estimated sea spray nuclei and sulphate nuclei. This provided excellent closure between CCN concentrations and cloud droplet number concentrations, with values having a correlation coefficient of 0.76. The author was responsible for all of the analysis of the particle size distribution data.

Paper 10: Contributing Author – minor role

Light scattering enhancement factors in the marine boundary layer (Mace Head, Ireland)

This paper presents measurements of light scattering enhancement factor as a function of relative humidity, as well as additional optical properties such as the backscatter fraction and single scattering albedo, from a one month field measurement campaign (January 2009 – February 2009) carried out at Mace Head. The measured particle size spectra during this period were used to calculate the scattering enhancement as a function of RH, using Mie theory. During the measurement period, the mean $f(\text{RH} = 85\%)$ for marine air masses at the wavelength of 550 nm was $2.22 (\pm 0.17)$ and $1.77 (\pm 0.31)$ for polluted air. Also during the period, the backscatter fraction decreased by about 20%, and the single scattering albedo increased on average by 1%–5% at 85% RH compared to dry conditions. The author was responsible for all of the analysis of the particle size distribution data.

4 Conclusions

In the course of this work a detailed study of aerosols in the coastal and marine environments with a focus on new particle formation has been carried out.

Several aerosol measurement instruments based on particle detection by electrical mobility were built throughout the course of this study. Principally, the development of the nano scanning mobility particle sizer, in conjunction with a scanning mobility particle sizer conforming to EUSAAR (European Supersites for Atmospheric Aerosol Research) standards, allowed for the measurement of particle size distributions in the range of 3nm – 500nm with a temporal resolution of 2 minutes and 30 seconds for the two instruments respectively. This component ensured that the right tools with the right accuracy were built, tested, evaluated and deployed correctly for the field and laboratory studies.

In the course of the current work, a longer time series of aerosol and meteorological measurements were collected over an entire year. This allowed for a detailed look at the dynamics affecting aerosol in air masses that had advected over the north Atlantic prior to detection. In this analysis of North East Atlantic particle size distributions detected at Mace Head for the year 2008, 12 clusters were identified as regularly occurring. These 12 clusters could be further broadly categorised as coastal nucleation, open ocean nucleation, background clean marine and anthropogenic aerosol size distributions, and showed that 53.9% (21.3% coastal nucleation and 32.6% open ocean nucleation) of the time coastal and open ocean nucleation size distributions were detected. Throughout this period the open ocean nucleation was seen to occur more often during May, June and July. This is further corroborated by the frequent detection of extended particle plumes and growth from the North East Atlantic, and points to a significant open ocean particle production mechanism, most likely as a result of large scale secondary particle production rather than entrainment from the free troposphere. Examination of 7 years of aerosol size distribution data sets shows definitively that these plumes occur during the summer months, throughout

periods of high biological activity, suggesting a link to organic vapours driving growth. The link to organic vapours is further strengthened in that no inorganic vapours are present at the sustained concentrations that were calculated to be required for the observed growth. This study reports, for the first time, events during which a recently-formed nucleation mode (~15 nm diameter) was detected and is observed to grow into an Aitken mode (~50 nm diameter) over periods up to 48 hours. The results offer new insight into new particle formation over the open ocean and contributes significantly to the current understanding of these phenomena.

With regards to coastal nucleation events, iodine compounds have been implicated in new particle production events, in both its organic and inorganic form, and may provide a clue as to whether nucleation *via* iodine compounds is possible over the open ocean. Laboratory studies with the brown alga *Laminaria digitata*, encompassing tidal, light and O₃ exposure carried out during this work found a high potential for the formation of new particles, given that appropriate amounts of molecular iodine and ozone are available, with emission occurring at different stages during emersion of the alga from water. Over all particle concentrations as well as 3nm particle concentrations were found to vary linearly with I₂ concentrations, and an extrapolation down to particle concentrations frequently measured at Mace Head predicted I₂ levels in the range of 6-93ppt, similar to mixing ratios found in previous coastal studies. This confirms that iodine compounds are, most likely predominantly I₂, the main particle precursor in coastal nucleation events. Tidal effects however are not applicable over the open ocean, and the question as to which iodine compound, and its ability to initiate or contribute to new particle formation, dominates in this environment, is still open. The measurements presented in this work however, show definitively that molecular iodine has the ability to produce atmospherically relevant numbers of new particles and measurements in different phases simultaneously contributed to the knowledge of the subject by yielding valuable information about rates of formation and the time scales involved with the various processes affecting the aerosol size distribution.

In a group of simulations investigating the feasibility of using a modal model in an analysis of these open ocean particle production events, it appears that a relatively small concentration of I_2 can result in significant enhancement of Aitken mode particle number concentrations. This enhancement is increased when nucleation is assumed to be OIO activation by H_2SO_4 , and further still when this OIO- H_2SO_4 nucleation happens in the presence of a low volatility organic vapour. In simulations where peak OIO and H_2SO_4 vapour concentrations were both limited to 0.22 ppt (6×10^6 molecules cm^{-3}) at noontime and where the peak organic vapour concentration was limited to 0.45ppt (12×10^6 molecules cm^{-3}), particle concentrations were predicted to increase from a base case particle concentration of 222 cm^{-3} at radii >15 nm, to 366 cm^{-3} from the OIO-OIO case, 722 cm^{-3} for the OIO- H_2SO_4 case, and 1584 cm^{-3} for the OIO- H_2SO_4 case with additional condensing organic vapours. Reproducing a previously measured open ocean plume detected at Mace Head confirmed that when this additional organic vapour, if present at concentrations in the order of 0.37 ppt (10^7 molecules cm^{-3}), was involved in the growth of the newly nucleated particles, the levels of both OIO and H_2SO_4 needed to simulate the measured plumes approached previous measurements over the open ocean. These simulations confirmed the sensitivity of the nucleation mechanism to each compound as well as verifying measurements by elucidating the concentrations of gas phase precursors needed to reproduce published measurements.

Organics in the marine atmosphere have a large contribution to the relative mass fraction of marine aerosols measured at Mace Head during periods of high biological activity. Despite being characterised by low water solubility, additional study in this work also shows that particles containing a large amount of organic matter in addition possess a high CCN activation efficiency. This suggests that both primary and secondary particles formed in the open ocean during periods of high biological activity, have the potential to increase CCN concentrations efficiently.

Further investigation into marine size distributions shows that when volcanic ash is present in the marine atmosphere, a bimodal aerosol size

distribution can be observed. In an examination of the Eyjafjallajökull ash plumes present in air masses arriving at Mace Head, a clear peak in the mass distribution at a diameter of 600 nm was observed, with the measured particles having been extremely hydrophilic. This implies that new particles in the marine boundary layer arising from volcanic eruptions, act as an infrequent but significant source of CCN.

These results provide new information about the underlying mechanisms of particle production in the marine environment, however throughout this work, different aerosol size distributions were detected among clean air masses suggesting that new particle production in marine air is a result of both primary and secondary processes, many of which are not yet fully understood. This work has elucidated some of the statistical characteristics of marine size distributions as well as provided new information on the underlying mechanisms of observed marine particle nucleation events. In terms of open ocean particle production, this study also offers fresh insight into the relative role of sulphuric acid, iodine oxide, and condensable vapours in this process, as well as the impact of organic matter on the physical characteristics of particles over the north Atlantic. Some open questions still remain however. Over the ocean, it is still not known which condensable vapour species dominates and drives growth of newly nucleated clusters, thus further *in situ* measurements are needed to properly quantify this particle production process. Also while organic matter has been found to have a significant contribution to the relative mass fraction of North Atlantic marine aerosols, the exact effects of particle uptake in the early stages of growth, as well as the question of the effects on particle distributions of different organic speciation, which changes both as a function of source location and seasonal biological variation, still needs to be elucidated.

Future Outlook

The analysis and discussion presented in this work were based on intensive field campaigns, laboratory chamber studies, and extensive modelling studies. Due to the confines in time and instrumental set-ups, future research could be advanced by a multi-dimensional study of air masses i.e. using a comprehensive suite of instrumentation to measure aerosol properties simultaneously. This would allow for a fuller understanding of the particle characteristics as well as information on the processes acting on the particles before advection over the measurement site. While this study provided a significant amount of new information regarding open ocean particle production, information relating to the critical first steps of formation and growth to a quasi-stable state is still largely non-existent. Measurement of gas phase species alongside high resolution measurements of particles < 20 nm would yield a large amount of data in terms of the particle numbers as a result of this nucleation, as well as the source rates of the main compounds involved. Accurate quantification of these gas phase constituents over the open ocean would aid greatly in advancing our knowledge of natural aerosol production and their impact on future climate scenarios.